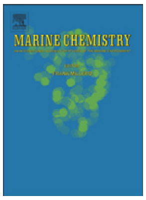
Marine Chemistry 113 (2009) 50–62

Contents lists available at ScienceDirect

Marine Chemistry

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



Benthic fluxes in a tidal salt marsh creek affected by fish farm activities: Río San Pedro (Bay of Cádiz, SW Spain)

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ARTICLE INFO

Article history:
Received 23 January 2008
Received in revised form 5 December 2008
Accepted 5 December 2008
Available online 14 December 2008

Keywords:
Benthic fluxes
Carbon mineralization
Nutrients
Dissolved inorganic carbon
Methane
Nitrous oxide
Salt marsh creek
Aquaculture

ABSTRACT

Benthic fluxes of dissolved inorganic carbon, total alkalinity, oxygen, nutrients, nitrous oxide and methane were measured in situ at three sites of Río San Pedro salt marsh tidal creek (Bay of Cádiz, SW Spain) during three seasons. This system is affected by the discharges of organic carbon and nutrients from the surrounding aquaculture installations. Sediment oxygen uptake rates and inorganic carbon fluxes ranged respectively from 16 to 79 mmol O_2 m^{-2} d^{-1} and from 48 to 146 mmol C m^{-2} d^{-1}. Benthic alkalinity fluxes were corrected for the influence of NH_4^+ and $NO_3^-+NO_2^-$ fluxes, and the upper and lower limits for carbon oxidation rates were inferred by considering two possible scenarios: maximum and minimum contribution of $CaCO_3$ dissolution to corrected alkalinity fluxes. Average C_{ox} rates were in all cases within ±25% of the upper and lower limits and ranged from 40 to 122 mmol C m^{-2} d^{-1}. Whereas carbon mineralization did not show significant differences among the sites, C_{ox} rates varied seasonally and were correlated with temperature ($r^2=0.72$). During winter and spring denitrification was estimated to account for an average loss of 46% and 75%, respectively, of the potentially recyclable N, whereas during the summer no net removal was observed. A possible shift from denitrification to dissimilatory nitrate reduction to ammonium (DNRA) during this period is argued. Dissolved CH_4 and N_2O fluxes ranged from 5.7 to 47 μmol CH_4 m^{-2} d^{-1} and 4.3 to 49 μmol N–N_2O m^{-2} d^{-1}, respectively, and represented in all cases a small fraction of total inorganic C and N flux. Overall, about 60% of the total particulate organic matter that is discharged into the creek by the main fish farm facility is estimated to degrade in the sediments, resulting in a significant input of nutrients to the system.

1. Introduction

Coastal sediments are in general sites of intense organic matter mineralization and nutrient recycling, and therefore play a key role in controlling coastal biogeochemistry (e.g., Berelson et al., 1998; Hopkinson et al., 1999; Codispoti et al., 2001). The measurement of solute fluxes across the sediment-water interface gives information about the role of sediment diagenesis and about the preferential pathways of organic matter mineralization. In sediments the organic matter is degraded to inorganic constituents through a vertical sequence of diverse microbial processes that use different terminal electron acceptors as oxidants (Froelich et al., 1979; Canfield, 1993). Although the most efficient of these processes is the aerobic oxidation of organic matter, in coastal sediments with high organic content the oxygen is rapidly consumed within the first millimeters of sediment (Revsbech et al., 1980) and thus microorganisms use other terminal acceptors as oxidants, such as NO_3^-, oxides of Mn and Fe, and $SO_4^=$ (Froelich et al., 1979; Canfield, 1993). Some of the NH_4^+ released from organic matter degradation is oxidized to NO_3^- in the presence of oxygen during nitrification, which can be subsequently reduced to N-gases (N_2 and N_2O) during denitrification. Coastal sediments are considered in general as favorable sites for denitrification due to the high loading of nutrients and organic matter and the low oxygen concentrations (Seitzinger et al., 1984; Seitzinger, 1988). In addition to NO_3^- reduction by denitrifiers, bacteria can also use NO_3^- as electron acceptor in the dissimilatory nitrate reduction to ammonium (DNRA) (Jørgensen, 1989). Nitrous oxide (N_2O), which is a potent greenhouse biogas (Rodhe, 1990) that it is also involved in the destruction of stratospheric ozone (Cruzten, 1970), can be produced during nitrification, denitrification and DNRA. Below the sub-oxic zone, where sediments are very reductive, sulfate reduction becomes the dominating diagenetic process and generally accounts for about 50% of organic carbon oxidation in coastal sediments (Canfield, 1993; Thamdrup and Canfield, 2000). Once sulfate is depleted organic carbon is degraded in various fermentative processes and methanogenesis to CH_4 and CO_2. CH_4 can be subsequently oxidized anaerobically by sulfate-reducing bacteria (Martens and Berner, 1974), which limits its flux to the water column. In this way, besides CO_2 which is the main end-product of organic matter mineralization, N_2O and CH_4 are also produced in coastal sediments in amounts that are often insignificant for the N and C-cycles of the sediments (e.g., Hopkinson et al., 1999; Alongi et al., 2005) but that may be significant for the global warming potential of coastal environments. Several authors

