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# Seasonal study of dissolved $CH_4$, $CO_2$ and $N_2O$ in a shallow tidal system of the bay of Cádiz (SW Spain)

S. Ferrón *, T. Ortega, A. Gómez-Parra, J.M. Forja

*Departamento de Química Física, Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz,*
*Campus Río San Pedro, s/n. 11510, Puerto Real, Cádiz, Spain*

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## Abstract

During 2004, 10 samplings were performed in order to measure dissolved methane ($CH_4$), carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) in the surface waters of Río San Pedro, a tidal creek in the salt marsh area of the Bay of Cádiz (SW Spain). The inner partvs of the creek is affected by the inputs coming from an intensive fish farm and the drainage of an extensive salt marsh area.

Dissolved $CH_4$, $CO_2$ and $N_2O$ concentrations ranged from 11 to 88 nM, 36 to 108 μM and 14 to 50 nM, respectively. Surface waters were in all cases oversaturated with respect to the atmosphere, reaching values of up to 5000% for $CH_4$, 1240% for $CO_2$ and 840% for $N_2O$. Dissolved $CH_4$, $CO_2$ and $N_2O$ showed a significant tidal and seasonal variability. Over a tidal cycle, concentrations were always highest during low tide, which points to the influence of the inputs from the fish farm effluent and the drainage of the adjacent salt marsh area, as well as *in situ* production within the system. Dissolved $CH_4$, $CO_2$ and $N_2O$ seasonal patterns were similar and showed maximum concentrations in summer conditions. Using four different parameterizations to calculate the gas transfer coefficients [Liss, P.S. and Merlivat, L., 1986. Air-sea exchange rates: introduction and synthesis. In P. Buat-Ménard (Ed.), The Role of Air-Sea Exchanges in Geochemical Cycling. Reidel, Dordrecht, The Netherlands, p. 113–127.; Clark, J.F., Schlosser, P., Simpson, H.J., Stute, M., Wanninkhof, R., and Ho, D.T., 1995. Relationship between gas transfer velocities and wind speeds in the tidal Hudson River determined by the dual tracer technique. In: B. Jähne and E. Monahan (Eds.), Air-Water Gas Transfer: AEON Verlag and Studio, Hanau, Germany, pp. 785–800.; Carini, S., Weston, N., Hopkinson, G., Tucker, J., Giblin, A. and Vallino, J., 1996. Gas exchanges rates in the Parker River estuary, Massachusetts. Biol. Bull., 191: 333–334.; Kremer, J.N., Reischauer, A. and D'Avanzo, C., 2003. Estuary-specific variation in the air-water gas exchange coefficient for oxygen. Estuaries, 26: 829–836.], the averaged air–water fluxes of $CH_4$, $CO_2$ and $N_2O$ from the creek to the atmosphere ranged between 34 and 150 μmol $CH_4$ $m^{-2}$ $day^{-1}$, 73 and 177 mmol $CO_2$ $m^{-2}$ $day^{-1}$ and 24 and 62 μmol $N_2O$ $m^{-2}$ $day^{-1}$, respectively.

*Keywords:* Methane; Carbon dioxide; Nitrous oxide; Greenhouse gases; Coastal system; Air–water fluxes

## 1. Introduction

Methane ($CH_4$), nitrous oxide ($N_2O$) and carbon dioxide ($CO_2$) are important atmospheric gases that contribute to global warming. In the troposphere they act as greenhouse gases (Rodhe, 1990). $CO_2$ accounts for approximately 55% of anthropogenic greenhouse warming (Mackenzie, 1998). Despite their lower concentrations in the atmosphere, $CH_4$ and $N_2O$ absorb infrared radiation much more intensely than $CO_2$ (Lashof and Ahuja, 1990). They contribute, respectively, about 15% (Houghton et al., 1990) and 5–6% (Lashof and Ahuja, 1990; Rodhe, 1990) to the anthropogenic greenhouse effect.

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* Corresponding author. Tel.: +34 956 016164; fax: +34 956 016040.
*E-mail address:* sara.ferron@uca.es (S. Ferrón).

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Whereas $CO_2$ is practically inert in the atmosphere, $CH_4$ and $N_2O$ are key compounds in chemical reaction cycles in the troposphere and stratosphere. $CH_4$ reacts photo-chemically in the troposphere affecting $O_3$ and OH radical concentrations, and it is also an important source of stratospheric $H_2O$ (Crutzen, 1991). Stratospheric $N_2O$ is the major source of NO radicals which are involved in the depletion of stratospheric ozone (Crutzen and Schmailzl, 1983).

Atmospheric concentrations of $CH_4$, $CO_2$ and $N_2O$ have been increasing significantly since pre-industrial times (Weiss, 1981a; Barnola et al., 1987; Blake and Rowland, 1988), which indicates that sources are larger than sinks. The role of the oceans, and particularly coastal regions, to the global budgets of $CH_4$, $CO_2$ and $N_2O$ is still uncertain, in part due to the limited database available and the neglect of seasonal variability. The contribution of the oceans to global emissions of atmospheric $N_2O$ was estimated to be about 13% (Khalil and Rasmussen, 1992). In the case of $CH_4$, oceans play only a modest role in its global budget, accounting for 0.1% to 4% of the total atmospheric emissions (Crutzen, 1991). But these oceanic emissions of $N_2O$ and $CH_4$ are not homogeneously distributed. Hence, biological productive regions, such as estuaries and coastal areas contribute about 75% to the global oceanic $CH_4$ production (Bange et al., 1994) and 35–60% of oceanic $N_2O$ emissions (Bange et al., 1996a; Seitzinger et al., 2000).

On a global scale, the oceans are a net atmospheric sink for $CO_2$. The global ocean's net annual uptake of anthropogenic $CO_2$ is calculated to be 1.9–2.2 Pg C $\text{year}^{-1}$ (Sarmiento and Gruber, 2002; Takahashi et al., 2002). The coastal ocean, although it plays a key role in the global carbon cycle (Gattuso et al., 1998; Wollast, 1998), has largely been ignored by modelers in global carbon budgets. Some recent studies have shown that temperate continental shelves behave as significant sinks for atmospheric $CO_2$ (Tsunongai et al., 1999; Frankignoulle and Borges, 2001; Chen et al., 2003; Thomas et al., 2004), whereas tropical and subtropical shelves can act as sources of $CO_2$ (Cai et al., 2003; Ito et al., 2005). Estuaries are considered to be strong sources of $CO_2$ to the atmosphere (Cai and Wang, 1998; Frankignoulle et al., 1998; Raymond et al., 2000; Abril and Borges, 2004). A very comprehensive compilation of $pCO_2$ and air–water $CO_2$ fluxes in different coastal ecosystems is reported in Borges (2005) and Borges et al. (2005).

In near-shore coastal ecosystems, the increased nutrient load due to human activities can enhance net ecosystem production. If light becomes limited, respiration becomes the main metabolic process and the system becomes more heterotrophic and can turn into a potential source of $CO_2$ to the atmosphere (Gattuso et al., 1998). Reducing conditions in bottom waters associated with inputs of inorganic and organic nitrogen can increase denitrification and nitrification rates, and thus $N_2O$ production (Barnes and Owens, 1998). Due to the shallowness of these systems, a large fraction of labile organic matter can be deposited in the sediments (Wollast, 1998), which generate favorable conditions for the microbial production of methane (Bange et al., 1998). Biogenic methane is produced exclusively by a group of strict anaerobes (methanogens) during methanogenesis. This process occurs in the sediments, in the interior of suspended particles and in the guts of marine organisms (Wolfe, 1971).

