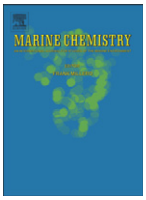
Marine Chemistry 110 (2008) 195–204

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem



Variability of the partial pressure of CO_2 on a daily-to-seasonal time scale in a shallow coastal system affected by intensive aquaculture activities (Bay of Cadiz, SW Iberian Peninsula)

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ARTICLE INFO

Article history:
Received 26 January 2007
Received in revised form 25 February 2008
Accepted 31 March 2008
Available online 9 April 2008

Keywords:
Carbon dioxide
Salt marshes
Seasonal variations
Air–water exchange
Aquaculture
Bay of Cadiz

ABSTRACT

The present study describes the temporal variability of the water fCO_2 as well as the different driving forces controlling this variability, on time scales from daily to seasonal, in the Rio San Pedro, a tidal creek located in a salt marsh area in the Bay of Cadiz (SW Iberian Peninsula). This shallow tidal creek system is affected by effluents of organic matter and nutrients from the surrounding marine fish farms. Continuous pCO_2, salinity and temperature were recorded for four periods of approximately one month, between February and September in 2004.

Major processes controlling the CO_2 variability are related to three different time scales. Daily variations in fCO_2 are controlled by tidal advection and mixing of the water from within the creek and the seawater that enters from the Bay of Cadiz. Significant cyclical variations of the fCO_2 have been observed with the maximum values occurring at low tide. On a fortnightly time scale, the amplitude of the daily variability of fCO_2 is modulated by the variations in the residence time of the water within the creek, which are related to the spring–neap tide sequence.

On a third time scale, high seasonal variability is observed for the temperature, salinity and fCO_2. Maximum and minimum values for fCO_2 were 380 µatm and 3760 µatm for February and July respectively. Data suggest that seasonal variability is related to the seasonal variability in discharges from the fish farm and to the increase with temperature of organic matter respiratory processes in the tidal creek. The fCO_2 values observed are in the same range as several highly polluted European estuaries or waters surrounding mangrove forests. From the air–water CO_2 flux computed, it can be concluded that the Rio San Pedro acts as a source of CO_2 to the atmosphere throughout the year, with the summer accounting for the higher average monthly flux.

1. Introduction

Despite their relatively modest surface area, coastal zones play a significant role in the carbon biogeochemical cycle because they receive massive inputs of terrestrial organic matter and nutrients; they are among the most geochemically and biologically active areas of the biosphere; and they exchange large amounts of matter and energy with the open ocean (Gattuso et al., 1998). The waters of salt marshes and their surroundings are significant sources of CO_2 to the atmosphere (Borges, 2005). The air–water CO_2 fluxes in this system are fuelled by net heterotrophy in the aquatic and sediment compartment, while aquatic primary production is usually low in most salt marsh systems and creeks, varying with geomorphology, water residence time, turbidity and nutrients delivery (Alongi, 1998; Gattuso et al., 1998; Borges, 2005).

The production of CO_2 in European coastal ecosystems, particularly estuaries, and the air-to-sea flux, has been studied in a few recent projects in the framework of EUROTROPH and the BIOGEST. Nevertheless, information on the production and

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doi:10.1016/j.marchem.2008.03.002

air–water exchange in other coastal ecosystems like salt marshes are rather scarce.

Future changes to the sea-air emissions of trace gases in the coastal zone are both directly and indirectly related to changes in socio-economic and natural drivers of global change (Pacyna and Mano, 2006). The direct relationship between relevant socio-economic drivers and coastal trace gas emissions is illustrated by the increasing input of precursors of nitrous oxide, methane, DMS and CO_2 to the sea. These precursors include organic matter and nutrients.

Alongi (2002) pointed out the significant impact of urban development and aquaculture on mangroves. Given the similarities between the two systems, salt marshes can be expected to suffer similar disturbances. Global production of farmed fish and shellfish in coastal zones has more than doubled in the past 15 years (Naylor et al., 2000) and as long as the human population continues to grow, present impacts will not diminish.

The Bay of Cadiz is becoming a focal point for intensive aquaculture in unlined ponds excavated from the natural soil. The total area devoted to aquaculture in 1994 in the Bay of Cadiz was 29.2 10^6 m^2 including extensive, semi-intensive and intensive farming systems (Marquez et al., 1996), and this has not changed significantly in the last decade. This development brings identified risks of negative environmental impact (Alongi, 2002). Attention has previously been focused on discharges of nutrients and organic matter, but thus far, only a limited number of studies are available on the CO_2 variability and air–water exchanges in these systems.

The main objective of the present paper is to investigate the variability on various different time scales of the partial pressure of CO_2 in the Rio San Pedro, a tidal creek running through the salt marsh area of the Bay of Cádiz; a secondary objective is to characterize the forces driving this variability, on scales from daily-to-seasonal periodicity. Daily air–water CO_2 fluxes have also been estimated.

2. Materials and methods

2.1. Study site

The Rio San Pedro is a tidal creek located in the Southwest of the Iberian Peninsula (Fig. 1). It used to be a distributary of the Guadalete River, but it was artificially blocked 12 km from the river mouth during the 1960s. Tidal exchange is usually the primary driving force for interactions between the tidal creek and the Bay of Cadiz. The main signature of the Rio San Pedro is seawater except for occasional freshwater inputs from rainfall and land drainage inputs. The Bay of Cadiz is a broad area of salt marshes subject to severe human pressure from increasing population density as well as from the aquaculture and other industries discharging into the Bay and the salt marsh inlets. Although the landscape surrounding the Rio San Pedro was originally formed by an extensive area of salt marshes, progressive exploitation by the human population, such as salt marsh desiccation by blockage, fish farm construction, salt production facilities, and other human activities, has significantly reduced the proportion of the area remaining as natural marsh. The actual channel of the Rio San Pedro is effectively isolated, laterally by means of an embankment that separates the channel from the various industries that exploit the salt marsh environment, and the more inland reaches of the creek are restricted by a dam, which allows some water exchange between the upper area of salt marshes and the tidal creek at times of very high water level. This human-made separation suggests that the influence of the salt marsh on the Rio San Pedro is only moderate. There is a fish farm located at the head of the creek (Fig. 1). Tovar et al. (2000b)

