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Characterization of atmosphere–water exchange processes of CO_2 in estuaries using dynamic simulation

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Abstract

CO_2 is one of the so-called "greenhouse effect" gases; therefore, its rates of water–atmosphere exchange are very relevant for studies of climate change. Coastal zones (which include estuarine systems) are of special interest in relation to the global carbon cycle. Thus, an estuary simulator, which operates in a dynamic mixing regime, is specifically applied in an initial study of the estuarine dynamic of inorganic carbon, focusing basically on the influence of salinity and pH on the water–atmosphere fluxes of CO_2 in these zones. The simulation has been performed under two assumptions: (i) considering that the system is subjected to a stationary gradient of salinity and (ii) taking into account the effect of the tides, owing to the daily oscillations introduced by this phenomenon in the process of CO_2 transfer between the water and the atmosphere. After analysing the results, it has been observed that a potential source of error exists when choosing the coefficients of gas exchange (k) for CO_2 studies. Nevertheless, the evolution of CO_2 fluxes along the salinity and pH gradients achieved shows the same trends with those observed in a wide variety of real estuaries described in the related literature.

Keywords: Estuaries; Simulation; CO_2; Atmosphere–water fluxes

1. Introduction

CO_2 is one of the so-called "greenhouse effect" gases; therefore, its rates of water–atmosphere exchange are very relevant for studies of climate change. In relation to the global carbon cycle, coastal zones (which include estuarine systems) are of special interest. The inventory of sources and sinks of atmospheric CO_2 in the zone known as "coastal ocean" is currently recognised as essential for better knowledge of the global carbon cycle (Frankignoulle et al., 2001). The overall picture in the "coastal ocean" is that temperate open continental shelves are net autotrophic (potential sinks for atmospheric CO_2) while near-shore system influenced by anthropogenic and/or terrestrial organic carbon inputs, in particular temperate estuaries, are net heterotrophic (Borges et al., 2004). It has been demonstrated in several studies that rivers and estuaries (with large anthropogenic influence) suffer a certain degree of oversaturation of CO_2 with respect to the atmosphere, with partial pressures that range between 500 and 9500 μatm (Martins and Probst, 1991; Raymond et al., 1997; Frankignoulle et al., 1998). In turn, CO_2 can present considerable temporal and spatial variations within the same estuary (Abril et al., 2000; Howland et al., 2000) due to the complexity of these littoral zones.

Given the large number of factors that affect the fluxes of CO_2 and the difficulty of integrating the

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influence of all of them simultaneously, it is very useful to utilise laboratory-controlled devices to be able to characterise the process of CO_2 exchange. Therefore, without denying the necessity of field work, it is possible significantly to reduce the length of time employed in real samplings by using laboratory simulations.

Thus, a piece of equipment (that enables the process of estuarine mixing to be reproduced dynamically mixing sea and river water continuously and progressively) has been employed to characterise the behaviour of inorganic carbon and the water–atmosphere fluxes of CO_2 that take place along different salinity and pH gradients under different assumptions.

Two different types of assay have been conducted in accordance with the two types of simulation that can be performed with the simulator. In the first approach, the distribution of species of inorganic carbon and the fluxes of CO_2 have been characterised when the system is subjected to a stationary gradient of salinity. Besides, with the objective of reproducing the importance of changes of pH values in the dynamics of inorganic carbon (owing to primary productivity for example), other simulation assays have been conducted at different fixed salinities when a stationary pH gradient exists. In a second approach, experiments were performed in which the effect of the tides was also taken into account, given the daily oscillations that this phenomenon introduces in the process of CO_2 transfer. In fact, the results of other authors (Reigner et al., 1997) indicate that techniques for the estimation of fluxes based only on assumptions of stationary state can introduce significant errors.

2. Materials and methods

2.1. Experimental device

Basically, the simulation of estuarine mixing is achieved by the cross-current mixing of sea water with river water. Fig. 1 is a diagram of the simulator, which is based on an original idea coinciding with that of Bale and Morris (1981). The mixture is performed in a series of eight tanks (each made of Plexiglas, cylindrical in shape and of 12 L capacity: 10 L of water and 2 L of air) interconnected under a hydrodynamic regime and situated at ascending levels. The lowest tank is supplied with seawater, and the highest tank is supplied with fresh water. From the lower to the upper tanks, there is a forced flow of water controlled by peristaltic pumps. In the inverse direction, filling the containers in series with fresh water generates a down-flow.