In this paper, we present for the first time the seasonal and tidal variations of dissolved $CH_4$, $CO_2$ and $N_2O$ concentrations in Río San Pedro, a tidal creek of the salt marsh area of the Bay of Cadiz (SW Spain). We also estimate the fluxes of these gases to the atmosphere.

## 2. Study area

The area of study is Río San Pedro, a shallow tidal creek located within the salt marsh area of the Bay of Cádiz (SW Spain) (36°23′–37′N, 6°8′–15′W) (Fig. 1). It is characterized by semi-diurnal mesotides (average tidal range 0.98–3.20 m). The tidal current flows from the bay along the creek where the freshwater inflow is not significant, except during heavy rains. The creek is 12 km long, its width ranges from 15 to 30 m and it has a maximum depth of 5–6 m. The water column is well mixed with no significant salinity differences between the surface and the bottom (González-Gordillo et al., 2003).

The system receives the inputs of organic matter and nutrients coming from the wastewater discharges of a fish farm located in the upper part of the creek. This farm, with an extension of about $5.7 \cdot 10^6$ $m^2$ (Tovar et al., 2000b), cultures in an intensive regime around $10^6$ kg $\text{year}^{-1}$ of *Sparus aurata*. Approximately 80% of its extension is occupied by ponds of about 1 m deep, which are dug directly into the ground. Thus, the inundated extension of the fish farm (~4.5 $km^2$) is about 10 times bigger than the total surface of the creek (~0.36 $km^2$). The total volume of water introduced daily by the fish farm ranges from 181,151 $m^3$ to 287,795 $m^3$ (Tovar et al., 2000b). Tovar et al. (2000b) estimated the total amount of dissolved nutrients, total suspended solids (TSS), particulate organic matter (POM) and biochemical oxygen demand ($BOD_5$) that the fish farm discharged into the receiving waters for each tonne of cultured fish. According to this, approximately $9.1 \cdot 10^6$ kg TSS $\text{year}^{-1}$, $8.4 \cdot 10^5$ kg POM $\text{year}^{-1}$, $2.4 \cdot 10^5$ kg BOD $\text{year}^{-1}$, $3.6 \cdot 10^3$ kg N-$NH_4^+$ $\text{year}^{-1}$,

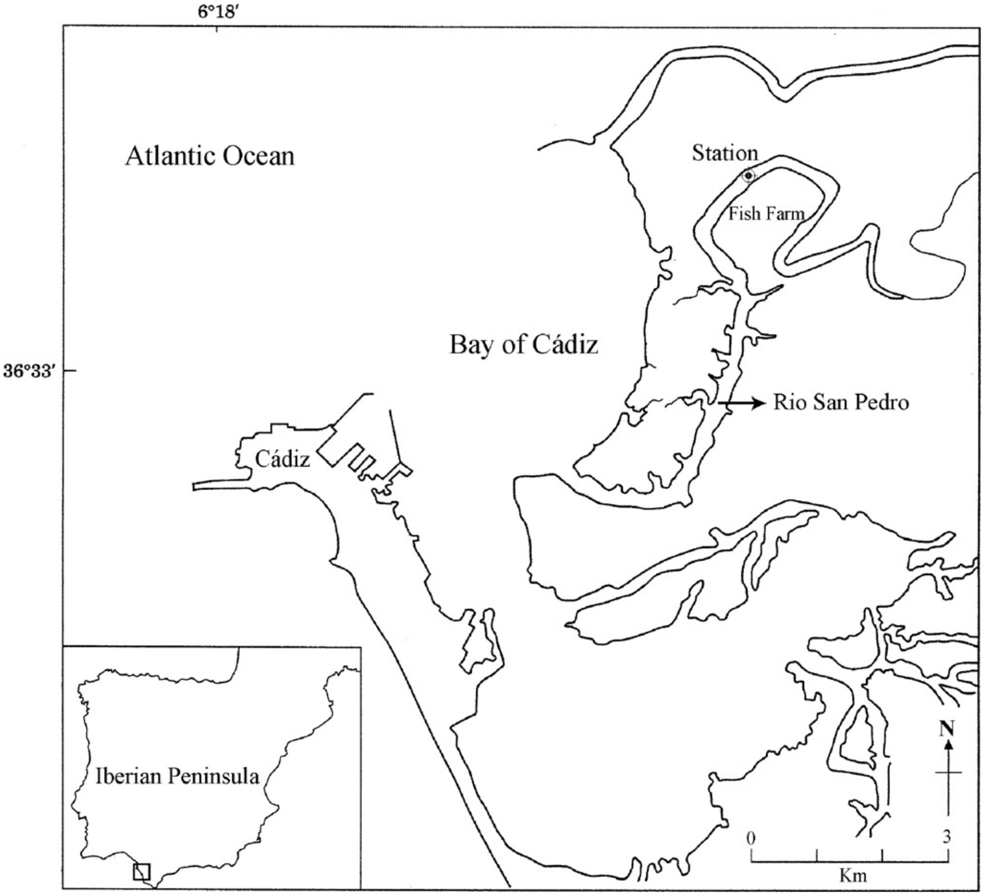

Fig. 1. Map of the Bay of Cádiz and the Río San Pedro creek, showing the location of the sampling station.

$5.0 \cdot 10^3$ kg N-$NO_2^-$ year$^{-1}$, $6.7 \cdot 10^3$ kg N-$NO_3^-$ year$^{-1}$ and $2.6 \cdot 10^3$ kg P-$PO_4^{3-}$ year$^{-1}$ are discharged annually into the environment.

Furthermore, the upper part of Río San Pedro also receives the drainage of an extensive but very shallow salt marsh area.

## 3. Materials and methods

Between February and October 2004, 10 samplings were performed at a fixed station in Río San Pedro, comprising different tidal conditions. Sampling dates and physicochemical parameters are detailed in Table 1. In each sampling, water samples were taken every hour at 1 m depth covering one tidal cycle (approximately 13 h). Samples were drawn in 100 ml air-tight glass bottles, preserved with saturated mercuric chloride to inhibit microbial activity and sealed with Apiezon® grease to prevent gas exchange. They were stored in the dark until analysis in the laboratory within a week of collection. All samples were collected and analyzed in duplicate. Temperature and salinity were continuously recorded at the station by a thermosalinometer (MicroTSG-SBD 45).

Dissolved gases concentrations were determined by gas chromatography. A head space technique was used to extract the dissolved gases from the water sample. A predetermined volume (approximately 20 ml) was equilibrated with a helium atmosphere in a 50 ml air-tight glass syringe. Equilibration was achieved by vigorously shaking the syringe at room temperature. This technique of compensation inside syringes has been used before by several authors (e.g., Jayakumar et al., 2001; Xie et al., 2002). The temperature of equilibration (±0.1 °C) was registered by a thermometer (P500 Dostman Electronic).

