A NUMERICAL STUDY OF CO_2 DYNAMICS IN THE TAGUS ESTUARY

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CHAPTER SYNOPSIS

Background
Among the most important current issues in marine and freshwater geochemistry are the fluxes, sources, and mechanisms of CO_2 transport and transformation. Data of water-air CO_2 fluxes are available for some Portuguese estuarine systems. However, a numerical modelling approach was never implemented in these systems. This chapter reports on the development of an algorithm to simulate CO_2 exchanges at the water-air interface, and its application in a study case in the Tagus estuary.

Results
The modelling approach can be considered successful, inasmuch as the CO_2 dynamics has been modelled in a realistic way. The major spatial and seasonal patterns of CO_2 dynamics (CO_2 partial pressure and fluxes across the water-air interface) were adequately reproduced.

Conclusions
Based on the results exposed in this study and the comparison between them and field data, it can be stated that the major objectives of this modelling exercise have been achieved, namely, the simulation of the basic patterns of CO_2 dynamics in the estuary and the magnitude of values found in nature. So, even with some limitations, the model as it is can be used in coastal management context for studies of CO_2 export/import flux across the water-air interface.

1 COASTAL AND ESTUARINE DYNAMICS OF CO_2

Carbon entering the estuaries can be transported by various means and has different fates. A fraction will be emitted to the atmosphere in the form of CO_2, other will remain in the water column and in the sediment and other fraction will be exported to the nearby coastal area. The flux and/or residence of carbon in each of these compartments depend on the characteristics of each estuary as well as on the season of the year and time of the day the study is carried out. For example, in Scheldt estuary approximately 60% of the respiratory CO_2 is released to the atmosphere, 26% is transferred to the sediment and only 14% remains in the water column [1]. Moreover, within the estuary, spatial variability plays an important role due to the hydrodynamic and geomorphological complexity of these littoral zones. Thus, among the most important current issues in marine and freshwater geochemistry are the fluxes, sources, and mechanisms of CO_2 transport and transformation.

An aspect of the recent compilation of available water-air CO_2 fluxes in inner estuaries [2], is that the west European inner estuaries have been the more extensively studied, representing 47% of the total results presented. Still, inter-annual and decadal variability of water-air CO_2 fluxes is, so far, undocumented in some estuarine environments. Concerning Portugal, a country localized at the eastern boundary of the Subtropical North Atlantic, few studies have been undertaken [3]. As a matter of fact, data of water-air CO_2 fluxes are available for four Portuguese estuarine systems, the Aveiro Lagoon and the estuaries Douro, Sado and Tagus [3]. However, none of these studies uses a numerical modelling approach.

This chapter reports on the development of an algorithm to simulate CO_2 exchanges at the water-air interface, and its application in a study case in the Tagus estuary (Figure 1). The skill of the model to reproduce the CO_2 dynamics is qualitatively assessed by comparing the results with field data. This was the first attempt to model CO_2 dynamics in the water and its fluxes at the water-air interface with the MOHID modelling system.

2 ACCOUNTING FOR DISSOLVED CO_2 IN THE MODEL

CO_2 concentration in the water is controlled by a variety of physical, chemical and biological processes. The role of biological processes in CO_2 concentration, namely photosynthesis and cellular respiration, is already parameterized in the biogeochemical model as sink and source terms in the mass balance equation for the functional groups (producers, consumer and decomposers). As such, this section describes the new processes added to the model, and the algorithms that have been implemented to account for the role of physical processes in the dynamics of CO_2. The chemical reactions that influence DIC concentration were not considered under the assumption that in most estuarine and coastal systems the CO_2 dynamics is mostly controlled by biological processes.