The temperature in each tank is controlled by means of coated dip heaters. The tanks are aerated by means of

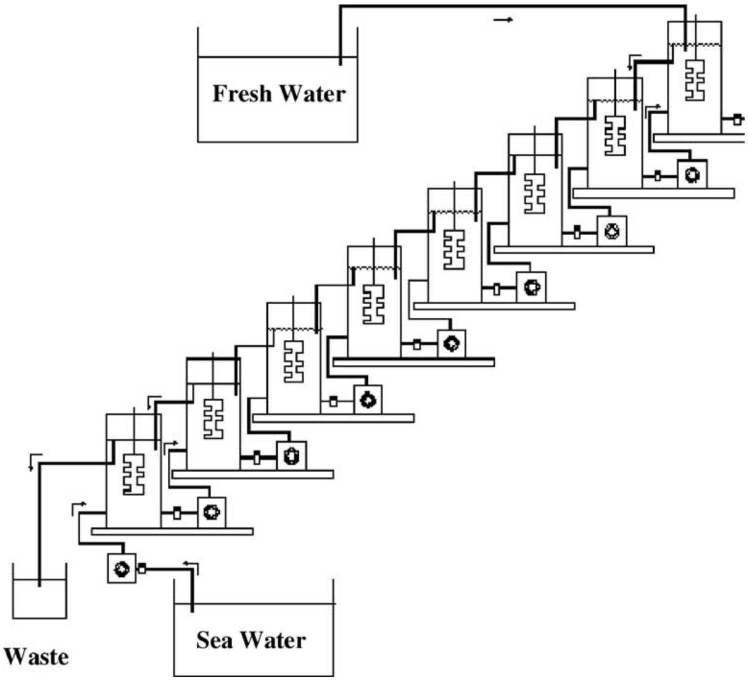

Fig. 1. Schematic representation of the estuarine hydrodynamic simulation system (adapted from García-Luque et al., 2003).

a blower system, with submerged diffusers, to ensure the correct oxygenation of the water in all the simulations performed. The mixture of the two types of water is kept homogeneous using mechanical agitators. In this way, the simulator reproduces the mixing that would take place in a vertically and laterally homogeneous estuary (type A of the classification of Beer, 1983).

The flow and temperature control is carried out by a personal computer using an AID 21-bit translation card. The regulation of flow involves setting up the peristaltic pumps (Masterflex, 7521-55) in phase with the flow meters (McMillan Company, 111), while the temperature is monitored by thermistor probes and adjusted by means of coated dip heaters.

More details about this system as well as other applications of the same are described in García-Luque et al. (2003, 2004).

2.2. Determination of partial pressure of CO_2 in air

In each tank of the simulator, a quantity of 10 L of water (equivalent to the ocean) was introduced, and a volume of 2 L of air (equivalent to the atmosphere) was left in the upper part. While the measurements were being made, the tanks were sealed hermetically.

The variations of the partial pressures of CO_2 (p_{CO_2}) and H_2O, the total pressure and the temperature of the air incubated in each tank were recorded continuously by means of an IRGA analyser (Licor-6262). Measurements were independent in each tank (the gas flow was not switched from one tank to the other). A non-linear calibration of the analyser was performed daily, using standards of 250, 500 and 1000 ppm (Air Liquide, Spain). Fig. 2 presents a diagram of the device employed for the determination of partial pressure of CO_2 in air at each tank of the simulator.

2.3. Determination of partial pressure of CO_2 in water

The p_{CO_2} in the water of each tank was determined from the pH (NBS) and the total alkalinity, obtained by means of potentiometric titration (Metrohm, 670 and 716 DMS) with HCl 0.1 M, utilising combined glass electrodes (Metrohm, 6.0210). The speciation of inorganic carbon was established utilising the constants proposed by Mehrbach et al. (1973). The validity of the method employed was proven utilising reference material (Batch#33, Scripps Institution of Oceanography). For the analysis of the samples, a mean value of 2010.6 ± 2.9 μM of inorganic carbon for a certified value of 2009.85 ± 0.85 μM was obtained.

The concentration of calcium was measured by a potentiometer (Metrohm, 670 and 716 DMS) with 5 mM EGTA, utilising a selective electrode (Metrohm, 6.1241) and a reference electrode with double saline bridge (Metrohm, 6.0726). The salinity was determined with an induction salinometer (Beckman, RS-10).