After equilibrium, a sample of the head space was injected into a gas chromatograph (Varian CX 3600). The configuration of the instrument, similar to the one described by Weiss (1981b), permits the simultaneous analysis of $CH_4$, $CO_2$ and $N_2O$. An electric valve allows the injection, with the same sample flow, into two different loops connected to different chromatographic columns and detectors. For $CH_4$ and $CO_2$, helium is used

Table 1
Sampling dates, number of samples ($N$), temperature, salinity, monthly averaged wind speed at 10 m height ($U_{10}$), daily averaged current velocity module ($W$), tidal coefficient ($m$), precipitation (mm month$^{-1}$) and evaporation (mm month$^{-1}$)

| Date | $N$ | Temperature (°C) | Salinity | $U_{10}$ (m s$^{-1}$) | $W^a$ (cm s$^{-1}$) | Tidal coefficient | Precipitación[b] (mm) | Evaporation[c] (mm) |
|---|---|---|---|---|---|---|---|---|
| 19/02/2004 | 13 | 10.0–16.4 | 31.75–32.45 | 4.8±3.0 | 16.06 | 0.94 | 2.4 | 62.6 |
| 01/03/2004 | 14 | 8.8–14.0 | 25.85–26.03 | 3.3±1.5 | 16.28 | 0.37 | 76.3 | 75.6 |
| 27/04/2004 | 13 | 16.4–22.0 | 34.30–34.57 | 4.1±1.8 | 15.89 | 0.32 | 39.0 | 86.4 |
| 04/05/2004 | 13 | 14.0–18.2 | 32.52–32.64 | 4.5±3.0 | 15.87 | 1.05 | 76.9 | 95.6 |
| 19/05/2004 | 13 | 16.4–22.0 | 31.18–33.87 | 4.5±3.0 | 15.87 | 0.76 | 68.6 | 95.6 |
| 01/07/2004 | 13 | 22.6–27.4 | 42.61–42.62 | 3.7±2.3 | 16.30 | 0.89 | 0 | 158.3 |
| 12/07/2004 | 13 | 19.7–27.0 | 43.32–43.35 | 3.7±2.3 | 16.25 | 0.49 | 0 | 158.3 |
| 26/07/2004 | 13 | 28.8–34.8 | 39.45–39.60 | 3.7± 2.3 | 16.05 | 0.56 | 0 | 158.3 |
| 07/09/2004 | 13 | 20.0–23.6 | 37.90–38.40 | 2.4±1.4 | 15.83 | 0.28 | 0.4 | 107.2 |
| 15/09/2004 | 13 | 18.4–21.2 | 38.40–38.80 | 2.4±1.4 | 15.89 | 0.97 | 0.4 | 107.2 |

[a] Provided by the Spanish Marine Hydrographic Institute.

[b] Precipitation accumulated 1 month before the sampling. Provided by the Spanish Meteorological Institute (INM).

[c] Monthly averaged evaporation. Provided by the Spanish Meteorological Institute (INM).

as the carrier gas (30 ml min$^{-1}$). The gases were separated on a 4.5 m × 1/8 in. stainless steel column packed with 80/100 Porapack N and a 1.5 m × 1/8 in. Molecular Sieve 5A column. A flame ionization detector (FID), operated at 300 °C, is used to measure $CH_4$ and $CO_2$. The $CO_2$ is detected after conversion to $CH_4$ by a nickel catalyst column (380 °C). For $N_2O$, a mixture of Ar/$CH_4$ (95%/5%) is used as carrier gas (30 ml min$^{-1}$), gases were separated by a 2.5 × 1/8 in. stainless steel Porapack N column (80/10), and $N_2O$ is detected by a $^{63}$Ni electron capture detector (ECD), operated at 300 °C. The detectors were calibrated daily using two standard gas mixtures which were made and certified by Air Liquide (France). Certified concentrations for $CH_4$, $CO_2$ and $N_2O$ were, respectively, 489 ppbv, 244.7 ppmv and 264 ppbv in the first gas mixture, and 2.53 ppmv, 998 ppmv and 1.55 ppmv in the second. The precision of the method, including the equilibration step, expressed as the coefficient of variation based on replicate analysis ($n$=25) of a seawater sample saturated with $CH_4$, $CO_2$ and $N_2O$, was 4.8%, 6.5% and 6.6%, respectively.

The concentrations of the gases in the water samples were calculated from the concentrations measured in the head space, using the functions for the Bunsen solubilities given by Wiesenburg and Guinasso (1979) for $CH_4$, and Weiss and Price (1980) for $CO_2$ and $N_2O$. The partial pressure of $CO_2$ ($pCO_2$) was determined from the concentration of dissolved $CO_2$, using the formulation given by Weiss (1974) to calculate the solubility coefficients.

Saturation values, expressed in %, were calculated as the ratio of the concentration of dissolved gas and the expected equilibrium water concentration.

Fluxes of $CO_2$, $CH_4$ and $N_2O$ across the air–water interface were estimated from:

$$F = k(C_w - \alpha C_a) \tag{1}$$

where $k$ (cm h$^{-1}$) is the gas transfer velocity (or piston velocity), $C_w$ is the concentration of dissolved gas in the water (mol l$^{-1}$), $\alpha$ is the Bunsen solubility and $C_a$ is the atmospheric gas concentration. A positive flux indicates a transfer of gas from the water to the atmosphere. The atmospheric concentrations of the gases were assumed

Table 2
Range of dissolved $CH_4$, $CO_2$ and $N_2O$ concentrations and saturation values for each sampling

| | $CH_4$ | | $CO_2$ | | $N_2O$ | |
|---|---|---|---|---|---|---|
| | Concentration (nM) | Saturation percent | Concentration (μM) | Saturation percent | Concentration (nM) | Saturation percent |
| 19/02/2004 | 12.7–45.4 | 514–1780 | 46.4–85.0 | 322–562 | 20.1–38.4 | 226–414 |
| 01/03/2004 | 23.2–56.8 | 886–2110 | 57.7–70.0 | 377–465 | 24.4–37.9 | 261–405 |
| 27/04/2004 | 13.3–30.4 | 583–1320 | 48.7–62.1 | 381–477 | 19.6–30.1 | 249–376 |
| 04/05/2004 | 13.3–33.1 | 574–1400 | 38.4–78.8 | 295–586 | 16.5–31.9 | 206–385 |
| 19/05/2004 | 13.0–29.3 | 586–1305 | 40.1–71.5 | 327–565 | 16.3–28.5 | 217–374 |
| 01/07/2004 | 17.3–50.0 | 894–2625 | 36.3–93.0 | 350–910 | 14.1–38.6 | 225–626 |
| 12/07/2004 | 33.9–61.8 | 1790–3210 | 57.4–115 | 566–1130 | 23.7–50.1 | 388–812 |
| 26/07/2004 | 47.0–87.5 | 2643–5000 | 61.8–114 | 660–1270 | 25.2–45.1 | 449–843 |
| 07/09/2004 | 35.2–57.6 | 1782–3010 | 59.4–108 | 562–1070 | 19.4–37.4 | 305–611 |
| 15/09/2004 | 22.5–75.0 | 1105–3780 | 28.8–102 | 264–955 | 12.7–35.4 | 191–546 |

to correspond to the annual average global concentration at Terceira Inland station (Azores, Portugal), taken from the National Oceanic and Atmospheric Administration/ Climate Monitoring and Diagnostics Laboratory/Carbon Cycle Greenhouse Gases Group (NOAA/CMDL/ CCGG) air sampling network (available at http://www.cmdl.noaa.gov/). The differences between these values and the local atmospheric concentrations are assumed to be small compared with the high dissolved concentrations in the surface waters of our study site.