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doi:10.1016/j.marchem.2008.12.002

have pointed out the importance of benthic mineralization processes as a major source of N_2O and CH_4 in coastal systems (Robinson et al., 1998; Seitzinger et al., 2000; Upstill-Goddard et al., 2000; Abril and Iversen, 2002; Bange, 2006). Whereas the oceans play a major role in atmospheric N_2O budget, accounting for about one third of global N_2O emissions (Seitzinger et al., 2000), oceanic CH_4 emissions are only a small term (2%) in the global CH_4 budget (Reeburgh, 2007). However, although continental shelves and estuaries occupy only a small portion of the world oceans, they contribute from 35 to 60% of oceanic N_2O emissions (Bange et al., 1996; Seitzinger et al., 2000) and about 75% to the global oceanic CH_4 emissions (Bange et al., 1994).

In this study organic matter oxidation and nutrient fluxes across the sediment-water interface were investigated. Benthic chamber flux incubations were performed in situ during different periods of the year in a shallow tidal creek located in the salt marsh area of the Bay of Cádiz (SW Spain). This environment is affected by the inputs of organic matter and nutrients coming from aquaculture. It has been reported that inputs of residual fish food and excreta from fish farms enhance total sediment metabolism (Hall et al., 1990) and may shift the dominant microbial processes in sediments (Christensen et al., 2000). The aim of this paper is to examine the stoichiometry of diagenetic reactions in this environment, the seasonal variability in benthic fluxes and the potential impacts of aquaculture waste inputs to the system. Direct benthic fluxes of N_2O and CH_4, which are very sparse in the literature, were also measured and discussed.

2. Materials and methods

2.1. Study area

Work was carried out in Río San Pedro creek, a shallow tidal inlet located within the salt marsh area of the Bay of Cádiz (SW Spain) (Fig. 1). The creek used to be a tributary of the Guadalete river until it was artificially blocked at 12 km from the mouth, so currently the only freshwater input into the creek comes from precipitation. It is characterized by a semi-diurnal tidal regime, with the tidal height ranging from 3.5 m at spring tide to 0.5 m at neap tide. The average depth ranges between ~3 and 5 m and the water column is well mixed. A considerable salt marsh area surrounds the creek, but it has been largely exploited by human activities so that at present Río San Pedro is considerably isolated from the marshes by human-made embankments and by a dam in the innermost part of the creek, which only allows water exchange in periods of high water level. Three fish farms are located on the banks of Río San Pedro creek. One of them, situated in the upper part of the creek (Fig. 1), is large enough to be considered as the main source of organic matter and nutrients to the system. This fish farm covers about $1.3{\cdot}10^6$ m^2, and supports a culture of around 10^6 kg yr^{-1} of gilthead seabream (*Sparus aurata)*. The total volume of water introduced daily by the fish farm ranges from 180,000 m^3 to 290,000 m^3 (Tovar et al., 2000). The fish farm consists of several batteries of shallow ponds excavated in the soil. The shallowness of the ponds, together with the high loading of organic matter due to the fish farming, is expected to cause a very intense benthic metabolism in their bottoms. The overlying water, enriched with the metabolic products coming from organic matter diagenetic processes, is directly discharged to the upper part of the creek. As a consequence, the concentration of nutrients and suspended solids in the creek is relatively high. Tovar et al. (2000) 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 ton of cultured fish. According to this, approximately $9.1\cdot10^6$ kg TSS, $8.4\cdot10^5$ kg POM, $2.4\cdot10^5$ kg BOD, $36\cdot10^3$ kg N–NH_4^+, $5.0\cdot10^3$ kg N–NO_2^-, $6.7\cdot10^3$ kg N–NO_3^- and $2.6\cdot10^3$ kg P–PO_4^{3-} are discharged annually into the environment. In addition, De la Paz et al. (2008b) observed strong dissolved inorganic carbon concentration gradients between the creek and the Bay of Cadiz, which they related to the inputs of the fish farm effluent. These authors found that Chl-a concentrations, which ranged from 1 to14 µg L^{-1}, increased at neap tides, due to an enhancement of phytoplankton growth with a higher residence time of the water inside the creek. However, primary production activity seemed to be patchy and depended on the balance between nutrients and turbidity, which changed with tidal movements. Overall, they observed a strong seasonality in dissolved inorganic carbon, pH and