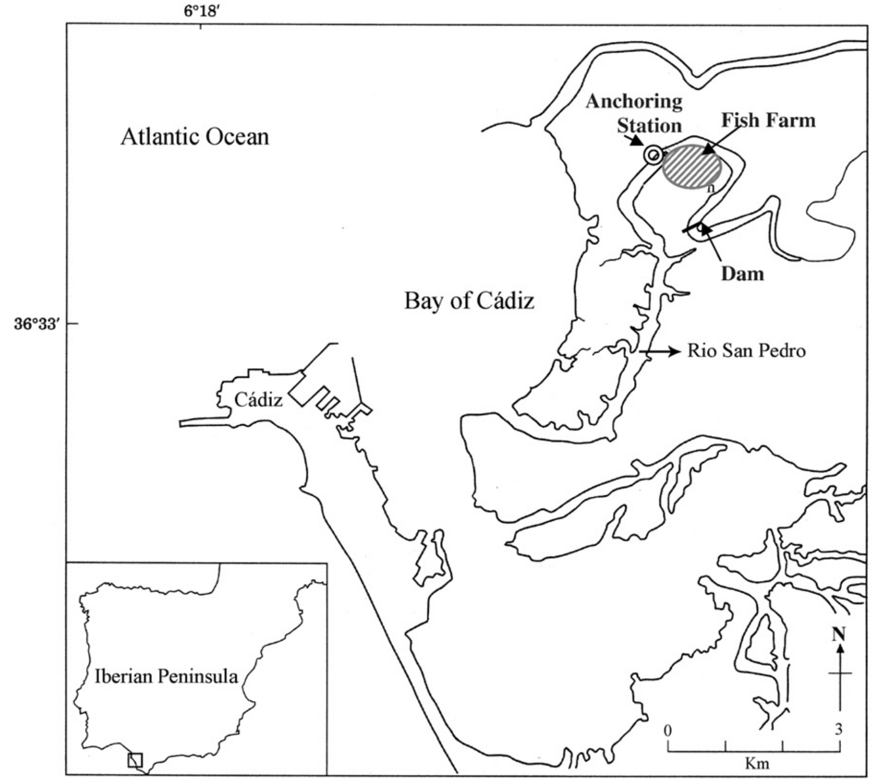

Fig. 1. Map of the Bay of Cádiz and the Rio San Pedro. Locations of the sampling station and the fish farms are indicated.

Table 1
Ranges of physico-chemical and meteorological data recorded for each sampling period

Sampling dates	Temperature (°C)	Salinity	Precipitation (mm month^{-1})	Wind speed (m s^{-1})	Evaporation (mm month^{-1})
February (13 Feb–8 Mar)	11.5–18.3	19.8–35.2	857	1–9.7	89
May (26 Apr–26 May)	16.5–24.0	31.0–35.7	674	1.9–12.2	173
July (29 Jun–29 Jul)	24.7–31.6	36.7–40.9	0	1–10.5	200
September (3 Sept–21 Sept)	22.2–27.3	35.6–39.7	0	0.5–7.7	125

determined the loading of large quantities of dissolved nutrients, organic matter and suspended solids in the effluents of the marine fish farm, which is dedicated to the intensive culture of gilthead seabream (*Sparus aurata*). According to this study, It was estimated that 9105 10^3 kg of suspended solids, 843 10^3 kg of particulate organic matter, 36 10^3 kg of N-NH^+_4, 5 10^3 kg of N-NO_2^-, 7 10^3 kg of N-NO_3^- and 3 10^3 kg of P-PO_4^{3-} dissolved in saline water were discharged annually to the Rio San Pedro (Tovar et al., 2000b). The total extension of the fish farm is about 1.3 km^2, where approximately 80% of this surface is occupied by water and its water volume is completely renewed once a day with the water of the Rio San Pedro.

2.2. Samplings and methods

The CO_2 partial pressure, salinity and temperature, of water pumped from 1–2 m depth to the surface, were continuously monitored at a fixed sampling station located 8 km distance from the mouth and 4 km from the head of the creek (Fig. 1, Table 1). Measurements were recorded, at a frequency of 1 min intervals. The sampling times were distributed seasonally in four separate periods of approximately 1 month: 13th February to 8th March, 26th April to 26th May, 29th June to 29th July, and 3rd September to 21st September.

Water salinity and temperature were measured, using a SeaBird thermosalinometer (Micro-SeaBird45), at the water intake of the pump and before its entry into the gas equilibrator. Temperature and salinity are estimated to be accurate to ±0.004 °C and ±0.005, respectively according to the SEABIRD calibration data. The equilibrator design is a combination of shower and bubble type similar to the system described by Körtzinger et al. (1996). The CO_2 mole fraction (xCO_2) was detected by means of a non-dispersive infrared gas analyzer (Li-Cor 6262) which was calibrated daily using two CO_2 standards of 523 ppm and 3000 ppm. Additional gas mixtures made and certified by Air-Liquide (France) were used; these have certified concentrations for CO_2 of 244.7 and 998 ppm. The temperature inside the equilibrator was measured continuously by means of a platinum resistance thermometer (PT100 probe). The temperature difference between the equilibrator and the water surface was around 0.7 °C. A highly accurate pressure transducer (Setra Systems: accurate to 0.05%) was used to monitor barometric pressure. The accuracy of the fCO_2 measurement system is <5 µatm.

The water saturated CO_2 fugacity (fCO_2) in the equilibrator was calculated from the xCO_2 in dry air, atmospheric pressure and equilibrium water vapour, according to the protocol described in DOE (1994). The formulation proposed by Takahashi et al. (1993) was employed for the partial pressure corrections to *in situ* water temperature.

In addition to the fCO_2 in the water, the atmospheric CO_2 molar fraction was measured at a frequency of 30 min. Monthly averaged atmospheric fCO_2 data were calculated for the CO_2 fluxes estimation.

Meteorological data including the daily precipitation, wind speeds (measured at 10 m height) and air temperature database were provided by the Instituto Nacional de Meteorología; data correspond to a meteorological station located about 15 km from the study site.

2.3. Hydrodynamic setting

The residence time of water within an aquatic system, or the length of time taken effectively to flush the system, is the strongest physical influence on water quality in the system. Residence time is often difficult to measure, so reliable estimates may be derived through the use of appropriate models (Sanford et al., 1992). In the case of the Rio San Pedro, this is a tidal creek where the only water input is by tidal exchange, not with the sea directly but with the Bay of Cadiz. The most predictable mechanism for flushing a small, well-mixed tidal system is the regular rise and fall of water of the astronomical tide, but a number of other factors also can affect the flushing, for instance winds, precipitation, and land drainage; however none of these are as predictable as the astronomical tides (Sanford et al., 1992).

Systems that are not well-mixed are likely to exhibit internal gradients of concentration, with areas remote from the open seawater mouth flushing more slowly than the rate predicted by tidal prism models. This is the case of the Rio San Pedro system, which presents a marked salinity gradient between the bay outlet and the inner creek part.