Monthly mean wind speed data, measured at 10 m height in a meteorological station located about 15 km from the study site, were provided by the Spanish Meteorological Institute (INM) and used to calculate the transfer coefficients of the gases.

## 4. Results and discussion

### 4.1. Tidal variation

Concentrations of dissolved $CH_4$, $CO_2$ and $N_2O$ in the creek under study ranged from 12.6 to 87.5 nM, 28.8 to 114.6 µM and 12.7 to 50.1 nM, respectively. The range of dissolved $CH_4$, $CO_2$ and $N_2O$ for each sampling is given in Table 2. Concentration values for the three gases were always above atmospheric equilibrium, indicating that the system behaves as a source of these gases to the atmosphere.

All data sets indicate a strong variability of the concentration of dissolved gases with tides. Fig. 2 shows the typical evolutions of dissolved $CH_4$, $CO_2$ and $N_2O$ over a tidal cycle, in two situations with two different tidal coefficients. In every case, dissolved gas concentrations increased when tidal elevation decreased, with maximum values during low tide. This pattern indicates that Río San Pedro water contains higher concentrations of dissolved $CH_4$, $CO_2$ and $N_2O$ than water from the Bay of Cádiz. We suggest that the major sources of these gases within the system are the inputs of from the fish farm effluent and the drainage of the adjacent salt marsh area, as well as in situ production, which may be enhanced by the high loading of organic matter and nutrient. Benthic metabolism in the fish farm ponds and the salt marsh might be very intense due to the broadness and shallowness of these zones and the high loading of organic matter that they support.

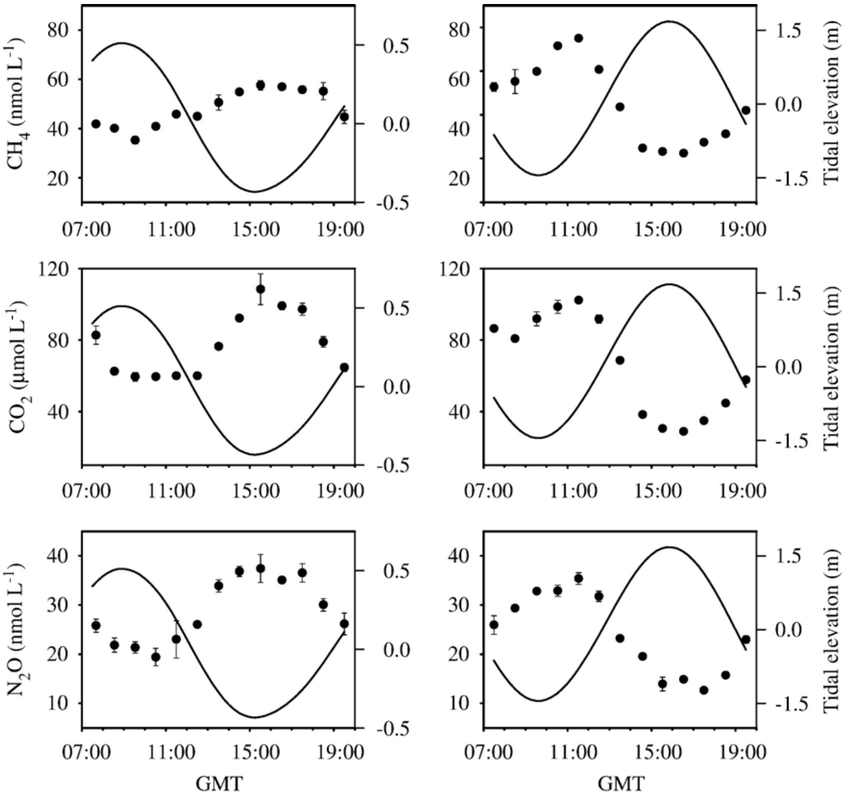

Fig. 2. Typical variations over a tidal cycle of dissolved $CH_4$, $CO_2$ and $N_2O$ concentrations and tidal elevation (solid line, referenced to the mean sea level). The three plots on the left correspond to the September 7th sampling (tidal coefficient = 0.28), whereas the plots on the right correspond to September 15th (tidal coefficient = 0.97).

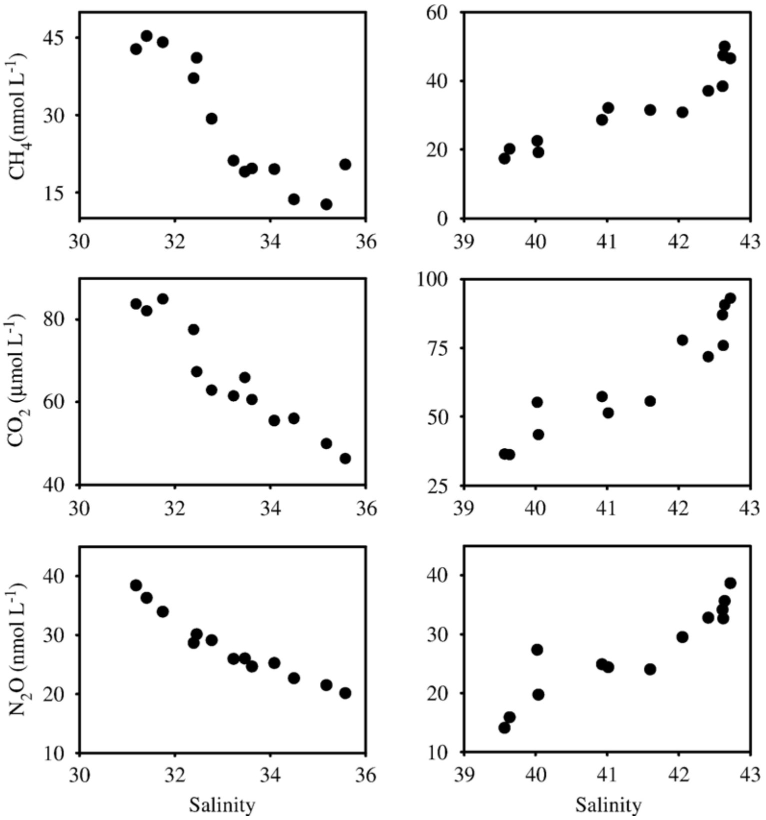

Fig. 3. Two examples of the variations of dissolved $CH_4$, $CO_2$ and $N_2O$ concentrations vs. salinity. The plots on the left correspond to the February 19th sampling (winter and spring pattern), whereas the plot on the right corresponds to July 1st.

Tovar et al. (2000a) evaluated the effects of intensive marine aquaculture on the water quality of Río San Pedro and observed a significant increase of the concentration of nutrients and suspended solids in the upper part of the creek, as well as a decrease of dissolved oxygen, which was attributed to the effluents from aquaculture activities together with a poor renovation of the water by the tides. These authors reported high values of $NH_4^+$ (up to 210 µM), $NO_2^-$ (up to 26 µM) and $NO_3^-$ (up to 35 µM).