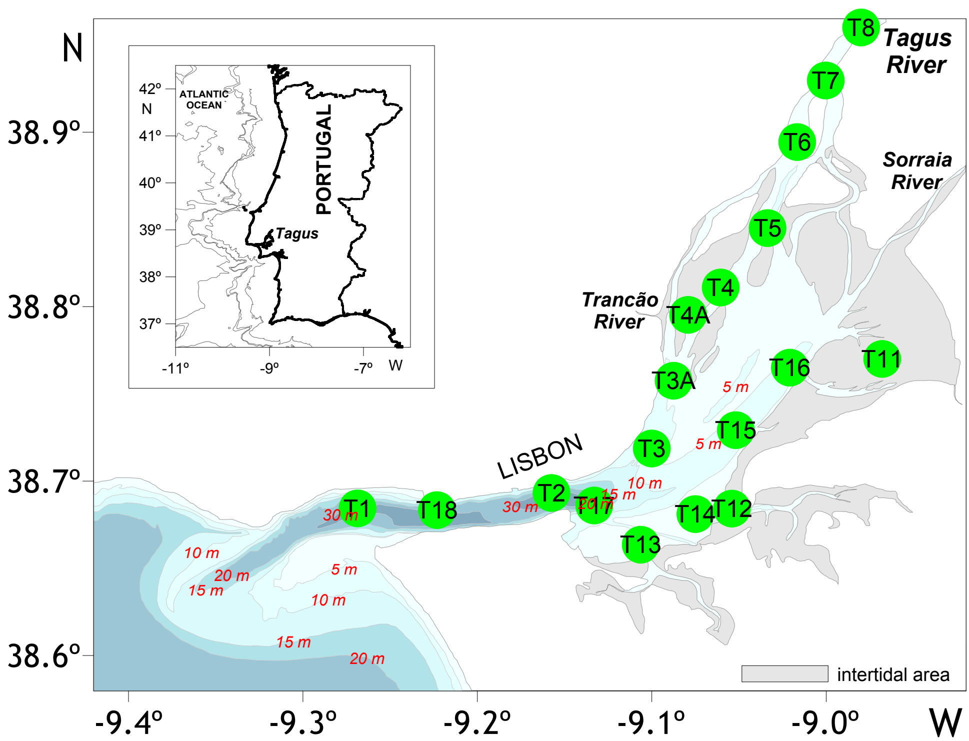

Figure 1. *Study site and the location of the sampling stations monitored.*

2.1 Modeling CO_2 fluxes in the water-air interface

As an integrated modelling system, the MOHID model has been used to study several processes in the Tagus estuary, including hydrodynamics, sediment dynamics, water quality, pollution and biogeochemical cycles in the water column [4-6]. However, the dynamics of CO_2 in the water and the fluxes of this gas across the water-air interface as never been studied before using MOHID. To accomplish this, the model had to be updated with new processes to link CO_2 dynamics in the water managed by the ecological/biogeochemical modules with the modules responsible for handling the gas fluxes in water-air interface.

The biogeochemical module at the base of this study consists in an algorithm that simulates the cycles of several elements such as nitrogen, phosphorus, silica and oxygen [7]. The module has 12 major components: producers, consumers, decomposers, organic matter (particulate, dissolved labile and semi-labile), nutrients (nitrate, ammonium, phosphate and silicate acid), biogenic silica and oxygen. Trophic interactions are expressed in terms of flux of carbon and nutrients by the model.

Borges et al. [8] constructed an empirical relationship to compute the gas transfer velocity of CO_2 (k, cm h^{-1}) that accounts for the contribution of wind and water current:

$$k = k_{OCD} + (1.0 + 2.58 \cdot u_{10}) \cdot \left(\frac{Sc\,(T,S)}{600}\right)^{-1/2} \tag{1}$$

where k_{OCD} is the conceptual relationship of O'Connor and Dobbins [9] for the water current, u_{10} (m s^{-1}) is the wind speed at 10 m above mean sea level, and $Sc(T,S)$ is the Schmidt number for CO_2 defined as a function of temperature and salinity.

O'Connor and Dobbins [9] formulation (k_{OCD}, cm h^{-1}) estimates the contribution of water current:

$$k_{OCD} = \left(1.719 \cdot \sqrt{\frac{v}{d}}\right) \cdot \left(\frac{Sc}{600}\right)^{-1/2} \tag{2}$$

where v (cm s^{-1}) is the water current, d (m) the mean depth of the water column, and Sc the Schmidt number determined using the polynomial relationship of Wanninkhof [10]:

$$\mathrm{Sc} = 2073.1 - 125.62 \times \mathrm{T} + 3.6276 \times \mathrm{T}^2 - 0.043219 \times \mathrm{T}^3 \tag{3}$$

Wind speed was referenced to a height of 10 m (u_{10}) using the algorithm given by Johnson [11]:

$$u_{10} = u \cdot \left(\frac{10}{z}\right)^{1/7} \Rightarrow \quad z \leq 20\,\mathrm{m} \tag{4}$$

where z (m) is the elevation above mean sea level at which the wind speed was measured.

The Schmidt number, a dimensionless ratio of the transfers of momentum and mass, was computed for a given salinity from the formulations for salinity 0 and 35 [10], and assuming that Schmidt number varies linearly with salinity:

$$Sc(T,S) = \frac{Sc(T,35) - Sc(T,0)}{35} \cdot S + Sc(T,0) \tag{5}$$

The $Sc(T, 35)$ and $Sc(T, 0)$ parameters are defined as:

$$Sc(T, 35) = 1953.4 - 128.0 \cdot T + 3.9918 \cdot T^2 - 0.050091 \cdot T^3 \quad (6)$$

$$Sc(T, 0) = 1800.6 - 120.10 \cdot T + 3.7818 \cdot T^2 - 0.047608 \cdot T^3 \quad (7)$$

2.2 Model setup

The geographic area of the model implementation is bounded by the coordinates 38°30' – 39° N and 8°51' – 9°51' W, stretching from the lower Tagus river section in the north, to the coastal area of the estuary mouth in the south. The modelled domain is composed of a variable step grid with 73×94 computation points, having higher resolution inside the estuary where the cells correspond to an approximated area of 372 km^2.