2.4. Calculation of fluxes of CO_2

The contained air in the tanks is recirculated through the IRGA by means of a peristaltic pump (flow: 105 $mL \cdot min^{-1}$) (Fig. 2). At the beginning of each determination, the partial pressure of CO_2 in the gaseous phase is reduced by introducing synthetic air free of CO_2, up to a value of close to 350 μatm. Under these initial conditions, for the greater part of the incubations performed, there is an output of CO_2 to the atmosphere.

In Fig. 3(A), the evolution of the partial pressure of CO_2 during one of these incubations is shown. There is an exponential increase of the p_{CO_2} with time, which is a consequence of the progressive decrease of the gradient of concentrations as the concentration of CO_2 in

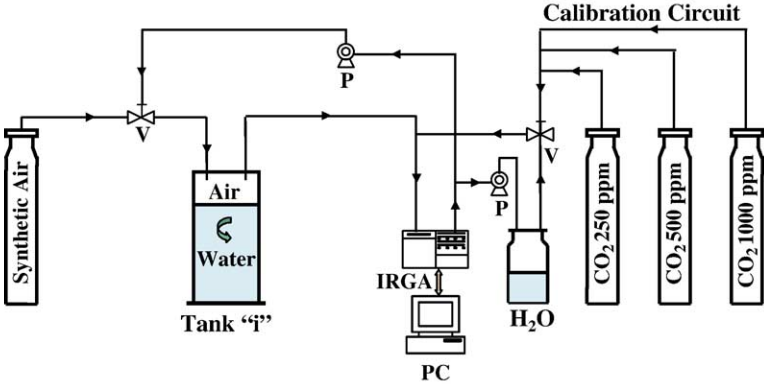

Fig. 2. Diagram of the device employed for determination of p_{CO_2} in air and quantification of CO_2 fluxes at each tank comprising the simulator (P: pump; V: valve).

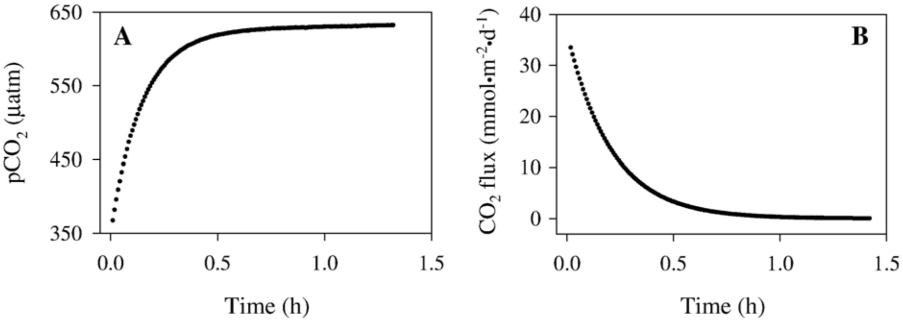

Fig. 3. (A) Evolution of p_{CO_2} over time during a tank incubation to quantify CO_2 fluxes between atmosphere and water. (B) Variation of quantified CO_2 flux with time during a tank incubation in one of the assays conducted.

the atmosphere increases. These curves tend towards an asymptotic value from 30 to 60 min, where the equilibrium is reached between the partial pressures in the water and in the air.

The flux of CO_2 between the water and the atmosphere has been obtained from the definition of flux itself:

$$F = \frac{1}{R} \cdot \frac{dC}{dt}$$

where R is the relationship between the area of the water surface film and the volume of the gaseous phase (16.13 m^{-1}). The substitution of the exponential equations that describe the dependence of the concentration with time within this expression gives, as the result, an exponential decrease of the flux with time (Fig. 3(B)), as a consequence of the decrease of the gradient of concentrations at the interface during the incubation. With the object of normalising the value of the flux, these expressions have been particularised for the moment of time when it is verified that the partial pressure of CO_2 is equal to 365 μatm; this pressure can be considered as the current world mean value in the atmosphere (www.cmdl.noaa.gov).