The water renewal, expressed as the percentage of water volume that leaves the tidal creek each tidal cycle, has been selected as the variable for relating the physico-chemical parameters of the Rio San Pedro with the water transport; actually this variable is the inverse of the flushing time:

$$\%\ \text{water renewal} = \frac{P}{P+V}$$

where *P* is the tidal prism volume–the water volume between low tide and high tide–and *V* is the water volume at low tide. Information must be available on the geometry of the channel and tidal elevations. The dimensions of the channel have been approximated to a constant width of 110 m, a datum depth of 3 m, and a length of 12 km. The heights at low and high tides have been obtained from the 2004 tide table provided by the Instituto Hidrográfico de la Marina.

The water budget can be complemented with the salt budget in order to perform a consistence test and to check the values obtained for *V* and *P* for

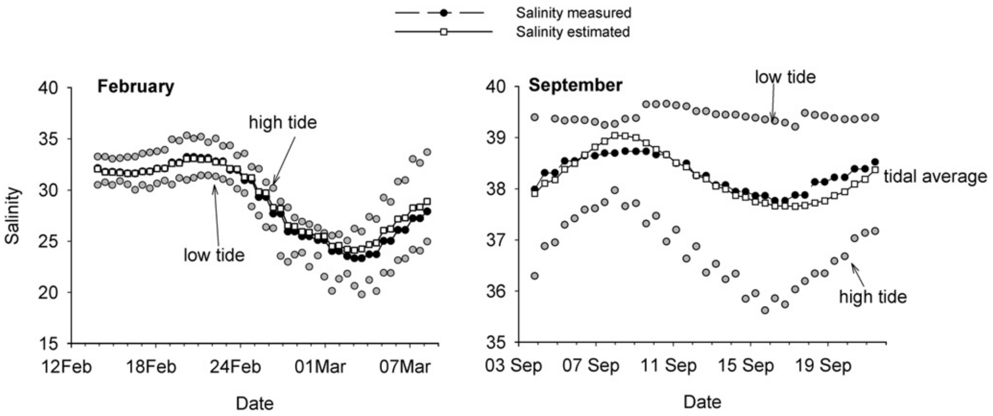

Fig. 2. Salinity measured at high tide, low tide, and daily average salinity for February and September. The calculated salinity (□) and measured salinity (●) have been included from the salt budget and tidal prism model.

each tidal cycle. Hence, a theoretical average salinity value can be calculated from the height at low and high tides and a constant salinity in both ends of the channel. The theoretical average salinity (S_T) can be formulated as:

$$S_T = (S_B P + S_C V)/(P + V)$$

where S_B and S_C are the salinity in the Bay of Cadiz and in the inner part of the San Pedro creek respectively.

The measured and theoretical tidal average salinity values can be compared in Fig. 2. The similarity between real and estimated salinity proves that on a fortnightly scale the variability in salinity is associated with the spring–neap tidal cycle; it also provides a check on the reliability of the V and P volumes estimated.

The maximum difference between the real and estimated value is around 1%, this is considerably less than the range of salinity values between high and low tides.

In order to assess the relative effects of the rain and water drainage on the water renewal rate, the salinity record for February and May has been analysed. The freshwater inputs have been determined as the water volume needed to dilute the average salinity with respect to a non-rainy initial situation for each month. The freshwater volume input (R) can be expressed as:

$$R = (V_M S_{T-NR})/S_{T-meas}$$

where V_M is the tidal averaged water volume ($V_M = V + P/2$); $S_{T\text{-}NR}$ is the non-rainy situation salinity calculated substituting S_B and S_C for two salinity constants measured before the rainy events in the expression (2), and $S_{T\text{-}meas}$ is the tidal averaged mean salinity measured. The estimation of the resulting corrected salinity for February has been included in Fig. 2.

3. Results

Fig. 3 presents the time series for temperature, salinity and CO_2 fugacity recorded, for the four periods sampled in 2004 in the Rio San Pedro. The ranges recorded for physico-chemical properties and meteorological data are also available in Table 1.

Temperature and salinity increase from February to July. The temperature of the system ranges between 12 °C on the first of March and 31 °C in July. The salinity value ranges between 20 in February and 41 recorded in July. The salinity in the tidal creek is strongly affected by the evaporation–precipitation ratio due to the shallowness of the system. February to May conditions are characterized by discrete precipitation, storms and diffuse land drainage inputs which make the water in the tidal creek fresher than the seawater of the Bay of Cádiz (Table 1, Fig. 1). The maximum salinity corresponds to a maximum in temperature and consequent higher evaporation in summer months (Table 1).

The fCO_2 data reflect the high seasonal variability in the creek. Minimum fCO_2 values occurred in February, ranging between 383 and 1595 µatm, and the maximum in July, with a range between 389 and 3763 µatm (Fig. 1). The amplitude of this oscillatory record increases significantly from February to July, indicating the considerable CO_2 variability of each end of the tidal creek.

4. Discussion

The factors governing the fCO_2 variability must be discussed in relation to each different time scale: daily, spring–neap tidal cycle, and seasonal.

4.1. Daily variability

In order to illustrate the daily variability the data recorded for salinity, temperature and fCO_2 in the Rio San Pedro have been plotted for one day in summer and winter as an example (Fig. 4). The tidal height is also given, displaying the semidiurnal signal typical of this area. Two patterns for salinity variability can be distinguished for winter and