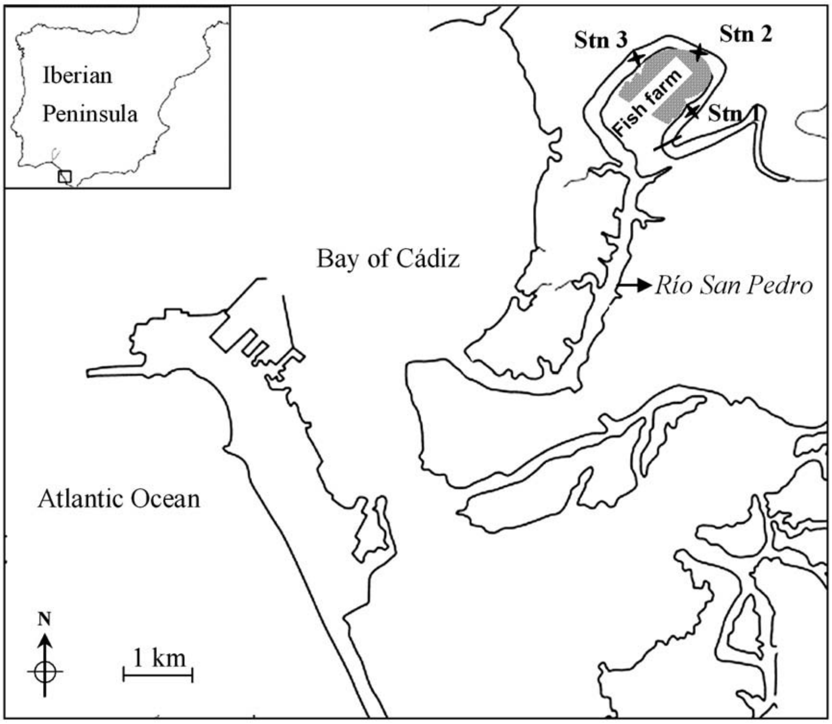

Fig. 1. Map of the Bay of Cádiz and Río San Pedro creek, showing the locations of the fish farm and the sampling stations.

dissolved oxygen concentrations, associated to an increase in metabolic rates with temperature, the alternation of storm events and high evaporation rates and the seasonal variability in the discharges from fish farms.

Three stations, characterized by silty sediment, were selected for the study of benthic fluxes in the upper part of the creek. Station 1 (Stn1) is located near the fish farm effluent, whereas stations 2 and 3 are progressively farther away towards the mouth (Fig. 1), at distances of approximately 1 km between them.

2.2. Sediment profiles

To study the vertical sediment profiles, 5 polycarbonate cores (50 cm long, 9.5 inner diameter) were taken by scuba divers at each of the three selected stations in October 2004. Cores were carefully maintained in vertical position during transportation and stored at 4 °C until analysis. One special sediment core in each station was used to measured redox potential (Eh) by inserting a Pt electrode (Methrom, ref. 6.0415.100) in holes at different depths.

Another sediment core was used to measure porosity and pore water solutes (ammonium, phosphate, silicate and sulfate). These cores were sliced at 1 cm intervals and immediately transferred to a tube provided with an inert atmosphere. Pore water was extracted by centrifugation at 15,000× g for 30 min at 4 °C (SIGMA 3K 30). Porosity was calculated from the weight of water loss after drying overnight a pre-weighed amount of wet sediment at 105 °C. Sulfate concentrations (±0.15 mM) in interstitial waters were measured by the gravimetric method (Grasshoff et al., 1983), adapted to a volume of sample of 2 mL. Ammonium (±0.5 μM), phosphate (±0.2 μM) and silicate (±0.2 μM) concentrations in pore water were measured after dilution by colorimetric techniques, following Grasshoff et al. (1983).

Pore water samples to analyze total alkalinity, dissolved inorganic carbon and nitrous oxide were extracted via a pressurized core barrel squeezer technique (Jahnke, 1988) to avoid degassing. For each station, one sediment core was assigned to analyze pH, total alkalinity and dissolved inorganic carbon, and two cores to measure nitrous oxide. Methane concentrations were not measured in interstitial waters.

2.3. In situ flux measurements

Twelve in situ benthic flux chamber incubations were performed successfully in the creek during June–July 2004, January–February 2005 and March–April 2006. The incubations were performed during the day and lasted from 5 to 6 h. During the samplings in 2004 and 2005 the incubations were made with a stirred benthic chamber (Ferrón et al., 2008). The cylindrical opaque PVC chamber (0.8 m inner diameter, 0.28 m height) covers 0.50 m^2 of sea-bottom and approximately 140 L of overlying water. The chamber is slowly lowered to the bottom from a small boat with a crane. An 8 cm rim assures the proper insertion of the chamber into the sediment. When the chamber contacts the sea-bottom and the rim sinks into the sediment, three methacrylate bases, located at the bottom collar surrounding the chamber, elevate three steel bars, making three reed switches contact with a magnet. This contact is checked by applying an electrical signal to the system. As these three devices are placed 120° apart, it is assumed that a signal coming from the three reeds indicates a correct horizontal landing of the chamber and, therefore, that the chamber is level and right side up. A similar procedure using reed switches is used to confirm the closure of three lids, which remain open during the landing process and are electronically closed when the chamber is placed on the bottom. Water inside the chamber is stirred by means of three external submersible centrifugal pumps, to avoid stratification and simulate natural conditions. Current velocity inside the chamber can be regulated from 2 to 5 cm s^{-1} (measured at 5 cm above the bottom). Discrete 50 mL samples are collected at programmable time intervals by means of a multiple water sampler provided with 12 syringes (KC Denmark). The volume of sample withdrawn, representing ~0.03% of the overlying solution, is compensated using a latex device that avoids the input of external water. Inside the chamber, sensors for temperature (SBE-39), pH (SBE-18), oxygen (SBE-43) and turbidity (Seapoint Turbidity Meter) give a continuous recording of these variables during the incubations. A two-way Global System for Mobile communications (GSM) was used for sensor data acquisition in real time, as well as to monitor samples withdrawn, pump rates, batteries and confirmation mechanisms during the incubation.