A two-dimension vertically integrated configuration was used, assuming that the intense mixing and shallowness of the estuary prevents the formation of vertical stratification. As such, only one vertical layer is used, having variable thickness depending on the bathymetry. Hydrodynamic and ecological models run with a time step of 60 s and 3600 s, respectively, during a 4-year period with repetitive annual forcing conditions.

2.2.1 Open boundary conditions and model forcing

Real wind conditions (direction and intensity) where prescribed as surface forcing, along with solar radiation and air relative humidity and temperature. Realistic river flow was used for rivers Tagus, Sorraia and Trancão. The effluent discharge of the waste water treatment plants (WWTP) inside the estuary is also considered in the application. All water inputs (rivers and WWTP) are characterized by flow, temperature, cohesive sediment concentration, and ecological parameters such as nutrients, organic matter, chlorophyll a (Chla), etc.

The values used to characterize water inputs and the open boundary conditions (OBD) were taken by similar previous studies of application of the model to the Tagus estuary [6, 12]. Given the importance of the wind regime in the gas fluxes at the water-air interface, a high-resolution forcing was adopted with hourly means calculated from a data set covering the period from 2001 and 2007 (Figure 2), measured at Portela Airport meteorological station in Lisbon.

2.2.2 Sampling

From 1999 to 2007 ten samplings were performed in Tagus estuary covering in an irregularly way the four seasons (Table 1). Nevertheless such samplings allowed characterizing the seasonal patterns of the estuary. Along the estuary a total of 18 stations were selected in order to study the spatial CO_2 distribution along the system (Figure 1). Surface seawater samples were collected during ebb conditions and along a salinity gradient with Niskin bottles.

In 2007 sampling was also performed at a fixed station (T18, see Figure 1) also covered four seasons and included two tide conditions (neap and spring). Surface water sampling was carried out at neap and spring tide every hour, for both tidal cycles (approximately 13 h). A total of 101 observations were recorded.

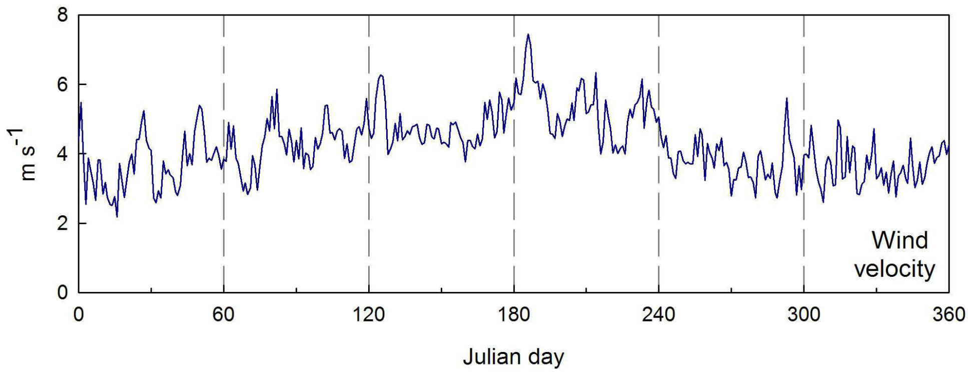

Figure 2. *Time-series for wind velocity prescribed as surface forcing in the model application. Hourly means calculated from a continuous time-series from 2001 to 2007, measured at the Portela Airport meteorological station in Lisbon.*

Table 1. *Sampling periods. Upwelling was present at the adjacent coastal shelf in the marked (*) periods.*

Season	Sampling periods	Season	Sampling periods
Winter	March 2001 February 2004	**Summer**	September 1999 * July 2001 * June 2002 *
Spring	May 2000 May 2003 * May 2006 * May 2007 *	**Autumn**	November 2006

3 MODEL RESULTS

The main purpose of this modelling experiment was to evaluate the skill of the model in reproducing the most relevant features and dynamics of CO_2 fluxes at the water-air interface in the estuary. As such, the results outlined here focus on the parameters and state-variables that determine or have a strong influence in this gas exchange. Accordingly, there is a significant quantity of results that are not addressed, considering that at the base of this application there is a rather complex biogeochemical model. Model validation for ecological and biogeochemical variables is also not presented here, since it is already presented in previous studies dealing with the modelling study of ecological processes in the Tagus [6, 12].