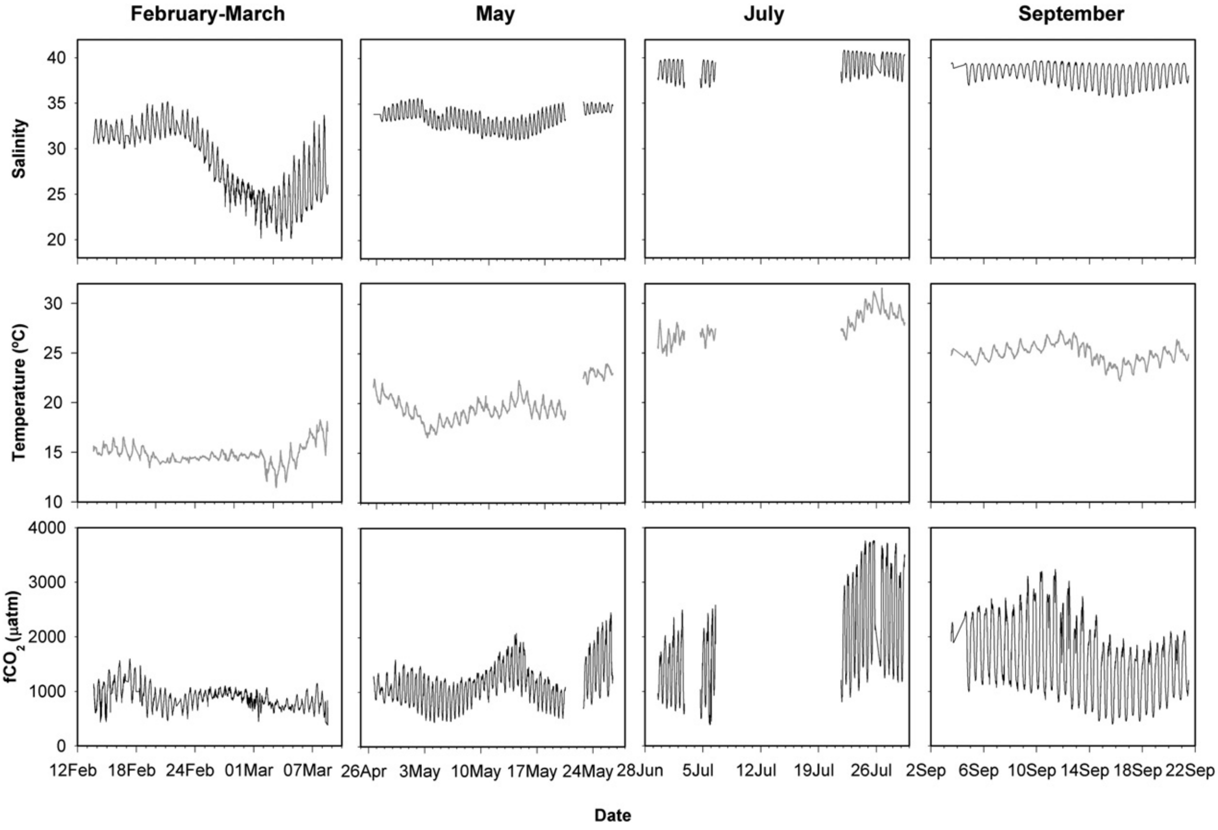

Fig. 3. Variations of salinity, temperature and fCO_2 recorded for the sampling periods.

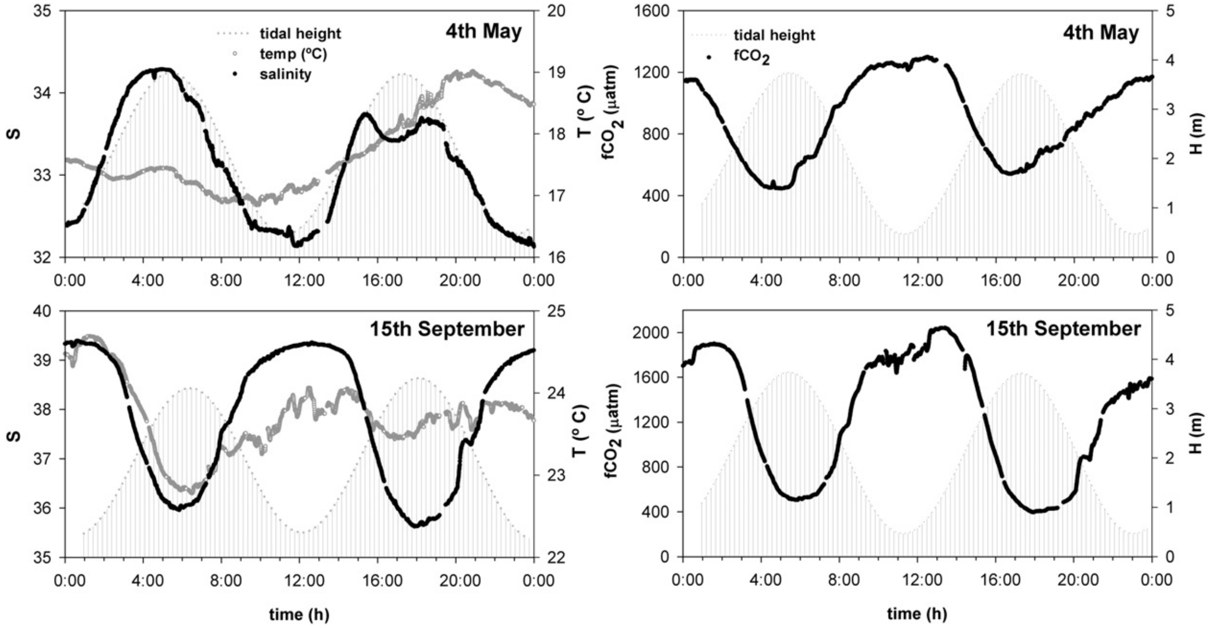

Fig. 4. Daily variation of salinity (S), temperature (T), tidal height (H) and CO_2 fugacity (fCO_2) for May and September.

summer situations inside the tidal creek. The common tendency is that salinity tracks the tidal advection with two maxima and two minima per day. Winter conditions are characterized by discrete precipitation, storms and lateral land drainage inputs making the water in the estuary fresher than the seawater of the Bay of Cadiz. The water of the Bay of Cadiz undergoes a smooth change in salinity compared to the tidal creek. Thus, the salinity shows a peak at high tide when the maximum water volume from outside has entered the creek. The summer situation is characterized by a total absence of freshwater inputs and the high temperature reached; as a result the creek water is more salty than the water from the Bay of Cádiz; thus high tide will be linked to a minimum in salinity. The daily temperature follows a day–night cycle and no temperature difference is observed between the two water masses (creek and bay). It presents high day–night variability (2–3 °C) in summer as well as in winter, probably due to the shallowness of the estuary. Consequently, the salinity closely tracks the tidal advection on a daily scale, even if there is a seasonal alternation in the sign of the slope of their relationship.

The CO_2 in the estuary is strongly influenced by the tidal advection and mixing of the two water masses of different CO_2 signature. On a daily time scale, the tidal cycle is the main mechanism responsible for CO_2 variations (Fig. 4). Maximum CO_2 values are linked to low tide, coinciding when the percentage of water from the inner creek is higher. Since the salinity changes its signature from winter to summer in the water of the creek, CO_2 peaks are linked to salinity minima in winter and to salinity maxima in summer.