During the samplings, dissolved oxygen saturation varied from 69% in the summer to 87% in the winter. This variation is related to the higher concentrations of dissolved and particulate organic matter during the summer in comparison to the winter. These parameters ranged, respectively, from 4.0 to 16.4 mg $l^{-1}$ and from 50 to 240 mg $l^{-1}$. The high loading of organic matter and nutrients from the effluent, together with the tidal regime that increases the residence time of the water inside the creek, may provide favorable conditions for

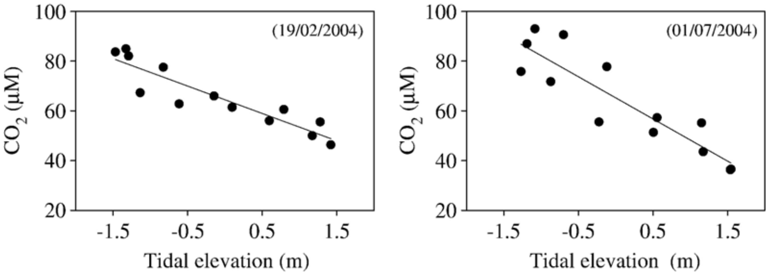

Fig. 4. Two examples of the variation of dissolved $CO_2$ concentration with tidal elevation. The plot on the left corresponds to the February 19th sampling whereas the plot on the right corresponds to July 1st. The similar linear pattern ($r^2$ = 0.85 and 0.81, respectively) was observed in both cases.

the production of $CH_4$, $CO_2$ and $N_2O$ within the creek and their emission to the atmosphere.

The plots of dissolved $CH_4$, $CO_2$ and $N_2O$ vs. salinity, shown in Fig. 3, present two different patterns. In winter and spring, concentrations decreased with increasing salinity. During this period, the minimum salinity corresponds to low tide, due to the freshwater inputs from rains in the system (Table 1). In the summer, we observed the opposite trend, the maximum salinity corresponded to low tide, due to evaporation processes inside the creek (Table 1). We can conclude that the dynamics of dissolved $CH_4$, $CO_2$ and $N_2O$ in the system is not controlled by salinity. Indeed, the tidal cycle has a major impact due to the displacement of different water masses. Fig. 4 plots the variations of dissolved $CO_2$ concentrations with tidal elevation for the two examples shown in Fig. 3. A linear diminution of $CO_2$ concentration with tidal elevation was observed in both situations. During low tide, there is no dilution with waters from the bay and the water column is shallower, so the influence of the inputs in the upper part of the creek (fish farm and salt marshes) and the *in situ* production of biogases become more evident.

Several authors have concluded that benthic mineralization processes can be a major source of $CH_4$ (e.g., Kelley et al., 1995; Bange et al., 1998; Abril and Iversen, 2002), $CO_2$ (e.g., Forja et al., 1994; Hammond et al., 1999; Cai et al., 2000; Forja et al., 2004) and $N_2O$ (e.g., Barnes and Owens, 1998; Dong et al., 2002) to the water column in different coastal systems. Another possible source of $CH_4$, $CO_2$ and $N_2O$ is the lateral transport from intertidal sediments during low tide (e.g., Kelley et al., 1995; Cai et al., 2000; Wang and Cai, 2004).

The range of variation of dissolved gases seems to be a function of the amplitude of the tides. For each season, higher variability was found when tidal ranges were higher. For example, on September 7th (tidal range = 0.28), the amplitudes of dissolved gas variations over the tidal cycle were 22.4 nM for $CH_4$, 49.0 μM for $CO_2$ and 24.5 nM for $N_2O$. On the other hand, on September 15th (tidal range = 0.97), the amplitudes observed were 52.5 nM for $CH_4$, 73.4 μM for $CO_2$ and 26.4 nM for $N_2O$. Thus, the variability of dissolved gases was higher with elevated tidal ranges for this summer period (average temperature = 26.2 °C). If we compare this to other seasons, this assumption might not be as evident. Over the tidal cycle on

Table 3
Range of $CH_4$ concentrations, saturations and air–water fluxes (parameterization used to derive the fluxes) reported in different coastal ecosystems

| Site | Concentration (nmol $l^{-1}$) | Saturation percent | Air–water flux (μmol $m^{-2}$ $day^{-1}$) | Date | Reference |
|---|---|---|---|---|---|
| *Estuaries* | | | | | |
| Humber and Tyne estuaries | 3.8–670 | 238–21,000 | – | November 1995; January, March, April, June, October, December 1996 | Upstill-Goddard et al. (2000) |
| Randers Fjord estuary (Denmark) | 28–4201 | 400–14,000$^{a,b}$ | 40–355$^{b}$ (CC98) | February–December 2000 | Abril and Iversen (2002) |
| European tidal estuaries (Elbe, Ems, Thames, Rhine, Scheldt, Loire, Gironde, Douro, Sado) | 2.1–1440 | 700–158,000 | 130$^{b}$ ($k_8$) | June, October, December 1996; April, July, September, November 1997; February, April, May, September, October 1998; February 1999 | Middelburg et al. (2002) |
| *Coastal waters and marginal seas* | | | | | |
| Aegean Sea | 2.9–11$^{b}$ | 118–231$^{b}$ | 3–167$^{b}$ (LM86) | July 1993 | Bange et al. (1996b) |
| Coastal waters of the southern Baltic Sea | – | 105–15,500 | 31–210$^{b}$ (LM86)<br>51–343$^{b}$ (W92) | June 1994–April 1997 | Bange et al. (1998) |
| North Sea | 2.0–67 | 74–2245 | – | August 1993, May 1995, October 1996, April 1998, March 1999 | Upstill-Goddard et al. (2000) |
| Arabian Sea | 2.6–48 | 140–2520 | – | April–May 1996<br>August–September 1997 | Jayakumar et al. (2001) |
| Gulf of Lions (Mediterranean Sea) | 8–1360$^{b}$ | – | – | March, June, September–November 1997; June 1998 | Marty et al. (2001) |
| NW Black Sea | 4–255 | 173–10,500 | 32–260 (LM86)<br>53–470 (W92) | July 1995 | Amoroux et al. (2002) |
| *Salt marshes* | | | | | |
| Río San Pedro creek | 13–88 | 514–5000 | 34–150 | February–May, July, September 2004 | This study |

Abbreviations are as follows: LM86, Liss and Merlivat (1986); W92, Wanninkhof (1992); CC98, Cole and Caraco (1998); $k_8$, using $k$ = 8 cm $h^{-1}$.

[a] Estimated if a saturation value was not explicitly given.

[b] Averaged values.

April 5th (tidal range = 1.05), the amplitudes of the variability of dissolved gases were 19.9 nM for $CH_4$, 40.4 µM for $CO_2$ and 18.3 nM for $N_2O$. On May 19th (tidal range = 0.76), the amplitudes of dissolved gas variations were 16.4 nM for $CH_4$, 31.4 µM for $CO_2$ and 13.5 nM for $N_2O$. Again we observe that, for this spring period (average temperature = 18.6 °C), the variation of dissolved gases with tide is greater if the tidal range is higher. But if we compare both periods this assumption does not hold. On comparing the September 7th and April 5th samplings, with tidal ranges of 0.28 and 1.05, respectively, the amplitudes of the variations of dissolved $CH_4$, $CO_2$ and $N_2O$ over a tidal cycle are higher on September 7th, even though the tidal range is significantly smaller. Therefore, the effect of tidal cycles on $CH_4$, $CO_2$ and $N_2O$ concentrations in Río San Pedro showed a seasonal variability. The influence of temperature on organic matter mineralization processes and biogas production appears to be stronger than the physical effects of tides.