Benthic fluxes during March–April 2006 were measured using two opaque plexiglass ellipsoidal chambers (Gómez-Parra and Forja, 1992; Forja and Gomez-Parra, 1998). These chambers enclosed 0.385 m^2 of sediment and between 78 and 90 L of overlying water, depending on the eccentricity of the ellipsoid. Stirring of the water inside the chambers was achieved using a pump. The chambers were carefully placed on the sediment by scuba divers, and water samples were collected from the surface using a water sampler equipment which was connected with polyethylene tubes to the benthic chamber and to a vacuum device controlled by valves. The dead volume of the system was about 140 mL. A detailed description of the equipment is provided by Gómez-Parra et al. (1987), who checked the system for potential degasification and changes in temperature.

Chamber water samples were analyzed following filtration (0.45 μm), except for N_2O and CH_4 samples, which were carefully drawn into 25 mL air-tight glass bottles, preserved with saturated mercuric chloride and sealed with Apiezon® grease. They were collected and analyzed in duplicate, and stored in the dark until analysis in the laboratory within a week of collection.

2.4. Analytical methods

Total alkalinity (TA) and pH were analyzed, in duplicate, in interstitial and benthic chamber samples using a potentiometric analyzer (Metrohm 670) with glass combination electrodes (Metrohm, ref. 6.0210.100). The titration was performed with 0.1 M HCl in 0.7 M NaCl. The pH was calibrated in the Free pH Scale (Zeebe and Wolf-Glasgow, 2001) and TA was computed from the second point of inflection of the titration curve by means of the Gran Function, taking into account the corrections for sulfate (Dickson, 1990) and fluoride (Dickson and Riley, 1979) interactions. For the dissociation of dissolved inorganic carbon (DIC) we used the acidity constants (K_1 and K_2) proposed by Lueker et al. (2000) in the Total pH Scale. The sample quantities analyzed were about 10 g for the benthic chamber samples and 2 g for the interstitial water samples (to a precision of ±0.001 g). The method was validated with reference standards provided by Dr. A. Dickson (Scripps Institution of Oceanography, San Diego, USA) to an accuracy of ±3 μM.

Ammonium, nitrate, nitrite, phosphate and silicate concentrations in benthic chamber samples were determined by segmented flow analysis with Alpkem autoanalyzers following Grasshoff et al. (1983), with some improvements introduced by Mouriño and Fraga (1985). The analytical errors were ±0.05 μmol kg^{-1} for nitrate, ammonium and silicate, ±0.02 μmol kg^{-1} for nitrite and ±0.01 μmol kg^{-1} for phosphate.

The dissolved oxygen (DO) concentration was continuously recorded with an oxygen electrode (SBE-43) in the incubations made during June–July 2004 and January–February 2005, whereas in March–April 2006 DO was measured by the Winkler method in discrete samples (±0.1 μM).

Dissolved N_2O and CH_4 concentrations were determined with a gas chromatograph (Varian CX 3600). In-syringe head space equilibration was used to extract the dissolved gases from the water samples. The temperature of equilibration (±0.1 °C) was registered by a thermometer (P500 Dostman electronic). For CH_4, helium was used as the carrier gas (30 mL min^{-1}) and gases were separated in 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, was used to measure CH_4. For N_2O, a mixture of Ar/CH_4 (95%/5%) was 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 was 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 and N_2O were, respectively, 489 and 264 ppbv in the first gas mixture, and 2.53 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 and N_2O, was 4.8% 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 N_2O.

Total C and N were measured in dried sediment on an elemental analyzer (CHNS-932-LECO). Organic C was determined after removing inorganic C by acidification following the method described by Hedges and Stern (1984).

3. Results

3.1. Solid phase and pore water data

The pore water distributions of SO_4^{2-}, N_2O, pH, DIC, TA, NH_4^+, SiO_2 (aq) and HPO_4^{2-}, and the sediment distributions of organic carbon, total nitrogen and C_{org}:N molar ratios are plotted in Fig. 2 for each station. Porosity (not plotted) ranged from 0.76–0.80 in the first cm decreasing