The thermodynamics of temperature effects can be assessed according to Takahashi et al. (1993) using an average temperature for each sampling period. This method gives a correction of only 2% of the measured value, on average. Hence, it is suggested that the difference in the magnitude of fCO_2 between day and night is due to the different tidal height and not to effect of thermodynamics. The high fCO_2 values found at the innermost part of the creek are related to the direct CO_2 discharge from the fish farm as well as its high content of particulate organic matter, which reinforce the respiratory processes in the benthic and pelagic compartments, especially in the vicinity of fish farm effluent outlets. Other authors (Cai and Wang, 1998; Wang and Cai, 2004) emphasize the relevance of the lateral inputs of organic and inorganic carbon originating from the adjacent salt marshes via drainage and diffusion as the principal mechanism for maintaining the high respiratory rates and CO_2 values encountered in pristine salt marsh systems. However, in the Rio San Pedro, this natural lateral CO_2 source to the tidal creek has been largely reduced.

4.2. Spring–neap tidal variability

The variability over the time scale of spring and neap tides needs to be assessed by analysing the water renewal processes in the Rio San Pedro. Fig. 5 displays the water renewal for each tidal cycle, the average daily salinity and the precipitation for the 4 samplings periods from February to September. The water renewal follows an oscillatory variation with fortnightly periods, and the amplitude depends on the tidal coefficient. It oscillates from 15% to 50% of water renewed from the Bay of Cádiz at neap and spring tides respectively. This corresponds to residence times for water in the tidal creek at the sampling station of 3.5 days to 1 day respectively. It is worth noting that a spatial gradient exists in the residence time (or water renewal) along the length of the channel, so the renewal will be much less in the innermost part of the channel.

The precipitation would directly affect the tidal averaged water volume and salinity of the creek.This can be observed in the salinity records of February and May, which show a continuous decrease in the average day salinity coinciding with the rainfall events (19–28 Feb) even though the decreased

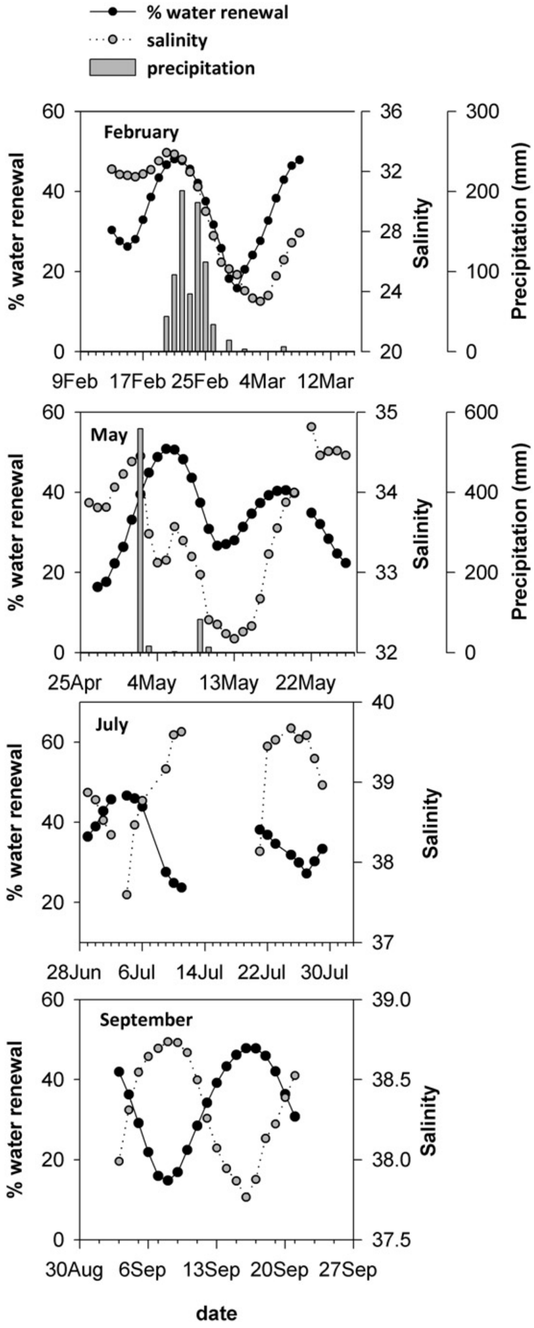

Fig. 5. Variations in water renewal (%), salinity and precipitation for the sampling periods.

salinity lasts for 10 days afterwards, due to lags in the land drainage freshwater input. The freshwater inputs estimated from the salinity record using expressions (2) and (3) lead to an increase of the water renewal by up to 4% for the 27th of February although on average it is around 2% from 23 February to 3 March. In May there is another rainfall event, which was more intense in quantity but only lasted 1 day, and resulted in a smaller decrease in average day salinity, which drops from 34.5 to 32.2. This freshwater input leads to an increase of the water renewal by up to 0.5% on 4 May, and on average it is 0.1%.The slight change in the water renewal suggests that rain and land drainage inputs are significant in terms of average salinity change but not very significant for the renewal of the water in the creek. Since the Rio San Pedro is subject to a moderate lateral isolation, the rain water mainly accumulates in the upper salt marsh area, which is subject to a periodic water exchange with the tidal creek, except when lateral inputs become more important as a result of storm events. The complex geometry of the salt marsh basin and the high surface/volume ratio in the zone of the fish farm causes a continuous and diffuse input of freshwater that is difficult to estimate. Apart from affecting the water and salt budgets, these salt marsh inputs also represent an important source of nutrients and organic matter. For February and May, higher water renewal rates are linked to higher tidally averaged salinities (Fig. 5). In the months of July and September, an inverse relationship can be observed between the average salinity and the % water renewal. These fortnightly spring–neap tide cycles can be significant in a long shallow channel and are a secondary mechanism of water mass movement along the tidal creek. This can have a major effect on the spatial distribution of dissolved compounds in salt marshes and mangrove systems (Dyer, 1997; Abril and Borges, 2004).

The salinity versus water renewal (%) (Fig. 6) shows that a direct relationship exists between high tide salinity and water renewal for dry months. In these periods, the salinity stays almost constant at low tide as a consequence of the low renewal of the water in the inner part of the creek. For rainy periods like February, salinity only loosely tracks the % water renewal.