3.1 Nutrients and chlorophyll

Model results show a seasonal trend in nutrient concentration inside the estuary (Figure 3), as well as a distinct longitudinal pattern characterized by a decrease in concentration seaward. Higher values (> 1 mgN L^{-1}) in the upper and middle estuary are a consequence of the Tagus river discharge and its variation throughout the year. The contribution from the river is also relevant for phosphorus and silica concentrations in the estuary, thus making possible to define as a general rule that nutrient concentrations decreases with increasing distance from the river.

Together, nutrient and light availability exert a strong control on primary production and, consequently, Chla concentration. Since both nutrients and light radiation have a clear seasonal pattern, Chla concentration also has a similar pattern, as seen in Figure 4. River flushing also determines Chla concentration by regulating the residence time inside the estuary. The results also show a spatial pattern described by higher mean concentration in the mid and lower estuary.

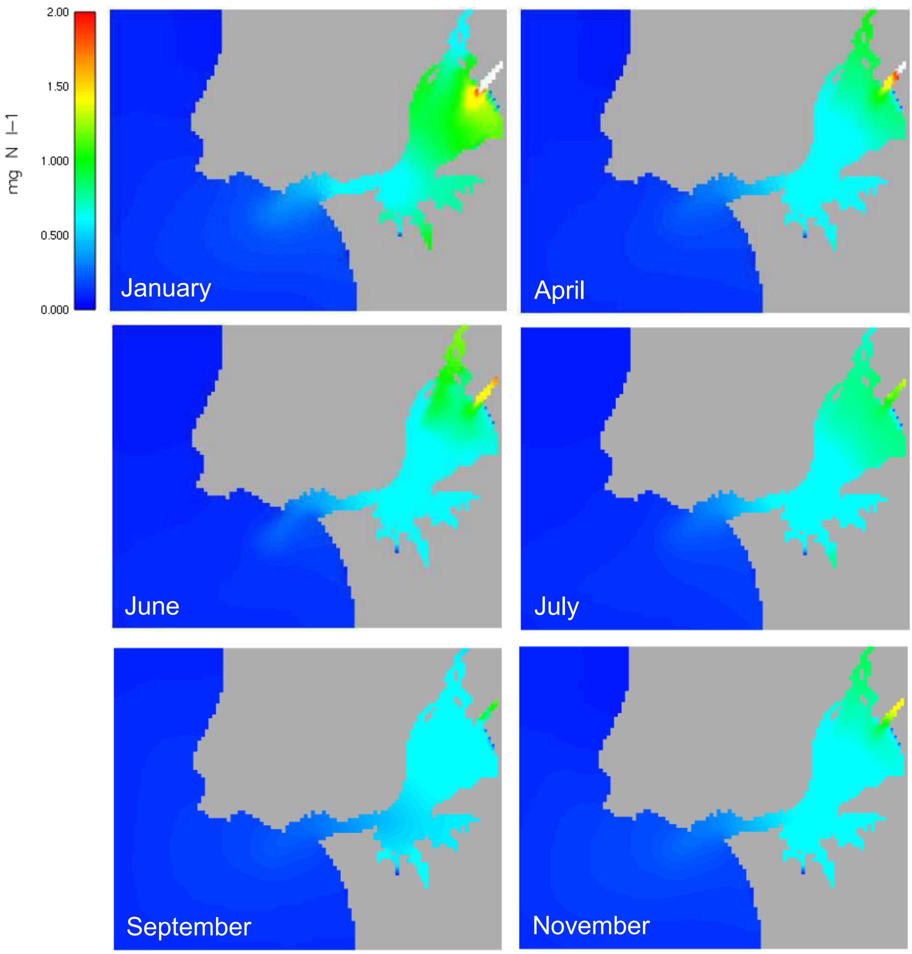

Figure 3. *Monthly means for nitrate concentration (mgN L^{-1}) calculated by the model from outputs with a temporal resolution of one hour.*