### 4.2. Seasonal variations

The ranges of $CH_4$, $CO_2$ and $N_2O$ concentration and saturation values for each sampling are listed in Table 2. Concentrations of dissolved $CH_4$ in the surface waters ranged from 13 to 88 nM, corresponding to saturations of 514–5000%. These values are within the range reported by other authors in different coastal environments (Table 3). Dissolved $CH_4$ concentrations in rivers, estuaries and coastal environments generally show a strong spatial and temporal variability (e.g., Bange et al., 1998; Upstill-Goddard et al., 2000; Jayakumar et al., 2001; Middelburg et al., 2002). Bange et al. (1998) reported $CH_4$ saturation values in the southern Baltic Sea and Bodden waters ranging from 105% to 15,500%. $CH_4$ measurements performed by Upstill-Goddard et al. (2000) in the coastal waters of the North Sea and the Humber and Tyne estuaries showed saturations in the range of 74–21,048%. A series of $CH_4$ measurements performed in nine tidal European estuaries (Elbe, Ems, Thames, Rhine, Sheldt, Loire, Gironde, Douro and Sado) by Middelburg et al. (2002) yielded saturation values of up to 158,000%.

Dissolved $N_2O$ concentrations in Río San Pedro varied from 13 to 50 nM, corresponding to saturations of 191% to 843%. These values are in good agreement with those reported by other authors in other coastal ecosystems (Table 4). For example, Bange et al. (1998) reported $N_2O$ saturation values in the southern Baltic Sea and Bodden

Table 4
Range of $N_2O$ concentrations, saturations and air–water fluxes (parameterization used to derive the fluxes) reported in different coastal ecosystems

| Site | Concentration (nmol $l^{-1}$) | Saturation percent | Air–water flux (µmol $m^{-2}$ $day^{-1}$) | Date | Reference |
|---|---|---|---|---|---|
| *Estuaries* | | | | | |
| Gironde estuary | 10–19 | 105–165 | – | November 1991 | Bange et al. (1996a) |
| Humber estuary | – | ~200–4000 | 43,200 (LM86) | January, February 1995; April, August 1996 | Barnes and Owens (1998) |
| Scheldt estuary | 10–338 | ~100–3100 | ~10–530 (C95) | October 1993, March 1994, July 1996 | De Wilde and de Bie (2000) |
| Colne estuary | 20–140 | 100–450 | – | February 1998 | Dong et al. (2002) |
| *Coastal Waters and Marginal Seas* | | | | | |
| Aegean Sea | 7.02–7.27 | 103–107 | 1.20–21.0 (LM86) | July 1993 | Bange et al. (1996b) |
| Central North Sea, and German Bight | 8.4–9.2 | 99–104 | – | September 1991, September 1992 | Bange et al. (1996a) |
| Southern Baltic Sea | – | 91–312 | 0.35–3.97 (LM86)<br>0.60–7.08 (W92)) | June 1994–April 1997 | Bange et al. (1998) |
| Tokyo Bay | 9–139 | 116–1630 | 1.5–153 (LM86) | May–October 1994 | Hashimoto et al. (1999) |
| Gulf of Lions (Mediterranean Sea) | 1.9–41 | 27–570[a] | – | March, June, September–November 1997; June 1998 | Marty et al. (2001) |
| NW Black Sea | 7.9–8.0 | 96–149 | 1.6–2.7 (LM86)<br>2.8–4.4 (W92) | July 1995 | Amoroux et al. (2002) |
| *Salt marshes* | | | | | |
| Río San Pedro creek | 13–50 | 191–843 | 24–62 | February–May, July, September 2004 | This study |

Abbreviations are as follows: LM86, Liss and Merlivat (1986); W92, Wanninkhof (1992); C95, Clark et al. (1995).

[a] Estimated if a saturation value was not explicitly given.

waters ranging from 91% to 312%, with a maximum in March. $N_2O$ saturations of up to 4000% were found in the Humber estuary, whereas in the pristine waters of the Tweed estuary they were close to atmospheric equilibrium (Barnes and Owens, 1998). In the Scheldt estuary and the Dutch coast, saturations ranged from 100% to 3100% (De Wilde and de Bie, 2000).

$p\text{CO}_2$ values in the creek ranged from 981 to 4680 µatm, corresponding to saturations of 264–1270%. These values are within the ranges reported in other coastal systems (Table 5). Particularly, the range of $p\text{CO}_2$ found in our system is very similar to the values reported by Wang and Cai (2004) in surface waters of the Duplin River (500–3000 µatm), a marsh-dominated estuary surrounded by intertidal salt marshes. Frankignoulle et al. (1998) and Ortega et al. (2005) reported $p\text{CO}_2$ values in different European estuaries, which were as high as 9728 µatm for the Scheldt estuary and up to 9425 µatm in the Cantabrian estuaries.

The concentration of dissolved $CH_4$, $CO_2$ and $N_2O$ in surface waters showed a strong seasonal variability. During winter, the highest observed values of dissolved $CH_4$, $CO_2$ and $N_2O$ were 56.8 nM, 85.0 µM and 38.4 nM, respectively. These values correspond to an oversaturation of 2110%, 562% and 414%, respectively. During summer, the maximum dissolved $CH_4$, $CO_2$ and $N_2O$ values increased to 87.5 nM, 115 µM and 50.7 nM, corresponding to oversaturation values of 5000%, 1270% and 840%, respectively. This shift in the oversaturation of $CH_4$, $CO_2$ and $N_2O$ from winter to

Table 5

Range of $p\text{CO}_2$ and air–water fluxes (parameterization used to derive the fluxes) reported in different coastal ecosystems

| Site | $p\text{CO}_2$ (µatm/ppm) | Air–water flux (mmol $\text{m}^{-2}$ $\text{day}^{-1}$) | Date | Reference |
|---|---|---|---|---|
| *Estuaries* | | | | |
| Altamaha and Satilla Rivers | ~400–8200 | ~41–700 (EM83) | October 1995 | Cai and Wang (1998) |
| European estuaries (Elbe, Ems , Rhine, Scheldt, Tamar, Thames, Gironde, Douro, Sado) | 125–9425 | 50–660[a] | March, July 1992; March, June 1993; March, April, November 1994; January, August, November 1995; September, October, December 1996; April, July, September, November 1997; February 1998 | Frankignoulle et al. (1998) |
| York River estuary | 113–3467 | −2.1–107 (R00) | April 1997, July 1996 | Raymond et al. (2000) |
| Cantabrian estuaries | 256–9728 | | June 1998 | Ortega et al. (2005) |
| *Coastal waters and marginal seas* | | | | |
| Gulf of Biscay and North Sea | 195–367 | −36.2–1.64 (LM86)<br>−71.2–384 (T90)<br>−58.4–2.43 (W92) | May, September 1993; May, April, November 1994; March, May, July 1995; April 1996; May, June 1997; January, July–August 1998; September 1999 | Frankignoulle and Borges (2001) |
| Galician Upwelling system (NW Spain) | 265–415 | 0.0 to −6.9 (LM86)<br>0.0 to −13.9(T90)<br>0.0 to −12.0 (W92) | June 1997, January 2000 | Borges and Frankignoulle (2002) |
| US Middle Atlantic Bight | ~200–650 | −2.47 to −1.10 (LM86)<br>−1.92 to −4.38 (W92) | 1994–2000 | DeGrandpre et al. (2002) |
| North Sea | – | −2.60 (LM86)<br>−4.60 (W92) | August–September, November 2001; February–March, May 2002 | Thomas et al. (2004) |
| South Brazil Bight | – | 0.3–9.8 (W92) | November 1997; January–February, June 1998 | Ito et al. (2005) |
| Gulf of Cádiz (SW Spain) | 152–340[b] | −0.41 (WT91) | March 2004 | Huertas et al. (2005) |
| *Salt marshes* | | | | |
| Duplin River | 500–3000 | 6.1–134 (W92)<br>9.4–158 (R00) | September 2000–April 2002 | Wang and Cai (2004) |
| Río San Pedro creek | 981–4680 | 073–177 | February–May, July, September 2004 | This study |