3. Results and discussion

3.1. CO_2 fluxes in stationary state

Seven assays were achieved in which the behaviour of the DIC has been characterized and the water–atmosphere fluxes of CO_2 over the length of the stationary gradients of salinity and pH have been calculated. Experiment 1, 2, 3, and 4 were performed simulating different gradients of salinity and pH. Experiment 5, 6, and 7 were performed at constant salinity and with relatively wide pH gradients that can be considered representative of the ranges of variation of pH found in real estuaries (Neal et al., 1998). In all cases, the sea water employed was collected from the Bay of Cádiz (SW Spain) and filtered at 10 μm. Fresh water is synthetic with a typical composition of average world standard river fresh water (Millero, 1992). All assays were conducted at a controlled temperature of 25 °C. Residence times, in all cases, were around 5.5 days. Duration of all assays ranged between 7 and 9 days. Table 1 shows the ranges of variation of salinity, pH, dissolved inorganic carbon (DIC), p_{CO_2}, and water–atmosphere fluxes in these experiments.

Table 1
Ranges of variation for salinity, pH, dissolved inorganic carbon (mM), partial pressure of CO_2 (μatm) and CO_2 fluxes water–atmosphere (mmol m^{-2} day^{-1}) obtained in the steady-state experiments

Experiment	Salinity	pH	DIC	p_{CO_2}	CO_2 flux	y_0	a	b	r^2
1	0–37	6.60–8.03	0.14–2.51	4026–516	71.2–10.7	18.8	24.2	0.12	0.84
2	0–10	7.12–8.09	1.34–1.47	1398–517	74.3–15.1	0	95.1	0.25	0.88
3	0–5	7.59–7.93	1.20–1.35	1317–490	93.2–15.6	16.1	306.9	3.85	0.98
4	0–10	6.52–8.23	0.34–2.60	1645–431	99.8–14.6	18.3	186.2	1.30	0.96
5	5	6.23–7.00	0.71–0.94	5340–3350	70.4–23.1	−13.8	147205.3	1.15	0.97
6	19	6.85–8.19	0.54–2.50	2600–210	42.2 to −2.1	−238.9	953.9	0.18	0.73
7	38	7.50–8.27	0.36–3.38	610–250	21.7 to −13.2	−322.9	1096.7	0.15	0.75

The best fit for the evolution of the CO_2 fluxes with salinity (or pH) is described by the exponential equation $\text{flux} = y_0 + a e^{-bx}$, where x is the salinity for Experiments 1, 2, 3, and 4 (or pH for Experiments 5, 6, and 7), and y_0, a, and b are the fitted parameters. Also shown is the correlation coefficient (r^2).

In general, the concentration of inorganic carbon grows linearly with the salinity, as can be observed in Fig. 4, which presents as an example a series of graphs that characterise the behaviour of inorganic carbon in one of the assays performed. This conservative behaviour of the DIC can be considered the most frequent found in studies conducted in real estuaries (e.g., Raymond et al., 2000). The pH usually presents an increase with the salinity, which causes a progressive decrease of the p_{CO_2}. At low salinities, a considerable oversaturation of p_{CO_2} has been observed, with values ranging between 500 and 4000 μatm. This range of variation of p_{CO_2} can be considered normal for estuarine systems (Frankignoulle et al., 1996; Raymond et al., 1997; Abril et al., 2000). In fact, values of p_{CO_2} as high as 9500 μatm have been measured in the zone of maximum turbidity of the river Scheldt estuary (Frankignoulle et al., 1998).

The increase of pH over the length of the salinity gradient causes a relative increase of the concentration of CO_3^{2-}. In turn, the concentration of Ca^{2+} increases linearly with the salinity, which causes an increase of the index of saturation of $CaCO_3$. Fig. 4 shows the variation of the degree of saturation of calcite in one of the experiments conducted, obtained from the product of solubility proposed by Mucci (1983). It can be observed how, in the more fluvial zone, conditions of undersaturation with respect to the formation of calcite usually exist and, at high salinities, values of oversaturation typical of coastal waters are reached.

The variation of the water–atmosphere fluxes of CO_2 in these experiments covers the range from 99.8 to 10.7 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. The variability of these fluxes is a consequence of the DIC and pH gradients established in each experiment. In all the cases, a decrease of the CO_2 fluxes with the increase of salinity is observed, as is shown in Fig. 5(A), by way of example, for one of the assays. This behaviour has been described in several European estuaries (e.g., the Elbe, Ems, Rhine, Scheldt, Tamar, Thames, Gironde, Duero, Sado) by various authors (Kempe, 1984; Kempe et al., 1991; Frankignoulle et al., 1998; Abril et al.,