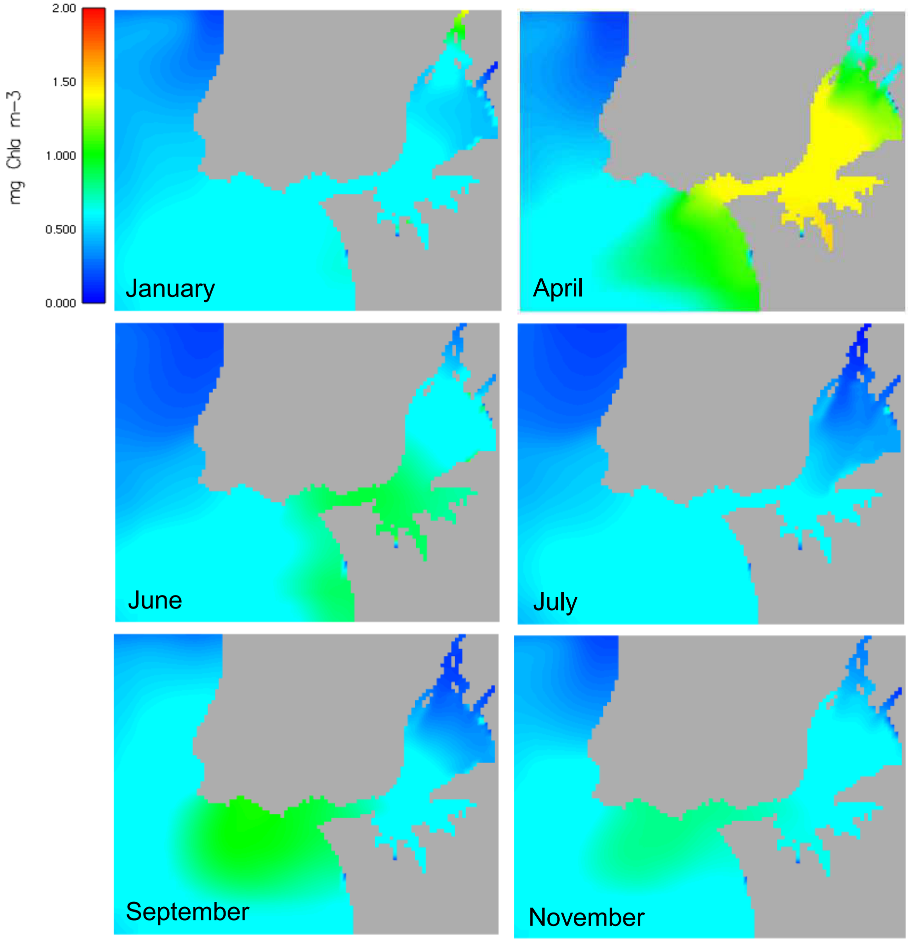

Figure 4. *Monthly means for Chla concentration (mg Chla m^{-3}) calculated by the model from outputs with a temporal resolution of one hour.*

Field data show that Chla concentration inside the estuary frequently peak at values around 12 to 15 mgChla m^{-3}. The values seen in Figure 4 are significantly lower because they correspond to monthly means, and not to discrete events. According to the results, higher values are observed in April, suggesting that the model may be anticipating optimal conditions for the growth of primary producers.

3.2 CO_2 partial pressure

Model predictions for the CO_2 partial pressure (pCO_2) in water are shown in Figure 5. There is a clear temporal and spatial variation in this property, with higher values ($\sim$500 μatm) usually found in upper estuarine areas all year around. In some parts under the direct influence of the Tagus river these concentrations are even higher. These results also show that