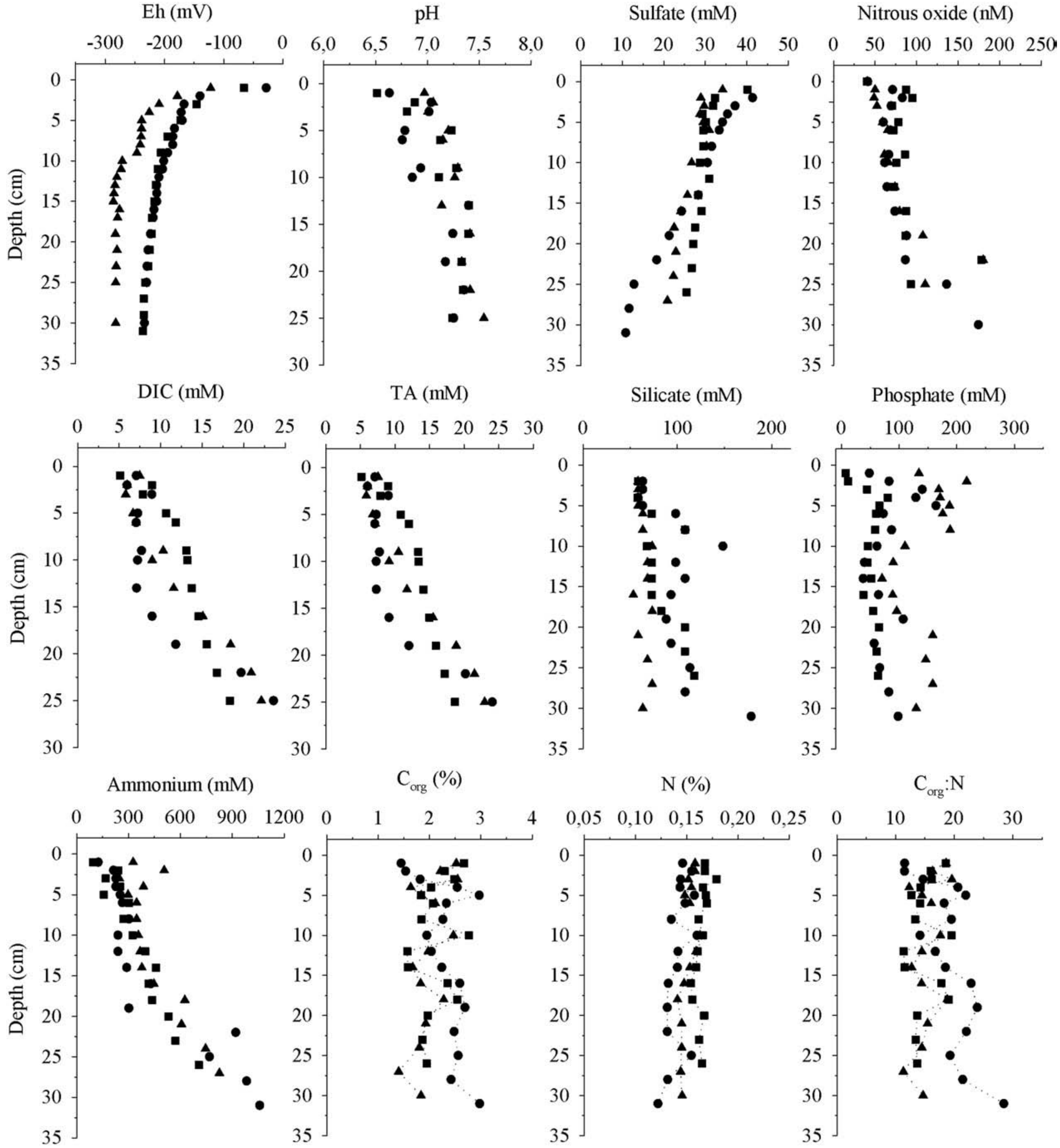

Fig. 2. Vertical pore water profiles of redox potential, pH, sulfate, dissolved nitrous oxide, dissolved inorganic carbon, total alkalinity, silicate, phosphate and ammonium at the three study sites in October 2003, as well as vertical profiles of sediment organic C and total N content, and the C_{org}:N ratio. Triangles: station 1, squares: station 2 and circles: station 3.