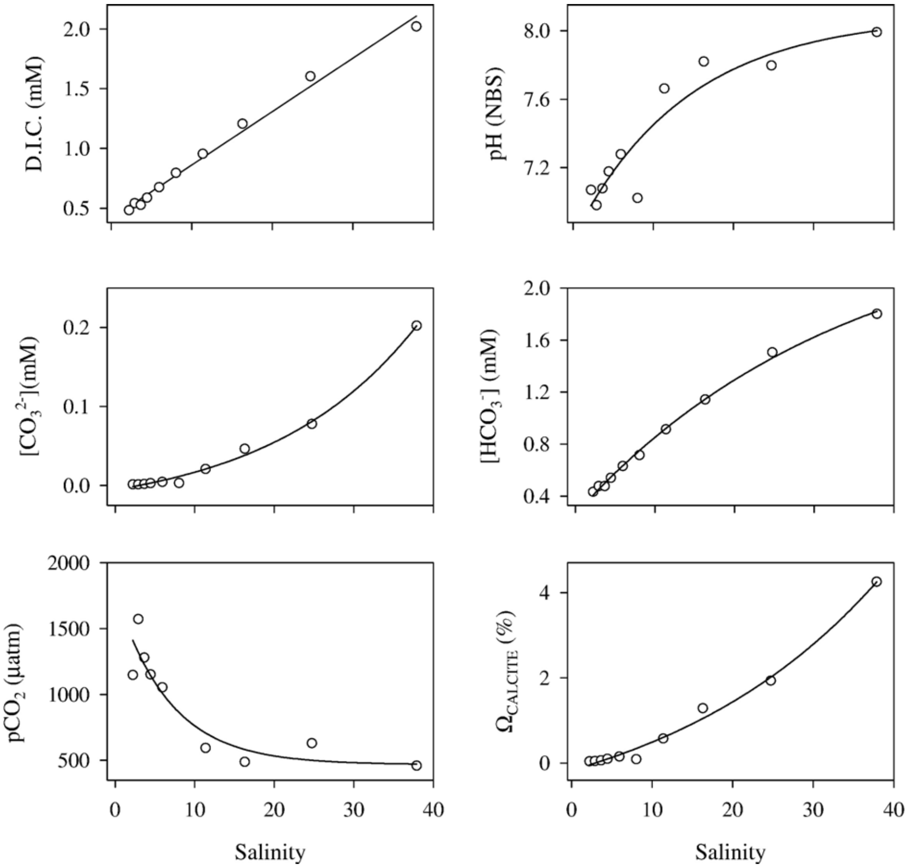

Fig. 4. Variation with salinity of the concentration of dissolved inorganic carbon (DIC), pH, CO_3^{2-}, HCO_3^-, p_{CO_2} and saturation index for calcite in one of the experiments described.

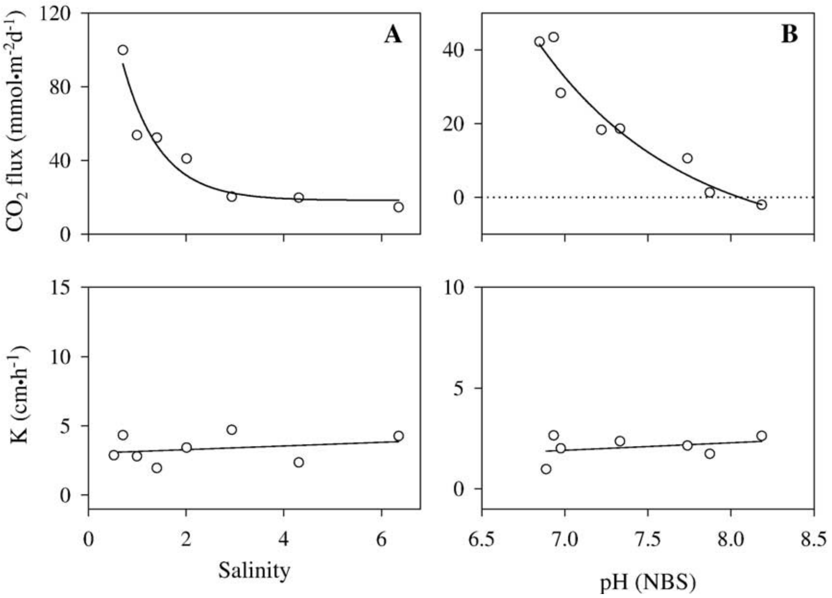

Fig. 5. (A) Evolution of CO_2 flux and gas-exchange coefficient (k) with salinity for a laboratory assay in which a certain salinity gradient was simulated. (B) Evolution of CO_2 flux and gas-exchange coefficient (k) with pH for a laboratory assay in which certain pH gradient was simulated (maintaining a constant salinity value in all tanks).