Fig. 6 shows the $f\mathrm{CO}_2$ high tide and low tide values for each tidal cycle versus % water renewal. In February and May the $f\mathrm{CO}_2$-water renewal dependence is very loose due to the lateral inputs from land drainage caused by rainfall. The values are higher at low tide than at high tide for all the samplings performed. Also, the maximum values correspond to lower water renewal rates (neap tide). The $f\mathrm{CO}_2$ high tide difference between spring and neap tides is 150 µatm in February, 180 µatm in May, 1300 µatm in July and 810 µatm in September; the value of these differences will depend on the seasonality of the two different endmember water masses. In July and September there is a closer relationship between $f\mathrm{CO}_2$ and water renewal due to the absence of land drainage inputs. In dry months high tide $f\mathrm{CO}_2$ variability seems to be linked to the amount of dilution from the waters of the external Bay, while low tide $f\mathrm{CO}_2$ variability is linked to the consequences of the reduced renewal: less dilution from fish farm discharges and an increase in the organic matter respiratory processes because of the longer residence time of the water in the inner part of the channel. It can be observed how, in the cycle from one high tide to next, the $f\mathrm{CO}_2$ can increase or decrease by up to 25% (depending on whether it is from neap to spring or from spring to neap).

Furthermore, the $f\mathrm{CO}_2$ at high tide and low tide versus salinity marks the difference in the water properties between the two ends of the tidal creek. Tovar et al. (2000a) studied the longitudinal distribution of various physico-chemical properties and found two zones. The first, with a length of about 8 km, extends from the mouth to the location of sampling station of this study, and the second zone from our station to the end of the creek (4 km length). Tovar et al. (2000a) found

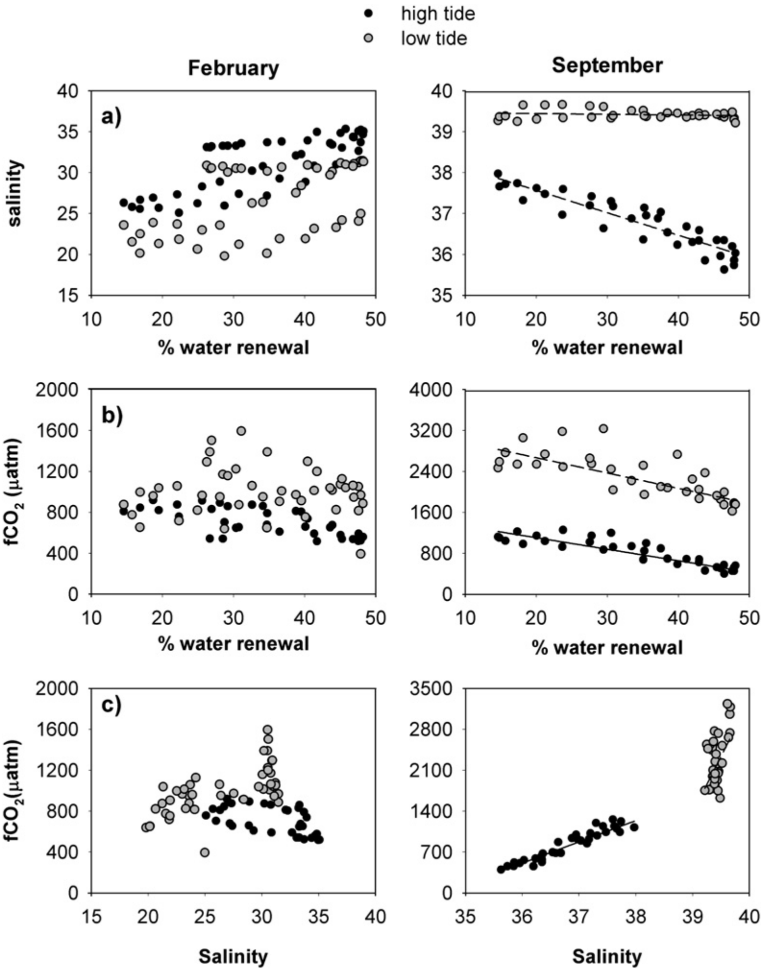

Fig. 6. For February and September, as extreme cases. Relationships between: a) Salinity and water renewal (%) obtained for February and September; b) fCO$_2$ and water renewal (%); c) fCO$_2$ and salinity.

that the inner zone was strongly affected by the discharges from the fish farm, and that the outer part was more controlled by tidal renewal.

Therefore, the spring–neap tidal variability on CO$_2$ seems to be controlled by the variability in the tidal water renewal in the creek, except for the rainy periods characterized by the allochthonous material inputs from diffuse land drainage.

4.3. Seasonal variability

As was shown in Fig. 4, the fCO$_2$ time series data reflect a high seasonal variability in the creek. In order to identify the factors driving this fCO$_2$ seasonality in the Rio San Pedro, the daily average values for salinity, temperature and fCO$_2$ have been calculated. Fig. 7 shows the daily average fCO$_2$ for the overall annual database versus salinity and temperature. The minimum values for daily average fCO$_2$ occurred in February with 610 µatm and the maximum values are 2940 µatm measured in July.

A direct relationship exists between the fCO$_2$ and the water temperature, with a minimum in February and a maximum in July. The evolution of fCO$_2$ values is the result of several different interrelated processes that increase the fCO$_2$. Firstly, the discharges of effluent from the fish farm are highly seasonal. Tovar et al. (2000b) studied the seasonality in the outflow of the fish farm over a two year period. In this study, an increase in the fish production cycle was observed with the temperature, with a maximum in summer and hence the maximum discharge of nutrients, dissolved organic carbon and particulate organic material to the tidal creek.

Secondly, the metabolic rates increase with the temperature in the water column of the tidal creek, which causes an increase in the respiratory rates, with a maximum in summer. This seasonal pattern, lower fCO$_2$ in winter and higher in summer months, has been described in several salt marsh systems like the Duplin River ((Wang and Cai, 2004) and the waters adjacent to salt marshes like the South Atlantic Bight (Cai et al., 2003). Wang and Cai (2004) suggested that temperature is probably a major factor mediating the respiratory release of inorganic carbon from the marshes. In contrast to the Rio San Pedro, the pristine Duplin River system studied by Wang and Cai (2004) is dominated by salt marshes and is characterized by high inputs of allochthonous dissolved

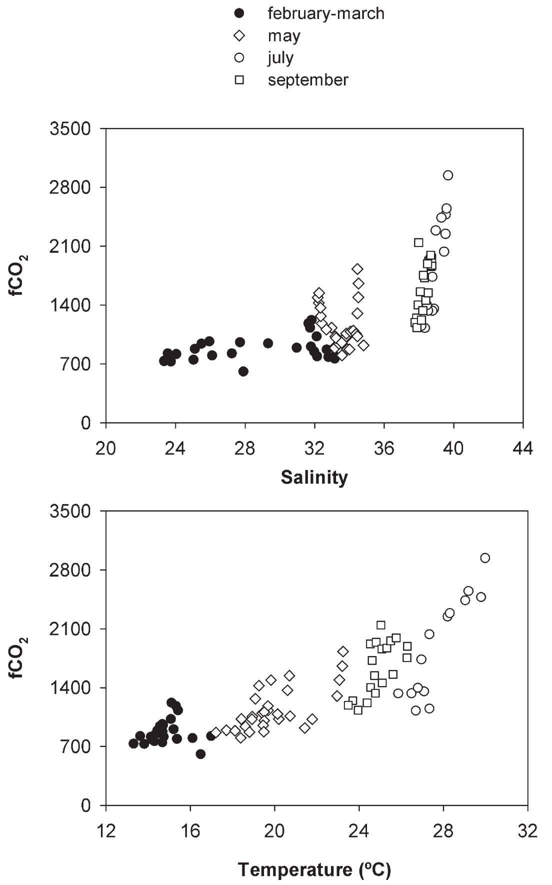

Fig. 7. Relationship between fCO_2 and salinity and temperature. Data were obtained by averaging daily records for the entire database available.

inorganic carbon (DIC) and organic matter as well as by the importance of organic carbon respiratory processes.