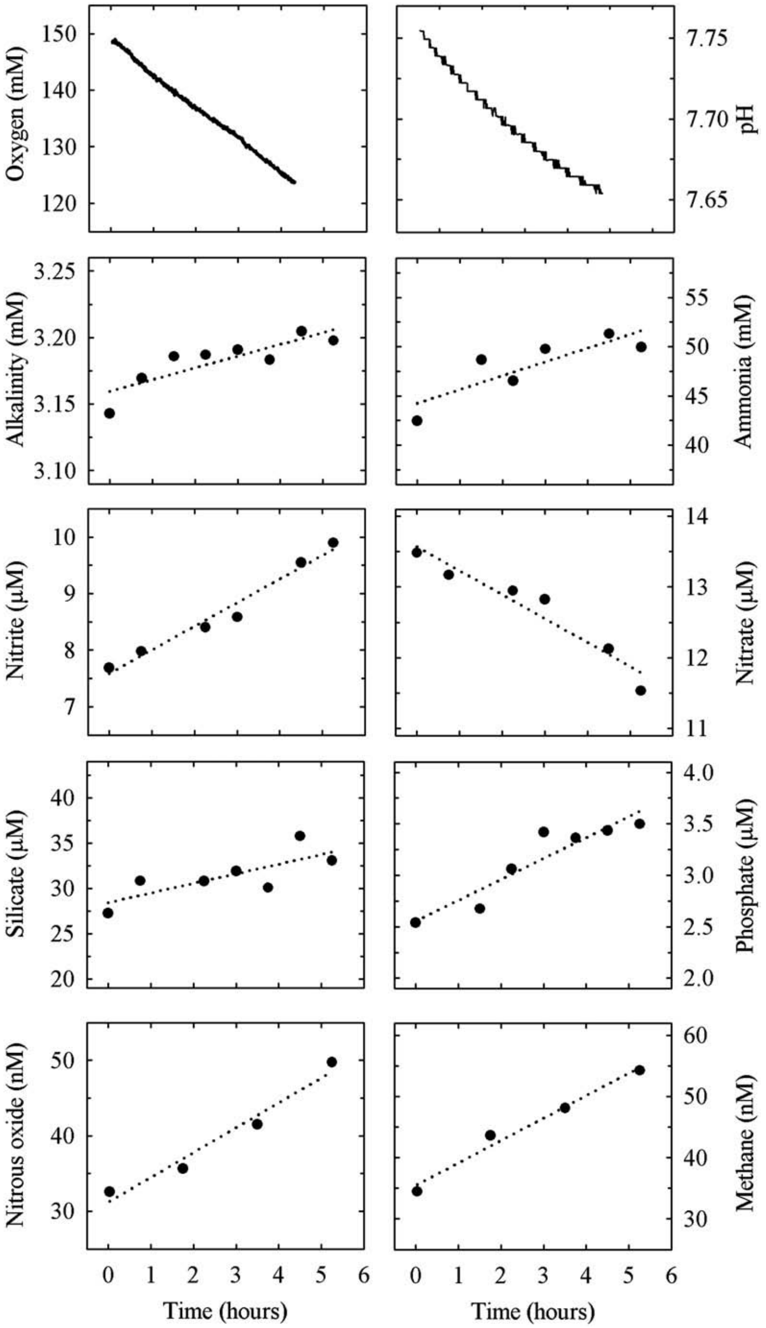

Fig. 3. Example of the evolution of dissolved oxygen, pH, methane, nitrous oxide, total alkalinity, dissolved inorganic carbon and dissolved nutrients in a benthic chamber deployment made in June 2004.

exponentially with depth to 0.62–0.69 at 15 cm depth. Sediments were highly reduced and showed negative redox potential values already in surface sediments, which decreased exponentially with depth. Surface redox potentials varied from −122 mV at stn1 to −66 mV at stn 2 and −28.3 mV at stn 3. The organic carbon content at the top cm of sediment ranged from 2.53% at stn 1 to 2.67% at stn 2 and 1.44% at stn 3. Sediment N content, ranging from 0.12 to 0.18%, was relatively small and constant with depth at all stations. C_{org}:N ratios ranged from 11.3 to 19.6 in stn 1 and 2. Stn 3 showed a pronounced increase of C_{org}:N ratio with depth, from values of 11.5 at the sediment surface to up to 28.5 at 30 cm.

DIC and TA values in pore water were relatively high and showed in all cases an increase with depth, reaching values of up to 22, 18 and 24 mM at 25 cm depth for stations 1, 2 and 3 respectively. However, at stn 1 and stn 3 DIC and TA profiles showed a slight decrease just below the sediment-water interface. Pore water pH values were lowest in surface sediments as a result of the aerobic degradation of organic matter and the re-oxidation of reduced species, and presented a general increase with depth.

The concentration of sulfate in pore water decreased with depth, as expected as a result of sulfate reduction. At stations 1 and 2 sulfate concentration gradients were steeper in the upper 4–5 cm of sediment, showing sulfate diminutions of 16–27% in this layer. On the other hand, within the first 25–27 cm of sediment, sulfate concentrations decreased 37–39% in stations 1 and 2, whereas at stn 3 a decrease of 69% was observed. In all cases, concentrations remained >10 mM, suggesting that sulfate availability was not limiting sulfate reduction.

Pore water NH_4^+ concentrations increased with depth in all stations, exceeding 1 mM in deeper sediments, in parallel to the increase of DIC. A similar pattern was observed for dissolved N_2O, which presented an overall increase with depth, with concentrations ranging from 40 nM