2000), where there are usually much more intense water–atmosphere fluxes of CO_2 in the more fluvial zone than at the mouth. However, the range of variation of the water–atmosphere fluxes of CO_2 found in estuaries is wide, and values higher than 1000 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ have been described in strongly anthropised estuaries (Frankignoulle et al., 1996). In the outer zone of estuaries, the water–atmosphere fluxes of CO_2 usually present a smaller range of variation (e.g., Frankignoulle et al., 1998).

The consistency of the values of CO_2 fluxes obtained in the simulator can be verified by analysing the gas-exchange coefficients (k) obtained in the different assays. These coefficients can be obtained from the fluxes of CO_2 by the expression

$$F = k\alpha(p_{\mathrm{CO_2SW}} - p_{\mathrm{CO_2AIR}})$$

where α is the solubility of CO_2 in function of the temperature and the salinity (Weiss, 1974), $p_{\mathrm{CO_2}}$SW is the partial pressure of CO_2 in the water of each tank, and $p_{\mathrm{CO_2}}$AIR = 365 μatm (www.cmdl.noaa.gov).

The values of k remained relatively constant with the salinity, as can be observed in Fig. 5(A). For this set of four experiments, an average value of k of 3.2 ± 1.0 $\text{cm} \cdot \text{h}^{-1}$ was obtained. If the experimental conditions are considered, these gas exchange coefficients of CO_2 would be compatible with those described at very low wind velocities. In this respect, the gas exchange coefficients at wind velocities lower than 2.4 $\text{m} \cdot \text{s}^{-1}$ remain relatively constant and are not well defined (Broecker et al., 1978; Wanninkhof et al., 1985). However, the values obtained are similar to those described by Ocampo-Torres et al. (1994) for wind velocities lower than 3 $\text{m} \cdot \text{s}^{-1}$ (k = 2.4–3.0 $\text{cm} \cdot \text{h}^{-1}$).

A certain turbulence degree in the air–water interface of the tanks can be found owing to two processes: the stirring system of each tank and the recirculation of the air contained in the tanks provoked by the IRGA system. Therefore, the k values estimated for each tank (average value = 3.2 ± 1.0 $\text{cm} \cdot \text{h}^{-1}$) correspond to a wind velocity value different from zero, although close to this value. These values seem to be too low for real environmental conditions close to the open sea.

To make comparisons, the gas-exchange coefficient (k) is often reported as k_{600} which is the k for CO_2 at 20 °C in fresh water, that is, k at Schmidt number of 600. While there are a number of measurement options and equations for choosing a value for k_{600}, the estimation of k_{600} is by far the most problematic term in the flux equation (Raymond and Cole, 2001). Developing accurate estimates of the gas-exchange coefficient in estuaries has become an important and controversial research goal in recent years (e.g., Carini et al., 1996; Raymond and Cole, 2001; Borges et al., 2004). Besides, Raymond and Cole (2001) suggested that the parameterization of k as a function of wind speed could be significantly different in estuarine environments from those developed in open oceanic waters (higher values of k in estuaries for the same wind speed).

Thus, it would be interesting to employ transfer velocity–wind speed relationships from the literature combined with wind speed data. This could allow comparing data of CO_2 fluxes estimated in the laboratory assays with data of fluxes extracted from literature. Owing to the controversy that implies the k estimation, we have selected two research studies (Raymond and Cole, 2001; Borges et al., 2004) since both have analysed a reasonably large data set of k values. Thus, CO_2 fluxes have been re-calculated employing the k_{600} values proposed by these authors to allow in this study the comparison to those of a real estuary.

Table 2 shows the ranges of variation of CO_2 fluxes water–atmosphere in the laboratory assays, employing different gas-exchange coefficients compiled from the bibliography.

As Table 2 shows, the lowest CO_2 fluxes are those obtained in this research, owing to the employ of the lowest k_{600} value since in laboratory assays k was obtained for a very low wind velocity. Obtained results prove the potential source of error when choosing a k for CO_2 studies. Substantial errors in flux computations are incurred if generic relationships of the gas transfer velocity as a function of wind speed are employed in estuarine environments (Borges et al., 2004). Extrapolation of laboratory data to obtain real values for CO_2 fluxes requires the employ of k values obtained in natural systems. It can be observed that the fluxes obtained are different depending on the employed k. Thus, it would be necessary to employ site-specific k values to avoid errors in flux calculations.