Abbreviations are as follows: EM83, Elsinger and Moore, 1983; LM86, Liss and Merlivat (1986); T90, Tans et al., 1990; WT91, Woolf and Thorpe (1991); W92, Wanninkhof (1992); C95, Clark et al. (1995); R00, Raymond et al. (2000).

[a] Fluxes measured on field by floating dome measurements or calculated using a $k=8$ cm $\text{h}^{-1}$.

[b] Values in ppm.

summer conditions indicates that these gases are closely linked to the seasonal temperature cycle.

Fig. 5 plots $CH_4$, $CO_2$ and $N_2O$ average saturation values for each sampling vs. temperature. It can be observed that the three gases follow a similar pattern. Below a temperature of approximately 20 °C, which corresponds to winter and spring conditions, there is no significant relation between dissolved gases concentrations and temperature. Above 20 °C, corresponding to July and September, saturation values for $CH_4$, $CO_2$ and $N_2O$ show a linear increase with temperature ($r^2=0.89$, 0.89 and 0.82, respectively).

Organic matter mineralization processes in the sediments, which constitute one of the main sources of trace gases in the system, show a high dependence on temperature (e.g., Aller, 1980; Aller and Benninger, 1981). Observations made in marine coastal areas with large variations in the temperature of the bottom water have revealed that low temperatures tend to reduce microbial activity (Shiah, 1994; Ortega et al., 2002) and hence the exchanges between sediments and the water column. Sediments of the Bay of Cadiz are basically clayey and their organic matter content is 2–3%. Benthic fluxes of inorganic carbon and nutrients are high in comparison to other littoral systems, owing to intensive bacterial colonization and a high density of benthic macro-fauna that significantly triggers diffusive fluxes (Forja et al., 1994; Forja and Gómez-Parra, 1998). A significant seasonal variation of benthic fluxes has been detected in the sediments of the interior part of the Bay of Cádiz (Forja et al., 1994, 2004), as well as an increase with temperature of the contribution of anaerobic routes of organic matter degradation (Forja et al., 2004). Thus, a rise in temperature implies a greater release of metabolic products to interstitial waters, including $CH_4$, $CO_2$ and $N_2O$, and consequently a higher rate of transfer of these gases to the water column.

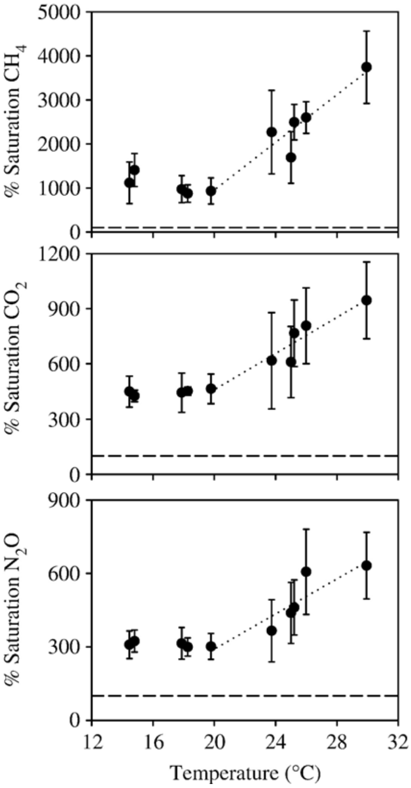

Fig. 5. Mean $CH_4$, $CO_2$ and $N_2O$ saturation values for each sampling vs. temperature. Above 20 °C, corresponding to July and September samplings, saturation values show a linear increase with temperature ($r^2=0.89$ for $CH_4$, $r^2=0.89$ for $CO_2$, $r^2=0.82$ for $N_2O$). The dashed line indicates equilibrium saturation (i.e. 100%).

### 4.3. Air–water exchange

The gas exchange between the surface waters and the atmosphere depends mainly on the concentration gradient and the gas transfer velocity, $k$. For sparingly soluble gases, such as $CH_4$, $CO_2$ and $N_2O$, $k$ mainly depends on turbulence in the water phase (Liss and Slater, 1974). In open oceans and lakes, wind stress appears to be the main source of water surface turbulence and $k$ is usually parameterized as a function of wind speed (e.g., Liss and Merlivat, 1986; Wanninkhof, 1992). In the case of shallow coastal sites, there are other important sources of turbulence (e.g., bottom friction, current velocity), and there is a lack of agreement on the relationships proposed in literature. Depending on the coastal system and the environmental conditions, one or more of these processes may control the air–water exchange. In macrotidal estuaries, tidal currents were found to significantly contribute $k$, in addition to wind stress (Zappa et al., 2003; Borges et al., 2004a,b). This can explain the high variability in the $k$-wind speed parameterizations found in estuaries of differing scale and hydraulic conditions. However, another source of uncertainty can be the inherent differences in the various measurement techniques. Zappa et al. (2003) and Borges et al. (2004a) showed that the contribution of water currents to the gas transfer velocity can be estimated by O'Connor and Dobbins (1958) relationship, which is based on fluid turbulence theory and where $k$ is parameterized as a function of water current and depth. Using this relation, Borges et al. (2004b) proposed an empirical equation that parameterizes the cumulative effects of wind speed and current velocity to calculate $k_{600}$ in the Scheldt estuary:

$$k_{600} = 1.0 + 1.719w^{-0.5}h^{-0.5} + 2.58u_{10} \quad (1)$$

where $k_{600}$ is the gas transfer velocity of $CO_2$ normalized to 20 °C (cm $h^{-1}$), $w$ is the water current (cm $s^{-1}$), $h$ is the depth (m) and $u_{10}$ is the wind speed at 10 m height (m $s^{-1}$).