A previous study by Ferron et al. (2007) was carried out in the same study periods and at the same sampling station in the Rio San Pedro using chromatographic techniques for discrete samples. The CO_2 database described in the present study undergo a systematic difference of 15 µmol kg^{-1} below the CO_2 values reported by Ferron et al. (2007), which is a consequence of the different sampling strategies as well as the techniques employed for the CO_2 equilibration analysis. This systematic difference for CO_2 concentrations are in the same order of magnitude of the standard deviation for both databases (±17.4 µmol kg^{-1} in Ferron et al. (2007) and ±16.3 µmol kg^{-1} in the present study). Despite these differences, Ferron et al. (2007) obtained similar behaviour for CO_2 and other biogases such as CH_4 and N_2O in the Rio San Pedro from daily-to-seasonal temporal scales, thus corroborating the result obtained in this study.

The seasonal dependence of the fCO_2 on the salinity is similar to its dependence on the temperature since salinity is a function of the precipitation–evaporation balance. Nevertheless, the relationship is strongly affected by the precipitation in the months of February and May (see Fig. 7).

In addition to the impact of temperature and fish farm effluent discharges on the high fCO_2 observed, the DIC dynamics in the water column of salt marsh systems are significantly affected by diagenetic degradation processes (Wang and Cai, 2004; Borges, 2005), and these in turn are subject to a high temperature dependence.

The fCO_2 range observed in the Rio San Pedro (380–3760 µatm) is significantly high in comparison with open coastal water systems but is of the same order of magnitude as other natural or pristine ecosystems, like the mangrove and surrounding waters, where fCO_2 values range from 380 to 4800 µatm (Borges et al., 2003) or other estuaries dominated by natural salt marshes, where maximum fCO_2 values are reached in summer and fall; values range from 2000 to 3000 µatm in the Duplin River (Wang and Cai, 2004) and up to 6000 µatm in the Satilla River (Cai and Wang, 1998). Similarly, the fCO_2 values obtained in the Rio San Pedro are comparable to some highly polluted European estuaries for which information was compiled in several reviews of fCO_2 in coastal waters (Borges, 2005; Borges et al., 2006). The progressive human alteration of the natural salt marshes landscape adjacent to the Rio San Pedro suggests that CO_2 of natural origin plays only a moderate role, in comparison to the effects of fish farming on this tidal creek. At the present time, there are few studies on the effect of human-induced activities on the CO_2 dynamics in salt marshes, which reduces the possibilities for comparing the data of this study with those of similar systems.

4.4. Air–water CO_2 exchange

The CO_2 flux to the atmosphere is a function of the CO_2 partial pressure air–water gradient (ΔpCO_2) and the gas transfer velocity (k). Despite the availability of highly accurate and precise methods for determining ΔpCO_2, the greatest source of uncertainty in the calculation of gas flux arises from the rate term k in both open and coastal environment processes (Borges et al., 2004b). Rivers and estuaries are systems where wind and boundary friction act as sources of turbulent energy. Therefore, two different parameterizations have been used in the computation of k: a) the relationship of k as a function of wind speed, given by Carini et al. (1996) and based on a SF_6 experiment in the Parker River, and b) the relationship from O'Connor and Dobbins (1958) for k as a function of the water current. The result obtained by Zappa et al. (2003) and Borges et al. (2004a) in estuaries emphasized the relevance of the water current contribution to water turbulence, especially under low wind conditions and it is concluded that the best k in estuaries is the site specific measurement. The CO_2 flux has been computed from the daily average data for water fCO_2, the wind speed and water current module, as well as the monthly averaged value for atmospheric fCO_2. The daily values for the sampling periods computed for the different gas transfer velocities, the air–water CO_2 gradient and the air–water CO_2 flux using the k proposed by Carini et al. (1996) are shown in Fig. 8.

The water current ranges between 5 and 20 cm s^{-1}, and the gas transfer velocities calculated using the formulation of O'Connor and Dobbins (1958) reach a maximum value of 3.3 cm h^{-1} (Fig. 8). On the other hand, the k calculated with the wind speed relationship of Carini et al. (1996) has a maximum value of 23 cm h^{-1}. Because of the low values of water current speed found in the Rio San Pedro, it has been considered that the water current contribution is not significant for the gas

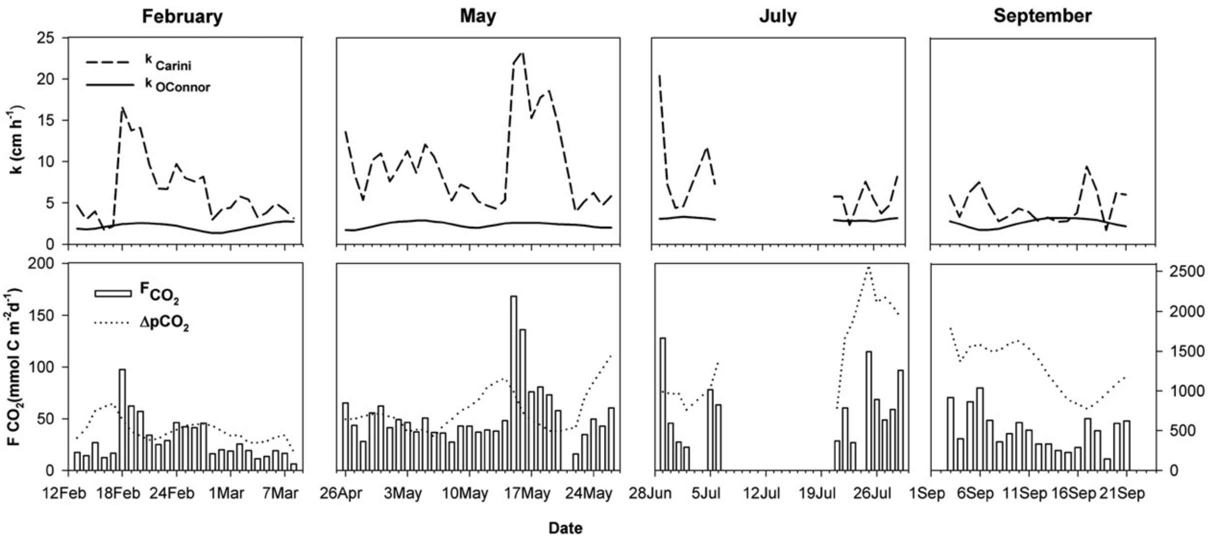

Fig. 8. Annual variations in gas exchange velocity obtained with different parameterizations, air–water CO_2 gradient (ΔpCO_2) and air–water CO_2 flux.