Table 2

Ranges of variation for CO_2 fluxes water–atmosphere (mmolm^{-2} day^{-1}) obtained in the laboratory assays, employing different gas-exchange coefficients compiled from the bibliography

Experiment	Flux 1	Flux 2	Flux 3
1	71.2–10.7	300.5–8.9	1141.2–33.9
2	74.3–15.1	141.5–20.5	537.8–77.6
3	93.2–15.6	134.2–33.4	509.9–127.2
4	99.8–14.6	201.3–27.1	765.1–102.7

Flux 1 was obtained employing the K_{600} average value estimated in this work (3.2 ± 1.0 cm · h^{-1}). Flux 2 was obtained employing a K_{600} value of 4 cm · h^{-1} according to Raymond and Cole (2001). They consider that this is a plausible value for an average estuary (based on the data available) with an average wind velocity of 4.6 m · s^{-1} (from wind data compiled for 39 coastal cities). Flux 3 has been obtained from average regression function between the gas-exchange coefficient (K_{600}) and wind speed at 10-m height (u_{10}) proposed by Borges et al. (2004). In order to compare data from flux 2 and flux 3, the same wind velocity of 4.6 m · s^{-1} has been employed. A K_{600} value of 15.2 was obtained.

Other processes that influence the behaviour of inorganic carbon in estuaries are primary production and the mineralisation of organic matter. In this respect, the outer part of estuaries frequently presents conditions of undersaturation with respect to atmospheric CO_2, related to high levels of phytoplankton activity (Frankignoulle et al., 1998; Borges and Frankignoulle, 1999) and with the presence of macroalgae deposited at the bottom (Howland et al., 2000). Furthermore, the respiration processes of organic matter and nitrification produce an acidification of the medium and an intensification of the fluxes with the atmosphere (Frankignoulle et al., 1996). All these biological processes can originate changes in pH values, which affect the dynamics of inorganic carbon and, therefore, to CO_2 fluxes. These changes in pH values can be studied in an approximate way by means of simulation assays. For this, Experiments 5, 6, and 7 were performed at constant salinity and with relatively wide pH gradients (Table 1) that can be considered representative of the ranges of variation found in real estuaries (Neal et al., 1998). Nevertheless, influence of primary producers and of sediment–water interaction is not possible to examine directly in this work.

In Fig. 5(B), it is shown how the CO_2 fluxes decrease with the increase of pH, with even inversions in the direction of the CO_2 flux appearing at a pH of 8.15 and above. These levels of pH producing inversion of CO_2 flux are similar to those found by Portielje and Lijklema (1995) in “ditches” with a high primary productivity associated with the abundance of macrophytes and benthic algae. It can also be observed in Fig. 5(b) how the values of k remain relatively constant over the length of the pH gradient in one of these experiments. The mean value of k for the set of three assays is 2.4 ± 0.3 cm · h^{-1}; this can be considered within the range of variation described at low wind velocities.

3.2. CO_2 flux in tidal regime

In addition to the assays in stationary regime, an experiment in the dynamic regime was conducted to verify the influence of the tidal regime on the water–atmosphere fluxes of CO_2. Fig. 6 shows the evolution of the salinity and pH with time during the course of 24 h of experimentation in four tanks of the simulator. It is observed how, in all the cases, both variables describe a sine-type function.

Having continuously measured the salinity, pH, and temperature and assuming that the inorganic carbon is conservative (Raymond et al., 2000), the evolution of the p_{CO_2} in the water over time has been estimated. In

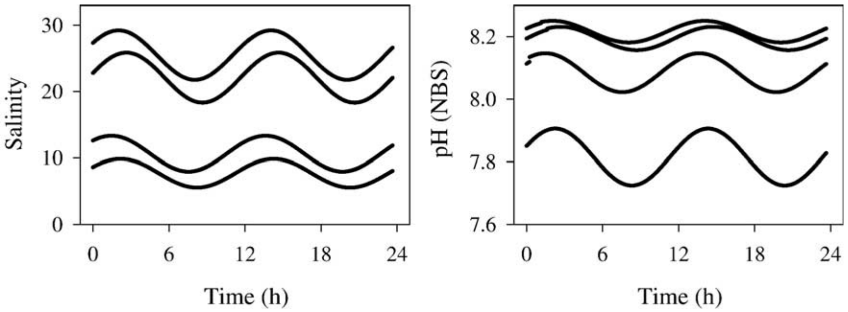

Fig. 6. Evolution of salinity and pH vs. time for four tanks of the simulator during 24 h of tidal regime assay.