To bracket the most likely value for $k$, we chose several parameterizations proposed by different authors in estuaries and coastal systems: (1) Clark et al. (1995) relationship (hereinafter referred to as C95), based on $SF_6$ release experiments in the Hudson River estuary and $^{222}Rn$ mass balance in San Francisco Bay, (2) Carini et al. (1996) relationship (hereinafter referred to as C96), based on $SF_6$ release experiments in the Parker River estuary, (3) Kremer et al. (2003) relationship (hereinafter referred to as K03), based on floating dome $O_2$ measurements in Childs River and Sage Lot Pond estuaries, and (4) Borges et al. (2004b) relationship (hereinafter referred to as B04), based on floating dome $CO_2$ measurements in the Scheldt estuary, taking into account the contribution of the water current from the conceptual relationship of O'Connor and Dobbins (1958) (Eq. (1)). The choice of these formulations was motivated by the relative similarity of these systems to Río San Pedro from the point of view of physical characteristics (e.g., shallow, well-mixed, influenced by tides).

Gas transfer velocity depends on temperature and it is different for each gas. From the $k$ estimated using the different algorithms, we calculated the $k$ for our gas of interest at a given temperature using the following expression:

$$k_1/k_2 = (Sc_1/Sc_2)^n$$

The Schmidt numbers ($Sc_i$) were calculated for the respective gases evaluated from the formulations given by Wanninkhof (1992) for salinity 0 and 35, assuming that $Sc_i$ varies linearly with salinity. We assumed a dependency of $k$ proportional to $Sc^{-0.5}$.

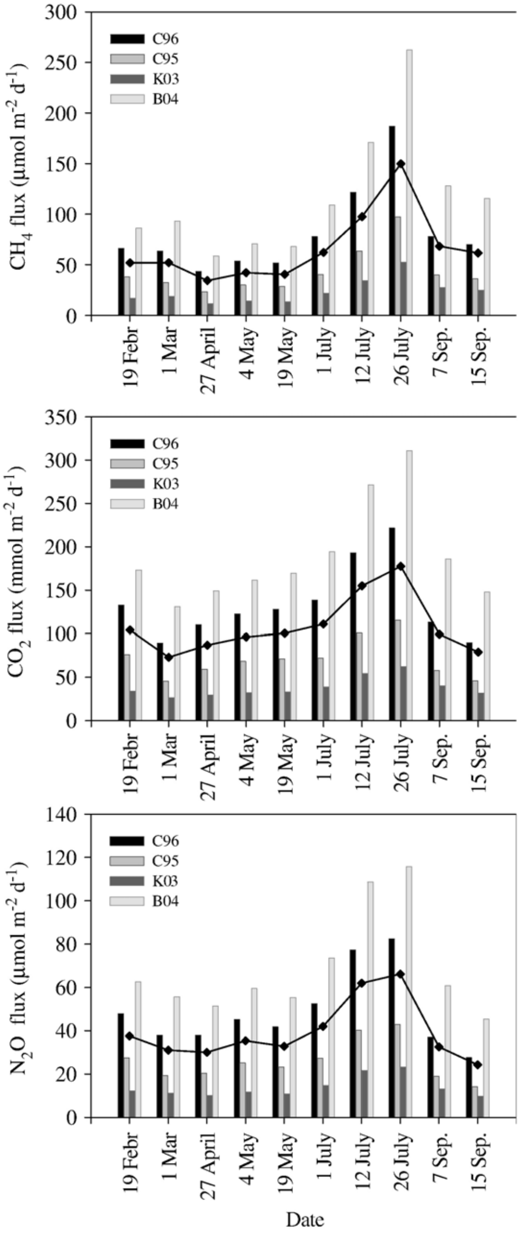

Fig. 6. Average $CH_4$, $CO_2$ and $N_2O$ air–water fluxes for each sampling: C95: air–water fluxes calculated according to Clark et al. (1995); C96: air–water fluxes calculated according to Carini et al. (1996); K03: air–water fluxes calculated according to Kremer et al. (2003); B04: air–sea fluxes calculated according to Borges et al. (2004b). The diamonds correspond to the averaged air–water fluxes for the four parameterizations.

The averaged air–water fluxes of $CH_4$, $CO_2$ and $N_2O$ for each sampling, calculated with the different relationships, are presented in Fig. 6. The magnitudes of these fluxes differ significantly depending on the gas transfer velocity used, and these differences are greater with increasing wind speed. However, no matter what parameterization is used, fluxes show in all cases a similar seasonal pattern. In general, fluxes estimated with the B04 relationship are as much as a factor of 5 higher than those with K03. The fluxes estimated from the C95 and C96 parameterizations fall between the latter two. But C96 fluxes are a factor of 2 higher than those estimated from the C95 relationship. Kremer et al. (2003) and Borges et al. (2004b) concluded that a simple parameterization of k as a function of wind speed is site specific in estuaries, and that the use of generic relationships to estimate the air–water flux can lead to substantial errors. Hence, we need to be very cautious when using *k* parameterizations to calculate air–water fluxes in coastal environments. The averaged $CH_4$, $CO_2$ and $N_2O$ air–water fluxes of all four parameterizations are also presented in Fig. 6, and ranged from 34 to 150 μmol $CH_4$ $m^{-2}$ $day^{-1}$, 73 to 177 mmol $CO_2$ $m^{-2}$ $day^{-1}$ and 24 to 62 μmol $N_2O$ $m^{-2}$ $day^{-1}$. These values are within the range reported by other authors in coastal environments (Tables 3, 4 and 5). For the three gases, maximum exchange values were registered in July, when the production of these gases within the system is more intense. Monthly mean wind speed varied slightly over the year and, therefore, differences in $CH_4$, $CO_2$ and $N_2O$ fluxes were mainly driven by the seasonal variability of dissolved $CH_4$, $CO_2$ and $N_2O$ in surface waters. As discussed before, the seasonal variations of dissolved $CH_4$, $CO_2$ and $N_2O$ are related to the temperature cycle, which affects the respiration processes and thus the production of biogases.

The system behaved throughout the year as a source of $CH_4$, $CO_2$ and $N_2O$ to the atmosphere, with annual averaged air–water fluxes of 66 μmol $CH_4$ $m^{-2}$ $day^{-1}$, 108 mmol $CO_2$ $m^{-2}$ $day^{-1}$ and 39 μmol $N_2O$ $m^{-2}$ $day^{-1}$, respectively.

## 5. Summary and conclusions

Dissolved methane ($CH_4$), carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) concentrations were measured in the surface waters of Río San Pedro. Waters were oversaturated with respect to the atmosphere during the whole year, reaching values of up to 5000% for $CH_4$, 1240% for $CO_2$ and 840% for $N_2O$. This indicates that the area is a net source of these gases to the atmosphere.

All data sets showed a strong tidal variability with higher values during low tide, indicating that Río San Pedro is richer in dissolved $CH_4$, $CO_2$ and $N_2O$ than water from the Bay of Cádiz. This is due to the direct inputs from the fish farm effluent and the drainage of the salt marshes in the upper part of the creek, as well as the *in situ* production of biogases, which is enhanced by the high loading of organic matter and nutrients. The concentrations of dissolved $CH_4$, $CO_2$ and $N_2O$ also showed a great seasonal variability, with maximum saturations in July, which is presumably due to the dependence of biological activity on temperature.

Annual averaged $CH_4$, $CO_2$ and $N_2O$ air–water fluxes, calculated using four different parameterizations, were 66 μmol $CH_4$ $m^{-2}$ $day^{-1}$, 108 mmol $CO_2$ $m^{-2}$ $day^{-1}$ and 39 μmol $N_2O$ $m^{-2}$ $day^{-1}$, respectively, which indicates that the system acts annually as a net source of these biogases to the atmosphere.

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