exchange in the Rio San Pedro compared to the wind speed; therefore the CO_2 flux has been calculated with the formulation of Carini et al. (1996).

The CO_2 flux ranges from 6 to 168 mmol m^{-2} d^{-1}, the minimum occurring in February and the maximum in May (Fig. 8). Similar CO_2 air–water fluxes were obtained by Ferron et al. (2007) using a combination of different gas transfer velocity parameters available in the literature, yielding CO_2 fluxes in the Rio San Pedro with values ranging from 73 to 177 mmol m^{-2} d^{-1}. The differences between the two studies may be due to differences in the parameterization and temporal resolution of each study. Throughout the year the water of the tidal creeks acts as a source of CO_2 to the atmosphere. The CO_2 flux does not follow a clear seasonal pattern due to the temporal evolution of the wind speeds. Despite the ΔpCO_2 showing a marked seasonal pattern, the highest wind speeds are recorded in May and hence are accompanied by maximum CO_2 flux. The highest monthly average CO_2 fluxes are in July as a result of the combination of high wind speeds and ΔpCO_2. Monthly variability in the CO_2 flux is controlled by the wind speeds.

4.5. CO_2 budget in the Rio San Pedro tidal creek

With the aim of comparing the various different CO_2 inputs and outputs in the Rio San Pedro tidal creek, the base of average annual data obtained in our study has been used. Additional information about the composition of fish farm discharges has been obtained from the existing literature. Tovar et al. (2000b) investigated the composition and net discharge of the effluent of the fish farm located in our study area, and reported average annual values of 235.40 10^3 kg of biochemical oxygen demand (BOD) and 843.20 10^3 kg of particulate organic matter (POM) per year. Assuming a respiratory quotient equal to 1, each mole of O_2 consumed liberates 1 mol of CO_2; hence the BOD discharge of 235.40 kg 10^3 O_2 yr^{-1} is equivalent to 7.35 10^6 mol CO_2 yr^{-1}.

On the other hand, the resulting annual CO_2 flux in this study is 46.23 mmol m^{-2} d^{-1}, and when this is multiplied by the water surface area of the Rio San Pedro, it represents an annual CO_2 emission of 22.16 mol CO_2 yr^{-1}. With this value it is possible to make an estimate of the percentage of the CO_2 flux in the Rio San Pedro due to the direct discharge from the fish farm; the result of this is that the fish farm is responsible for 33% of the CO_2 emission in the tidal creek.

In addition to the direct discharge of CO_2, the fish farm is also responsible for large quantities of CO_2 precursors in the form of particulate and dissolved organic material that are discharged into the tidal creek, where they are remineralized and produce more CO_2.

Apart from the air–water CO_2 fluxes, there are other mechanisms capable of exporting CO_2 from the system, such as the tidal exchange with the adjacent waters of the Bay of Cadiz. This exchange can be calculated from the tidal prism model following Sanford et al. (1992) substituting in expression (2) the CO_2 concentrations instead of salinity and assuming a volume exchange of P (tidal prism) for each tidal cycle. This CO_2 water export has been estimated to be 58 10^6 mol CO_2 yr^{-1}. This amount is double the average CO_2 emission to the atmosphere, and the finding suggests that the processes triggered by the fish farm discharges inside the tidal creek are also quite relevant. Although this budget is only a rough estimation, it gives an idea of the effect of the fish farm on the tidal creek, since there is no data available to differentiate the natural and anthropogenic components of the CO_2 fluxes in this system.

5. Conclusions

The results obtained in the present study describe the temporal variability of the water fCO_2 in the Rio San Pedro, as well as the different forces driving this variability on time scales from daily to seasonal. On a daily scale, tidal advection and mixing of two main water bodies are the main factors controlling the fCO_2 variations. Higher fCO_2 is always in phase with low tide waters, when the water of the inner tidal creek is measured. On a fortnightly time scale, a spring–neap tidal cycle is observed for the fCO_2 on the water surface. Neap tides lead to higher residence time of the water within the tidal creek, decreasing the direct outflows of the fish farm nutrients and organic matter effluent to the more open waters of the Bay of Cadiz, and this causes an increase in the *f*CO_2, due to organic matter respiratory processes. On the longest time scale considered, high seasonal variability is observed for the temperature, salinity and *f*CO_2. Maximum and minimum values for *f*CO_2 were 380 µatm and 3760 µatm for February and July respectively. Data suggest that seasonal variability is related to the seasonal variability of discharges from the fish farm and to the increase with temperature of organic matter respiratory processes in the tidal creek. The *f*CO_2 values observed are in the same range as several highly polluted European estuaries and waters surrounding mangrove forests. From the air–water CO_2 flux computed, it can be concluded that the Rio San Pedro acts as a source of CO_2 to the atmosphere throughout the entire the year, with the highest average monthly flux occurring in July. The net CO_2 output from the overall system of the tidal creek has been estimated from the air–water CO_2 fluxes and the tidal exchange. The CO_2 input directly discharged from the fish farm accounts for 8% of the total output. This finding highlights the relevance of *in situ* CO_2 generation in the tidal creek both by natural processes and by mineralization of the organic matter entrained with the fish farm discharges, but the separate effects of these processes cannot be discerned.

Acknowledgments

This work was supported by the Spanish CICYT (Comisión Interministerial de Ciencias y Tecnología) of the Ministerio de Educación y Ciencia under contract CTM2005-01364/MAR. Thanks are expressed to CYCEM “El Toruño” for providing the infrastructures and to Dr. O. Alvarez for his generous assistance with the processing of hydrodynamic data. Thanks to S. Ferrón for the help with the final version manuscript.

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