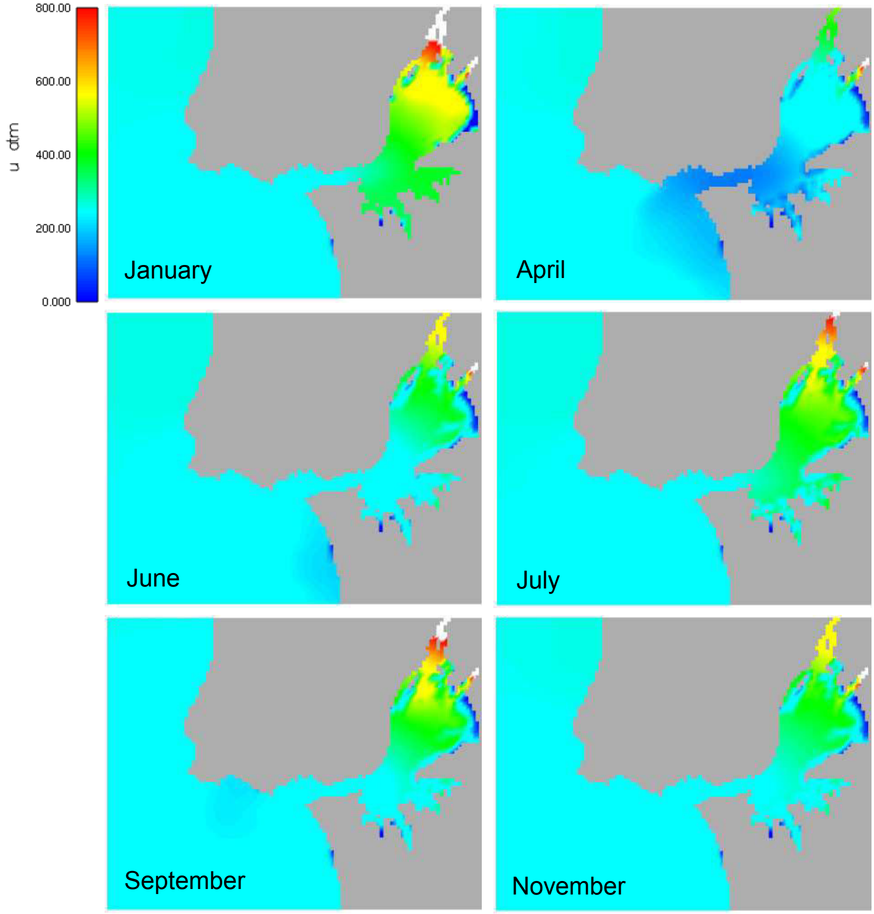

Figure 5. *Monthly means for CO_2 partial pressure (μatm) calculated by the model from outputs with a temporal resolution of one hour.*

the pCO$_2$ has its lower values ($<$400 μatm) during spring and early summer months in all estuarine range. The range of values seen in the model results are within the magnitude of values found in natural aquatic systems, denoting that the model is able to reproduce real CO_2 concentrations in water, both qualitatively and quantitatively.

The results for pCO$_2$ show that this property has an inverse relation with Chla concentrations. This inverse relation is particularly obvious during spring months, when the mean Chla concentration is higher and pCO$_2$ is lower. CO_2 and O_2 dynamics are both strongly conditioned by biological activity, specifically by means of primary production, cellular respiration and organic matter degradation (bacterial activity). During winter months, when respiration and organic matter degradation processes dominate, there is a surplus of CO_2 that is not absorbed by primary producers because ambient conditions are not favorable for growth. This explains the higher pCO_2 seen during those months. Primary production is eventually boosted in spring with the increase of light radiation, and since CO_2 is removed from the water during this process, consequently, pCO_2 decreases.

pCO_2 is also conditioned by water temperature, since the increase in temperature induces an increase in the metabolic rates (respiration) of organisms, thus intensifying O_2 consumption and CO_2 release. These processes may explain the pCO_2 values that are higher during July in the inner estuary, when compared with the values for September and December. The higher pCO_2 observed in the upper areas of the estuary can be the result of mineralization processes, given the higher concentrations of organic matter in this region. Finally, wind plays a decisive role in gas exchanges over the water-air interface, having a direct effect on pCO_2 in water. This process is addressed in the next section.

3.3 CO_2 fluxes in the water-air interface

Selected results for the CO_2 fluxes at the water-air interface are illustrated in Figure 6 for some of the monitored stations. Station selection for comparison purposes was based on their spatial distribution, in such a way to cover distinct zones of the estuary in terms of ambient conditions. These zones are the estuary mouth (T1), the north channel (T4A), the south margin (T12) and the river influence upper estuarine area (T6).

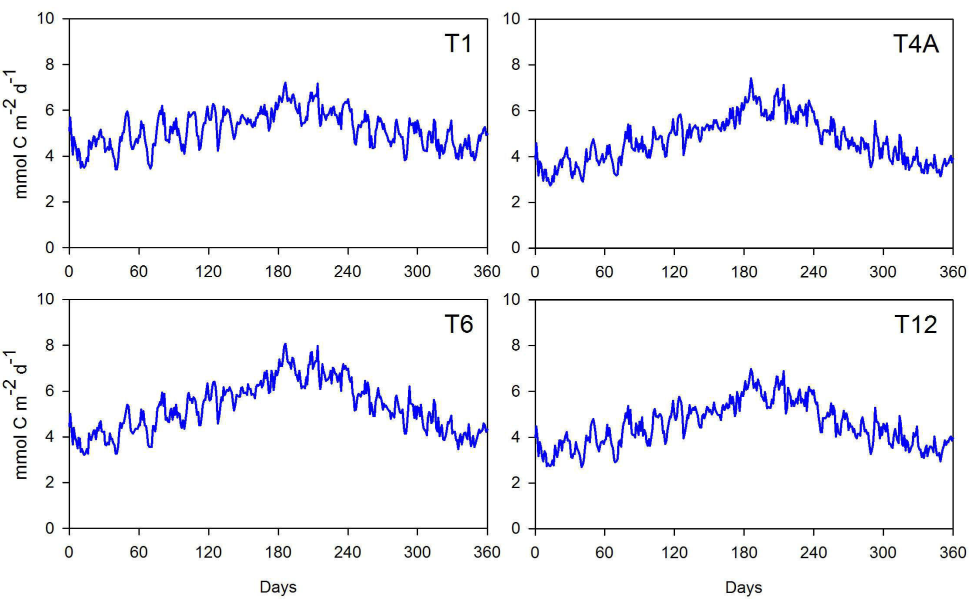

Figure 6. *Model results for mean water-air CO_2 fluxes (mmol C m^{-2} d^{-1}) at the estuary mouth (T1), the north channel (T4A), the south margin (T12) and the river influence upper estuarine area (T6) during an year of simulation.*