this experiment, the water–atmosphere fluxes of CO_2 in each tank were measured every 30 min during a complete tidal cycle. Fig. 7 shows the variation with time of the salinity and the water–atmosphere fluxes of CO_2 in four tanks of the simulator. It can be observed that the CO_2 fluxes vary cyclically with time and describe a sinusoidal equation (as do the other variables, salinity and pH).

Therefore, the CO_2 flux presents a dependence on the input and output of sea water in the estuary. In addition, the maximum values of CO_2 flux coincide with the minimum values of salinity and vice versa. When the minimum salinity is recorded, the marine influence in the estuary is at a minimum, and the pH values are also lowest, and as a result, the largest water–atmosphere fluxes of CO_2 take place. When the maximum salinity is recorded, exactly the opposite occurs.

Although the variations depend on each tank, the water–atmosphere fluxes of CO_2 are less than those obtained in the experiments conducted in stationary regime and range between 48.85 and 5.12 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. This is because the pH values are more alkaline than in the assays under stationary regime, and their ranges of variation are also smaller.

Borges and Frankignoulle (1999) discovered this same behaviour of CO_2 on the coast near the mouth of the Scheldt estuary. The daily variations of CO_2 flux that they found in this zone were related to two phenomena: the tidal cycle (of the semidiurnal type) and the biological activity. In our experiment in dynamic regime, biological activity has to be discounted due to the design of the experiment. Therefore, the temporal variations of the CO_2 fluxes in the estuary are only related to the tidal cycle. This hypothesis seems to be correct according to the correspondence between salinity and flux observed in Fig. 7.

The simulation of estuaries in the laboratory is presented as a technique capable of reproducing the char-

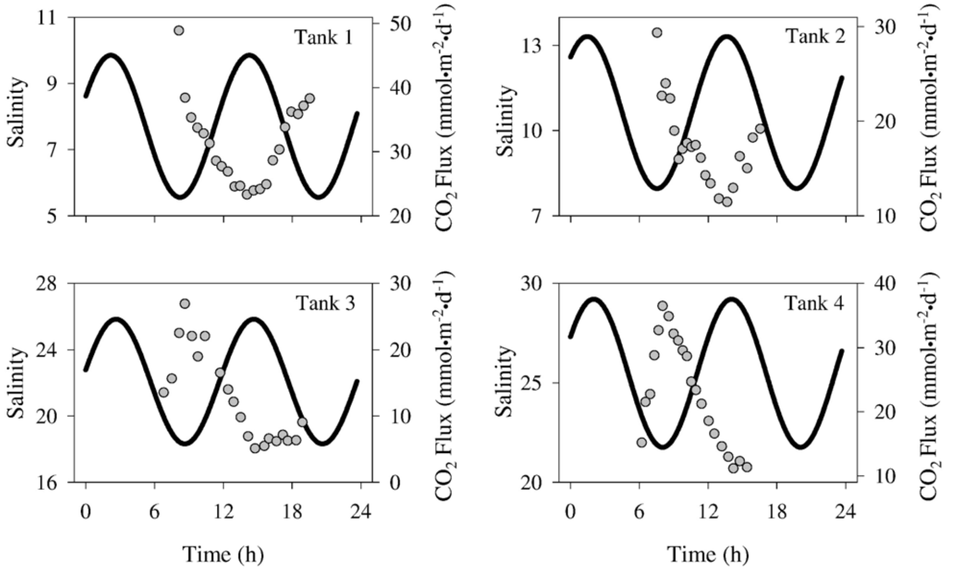

Fig. 7. Variation with time of salinity and CO_2 fluxes between atmosphere and water in four tanks of the simulator during one of the tidal regime assays.

acterization of certain atmosphere–water exchange processes of CO_2 in these areas. After analysing the results, it is concluded that a potential source of error exists when choosing the coefficients of gas exchange (k) for CO_2 studies. Nevertheless, the evolution of CO_2 fluxes along the salinity and pH gradients achieved show the same trends that those observed in a wide variety of real estuaries described in the related literature.

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