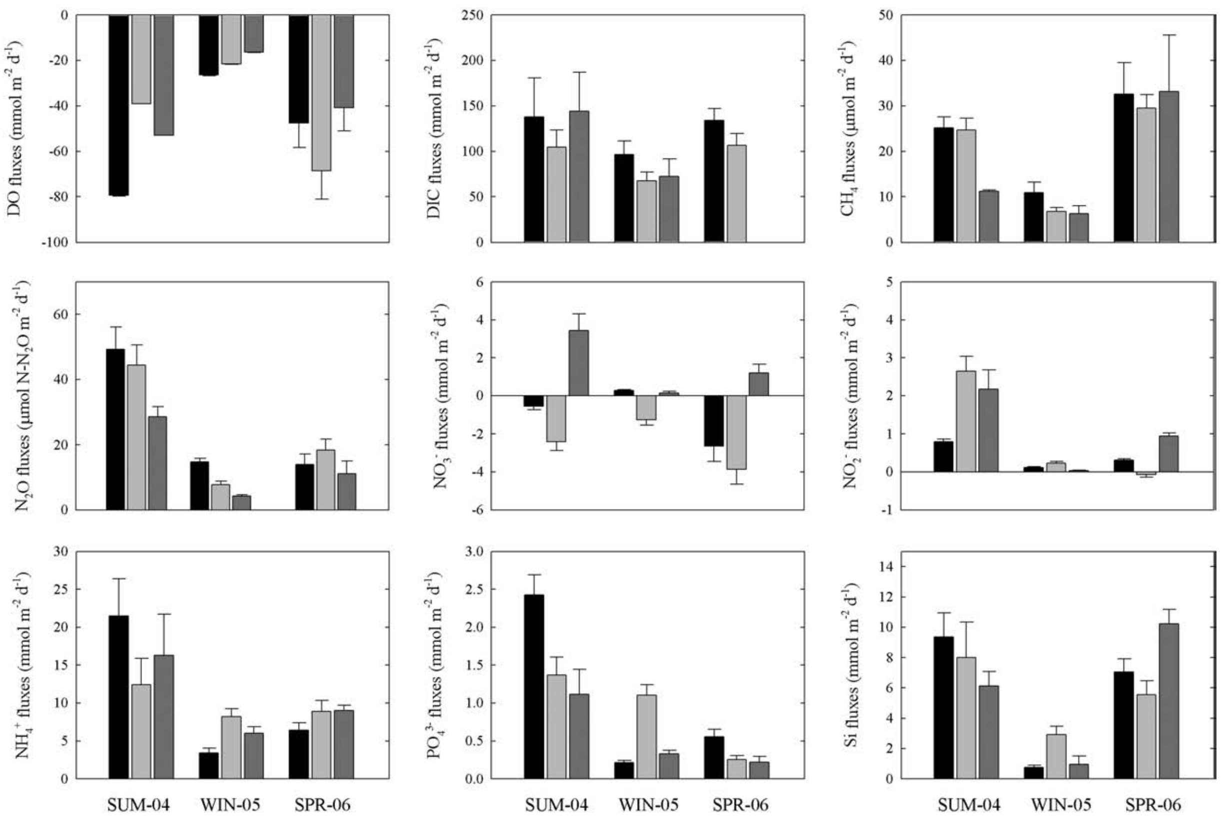

Fig. 4. Benthic flux measurements made at the three sites in summer (SUM), winter (WIN) and spring (SPR). Black bars represent station 1, light grey bars station 2 and dark grey bars station 3. Error bars are the uncertainties derived from the error in the slope of the data fit. In those cases in which replicates are available, the value plotted is the average.

to 180 nM. In the case of stn 2 and stn 3, vertical profiles of N_2O peaked at ~2 cm depth.

Dissolved phosphate pore water profiles showed in all stations an increase in the upper centimeters, with a maximum at around 5 cm depth and a subsequent decrease. Silicate profiles were characterized by an irregular shape, with a general trend to increase with depth.

3.2. Benthic fluxes

An example of the evolution of DO, pH, methane, nitrous oxide, TA and dissolved nutrients during a benthic chamber incubation is plotted in Fig. 3. Trends in the rest of chamber deployments were similar to this example. Benthic fluxes, calculated from the product of the slope of a linear regression of the time-series concentrations and the chamber's volume: surface ratio, are plotted in Fig. 4. Negative values denote fluxes into the sediment. Benthic fluxes measured in the creek did not statistically differ among the three stations studied. Water column characteristics at the beginning of each chamber incubation are summarized in Table 1. Water temperature varied from 8 °C in the winter months to up to 26 °C during the summer months. The concentrations of NO_3^-, NO_2^- and NH_4^+ in the water column were relatively high, as a result of the fish farm discharges (Tovar et al., 2000).

Oxygen fluxes ranged from −16 to −79 mmol m^{-2}d^{-1}, with lowest uptake rates during the winter months. DIC and TA effluxes presented a

Table 1
Water column characteristics at the beginning of each chamber incubation performed

	T (°C)	*S*	OD (µM)	CH_4 (nM)	N_2O (nM)	TA (mM)	DIC (mM)	NO_3^- (µM)	NO_2^- (µM)	NH_4^+ (µM)	PO_4^{3-} (µM)	Si (µM)
Summer 04												
Stn 1	26.2	37.0	151.7*	63.5 (4)	47.5 (4)	3.21 (7)	3.21 (7)	13.80 (6)	9.66 (4)	21.5 (8)	2.43 (8)	9.4 (8)
Stn 2	24.6	36.2	148.5*	35.5 (4)	31.2 (4)	3.16 (8)	3.13 (8)	13.65 (6)	7.57 (6)	12.4 (6)	1.37 (7)	8.0 (7)
Stn 3	25.6	40.3	154.8*	14.0 (4)	30.3 (4)	2.93 (8)	2.86 (8)	8.32 (8)	5.21 (8)	16.3 (8)	1.11 (7)	6.1 (6)
Winter 05												
Stn1	8.1	36.1	281.2*	16.8 (5)	12.4 (5)	3.11 (7)	2.88 (7)	0.13 (5)	0.01 (6)	3.4 (6)	0.21 (6)	0.7 (6)
Stn 2	10.0	37.4	259.9*	25.6 (5)	20.8 (4)	3.25 (6)	3.07 (6)	0.80 (4)	0.56 (6)	7.7 (7)	1.54 (7)	3.6 (7)
Stn 2	10.1	27.6	232.1*	24.8 (4)	17.4 (5)	3.06 (6)	2.94 (6)	–	0.31 (6)	8.7 (6)	0.66 (6)	2.2 (6)
Stn 3	9.6	35.2	274.1*	14.3 (5)	13.0 (5)	2.89 (6)	2.70 (6)	0.07 (5)	0.11 (5)	6.0 (5)	0.33 (6)	1.0 (6)
Spring 06												
Stn 1	22.6	35.8	163.9 (7)	56.8 (5)	39.9 (6)	2.73 (5)	2.65 (5)	4.02 (5)	2.52 (6)	7.5 (5)	0.42 (6)	5.4 (6)
Stn 1	22.6	35.8	158.8 (7)	62.5 (6)	41.0 (6)	2.79 (5)	2.72 (5)	4.88 (4)	2.91 (6)	5.4 (5)	0.69 (6)	8.7 (6)
Stn 2	21.8	34.8	169.1 (6)	54.3 (6)	34.9 (6)	2.80 (5)	2.73 (5)	9.24 (5)	3.47 (6)	7.6 (6)	0.21 (4)	5.7 (4)
Stn 2	21.8	34.8	167.9 (6)	72.4 (6)	36.4 (6)	2.88 (5)	2.78 (5)	7.22 (4)	3.16 (5)	10.2 (5)	0.30 (5)	5.4 (5)
Stn 3	20.7	35.5	170.8 (6)	49.6 (6)	34.5 (5)	–	–	3.71 (4)	2.36 (6)	9.0 (5)	0.22 (6)	10.2 (6)