An inter-station comparison shows low spatial variation with values ranging between 3 and 8 mmol C m^{-2} d^{-1} (mean daily values) at all station. Nevertheless, station T6 has higher mean values when compared to others, which can be attributed to the higher $p$$CO_2$ and lower salinity in this section of the estuary. Station T1, at the mouth of estuary, also has higher comparative values during winter, an occurrence that can be explained by the higher current velocities in this area, a factor that is determinant in the parameterization used to calculate the fluxes at the interface [8, 13].

Field data show marked differences between stations, not coinciding with model results. Among the factors that may help to explain this difference, the most important are:

1. Differences in the physical conditions;
2. In situ fluxes were calculated based on instantaneous salinity, temperature and wind values, while in the model the fluxes are calculated with daily means for wind, and estimates of temperature and salinity;
3. Lack of realism in the estimative of the organic loads that reach the estuary via Tagus river and waste water treatment plants effluents;
4. Limitations inherent to the model parameterization.

The strong correlation between wind intensity and the CO_2 fluxes is evident in all stations. Higher values for the flux (>6 mmol C m^{-2} d^{-1}) occur during the period when the wind intensity is also higher, between the Julian days 150 and 240 (June – August). This correlation is corroborated by field data, highlighting the significant weight of wind contribution in the algorithm used to estimate the flux [13].

The model calculates instant CO_2 fluxes, accounting for the marked variations throughout the day that characterize both wind and currents regime. The results presented here, however,

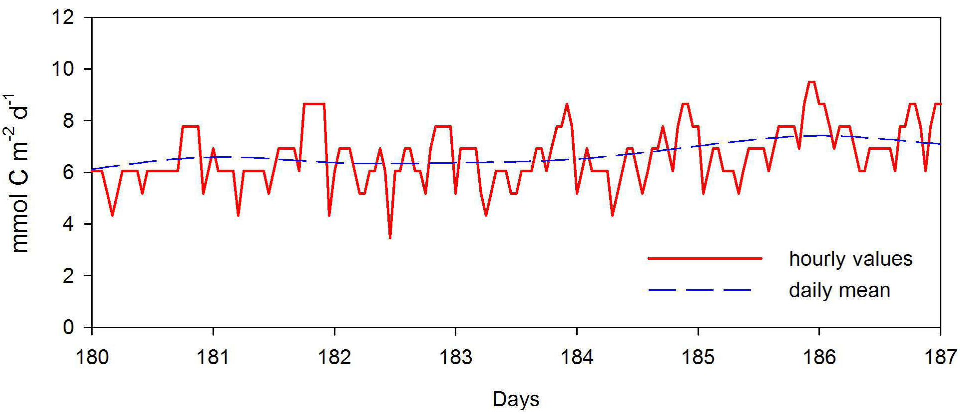

Figure 7. *CO_2 water-air flux variability at instant and hourly values (station T4A).*

correspond to daily mean values so that the daily variation is filtered, thus simplifying their analysis. This is illustrated in Figure 7 for a period of one week, where instant values (hourly resolution) for the flux are plotted together with daily mean values (Station T4A).

In some cases this variation can be even more accentuated, with fluxes varying between positive (water-air direction of the flux) and negative (air-water direction of the flux). This is observed in Figure 8, in which the flux varies between -15 and >35 mmol C m^{-2} d^{-1}. The results support the idea that, in respect to CO_2 dynamics, there are distinct zones in the estuary and adjacent coastal area, with some acting as both sources and sinks of CO_2 to the atmosphere. Given the relation between $p$$CO_2$ and the magnitude of CO_2 fluxes to and from the atmosphere, the distribution of $p$$CO_2$ is superimposed to all other processes affecting CO_2 fluxes. Model predictions show this relation in a clear way.

4 THE MODEL AS IT STANDS AND THE NEXT STEPS

The limitations of this initial attempt to model CO_2 dynamics in a coastal system are significant, as already discussed. Several code developments and model application improvements are needed for a more comprehensive and realistic modelling exercise of CO_2 fluxes in the Tagus estuary. Among the most relevant there is the:

- Development of a module to explicitly account for the kinetics of chemical reactions in the water and its control on pH variation;
- Increase of resolution and adequate temporal coverage in the forcing conditions, since the lack of adequate data imposed the application of mean conditions and not the values observed at the time of the campaigns;
- Inclusion of alternative parameterization and algorithms to calculate CO_2 fluxes;
- Simulate the temporal window of field campaigns using realistic forcing.

Despite all the limitation, this modelling approach can be considered successful, inasmuch as the CO_2 dynamics has been modelled in a realistic way. Based on the results exposed in this study and the comparison between them and field data, it can be stated that the major objectives of this modelling exercise have been achieved, namely, the simulation of the basic patterns of CO_2 dynamics in the estuary and the magnitude of values found in nature.

As a concluding remark from this work it can be said that even with the limitations, the model is adequate to be used for studies of CO_2 dynamics in coastal waters. In a coastal management context, the model may provide relevant information on the export/import flux across the water-air interface.

ACKNOWLEDGEMENTS

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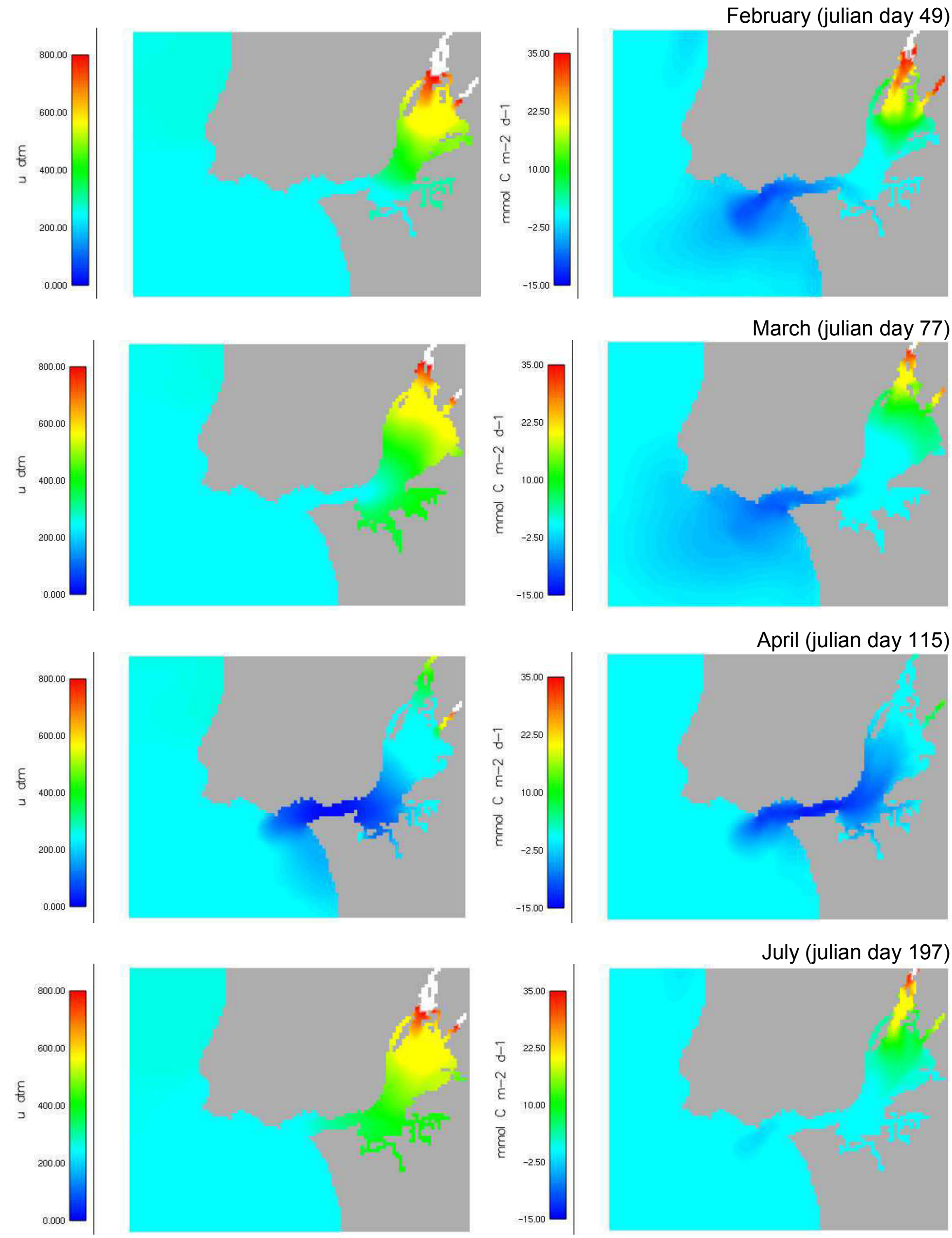

Figure 8. *Model results for instantaneous values of CO_2 partial pressure (μatm) and of CO_2 water-air fluxes (mmol C m^{-2} d^{-1}).*

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