The initial concentrations are derived from the linear regressions made to calculate benthic fluxes. The number of data points used in the linear fits in brackets.
*Continuous measurement.

greater range, from 47 to 147 mmol $m^{-2}d^{-1}$ and 41 to 126 mmol $m^{-2}d^{-1}$, respectively. NO_2^- and NO_3^- fluxes, which generally accounted for a considerable portion of total inorganic N fluxes, were highly variable and varied from −4.6 to 3.4 mmol $m^{-2}d^{-1}$ and from −0.4 to 2.2 mmol $m^{-2}d^{-1}$, respectively. Specifically, NO_2^- fluxes were very high, on some occasions even higher than NO_3^- fluxes. NH_4^+ fluxes were relatively high and always positive, ranging from 3.4 to 21.5 mmol $m^{-2}d^{-1}$, with significantly higher values during the summer months. Phosphate and silicate fluxes were always directed out of the sediment, and ranged between 0.2 and 2.4 mmol $m^{-2}d^{-1}$ and 0.7 and 10.2 mmol $m^{-2}d^{-1}$, respectively.

Benthic fluxes of methane and nitrous oxide were always positive and ranged from 5.7 to 47 µmol CH_4 $m^{-2}d^{-1}$ and from 4.3 to 49 µmol N–N_2O $m^{-2}d^{-1}$, respectively.

In general, benthic fluxes in Río San Pedro creek were lower than those measured seasonally in previous studies at other polluted sites of the Bay of Cádiz (Forja et al., 1994, 2004), even though the organic carbon contents of those sediments were relatively similar to the ones in our study site. Forja et al. (2004) reported fluxes which varied from 154 to 295 mmol m^{-2} d^{-1} for dissolved inorganic carbon, from 114 to 204 mmol m^{-2} d^{-1} for total alkalinity and from 106 to 146 mmol m^{-2} d^{-1} for oxygen uptake. A possible explanation for this difference may be that the organic matter reaching Río San Pedro creek is more refractory, as it is probably being partially degraded in the fish ponds before it is discharged to the creek and/or in the water column before it settles to the bottom.

It should be noted that the chambers used for the in situ incubations were opaque, which means that, if any light reached the sediments, our measurements would not integrate net metabolism but only respiration.

3.3. Seasonal variability

Benthic fluxes showed a strong seasonal variation. Fig. 5 shows the averaged benthic fluxes for each season versus temperature. Fluxes of dissolved oxygen, inorganic carbon, methane and silicate showed the same seasonal pattern, being significantly lower in the winter than in the summer or spring ($p<0.03$). However, none of them showed any statistical differences between summer and spring. Hence, their seasonal variability seemed to be related to temperature changes, as indicated by their linear correlation with water column temperature ($r^2=0.66$, $r^2=0.65$, $r^2=0.41$ and $r^2=0.71$). Alkalinity fluxes did not show any clear seasonal pattern.

Nitrous oxide fluxes and nitrite fluxes were significantly higher in the summer compared to spring and winter ($p<0.02$), whereas nitrate fluxes did not show any statistical differences between the seasons. Similarly phosphate benthic fluxes were highest during the summer, although significant differences were only observed between summer and spring ($p<0.01$).

4. Discussion

4.1. Sediment profiles

The vertical distributions of pore water pH, DIC, TA, NH_4^+, SO_4^- and HPO_4^{2-} are consistent with the sequence of processes involved in the oxidation of organic matter. For example, the aerobic degradation of organic matter results in the release of DIC, NH_4^+ and HPO_4^{2-} to the pore water, and leads to a decrease in pH, which can induce $CaCO_3$ dissolution (Mucci et al., 2000). In our sediments this initial pH diminution was not observed, probably due to the lack of sediment depth resolution, although the lowest pH values were in all cases recorded in the first cm of sediment. There are several suboxic oxidation reactions, such as manganese and iron/oxyhydroxide reduction processes, that result in an increase of pore water pH. On the other hand, sulfate reduction results in a small decrease of pH, but this acidification can be buffered by the precipitation of iron sulphide minerals such as pyrite (Mucci et al., 2000). Sulfate reduction is one of

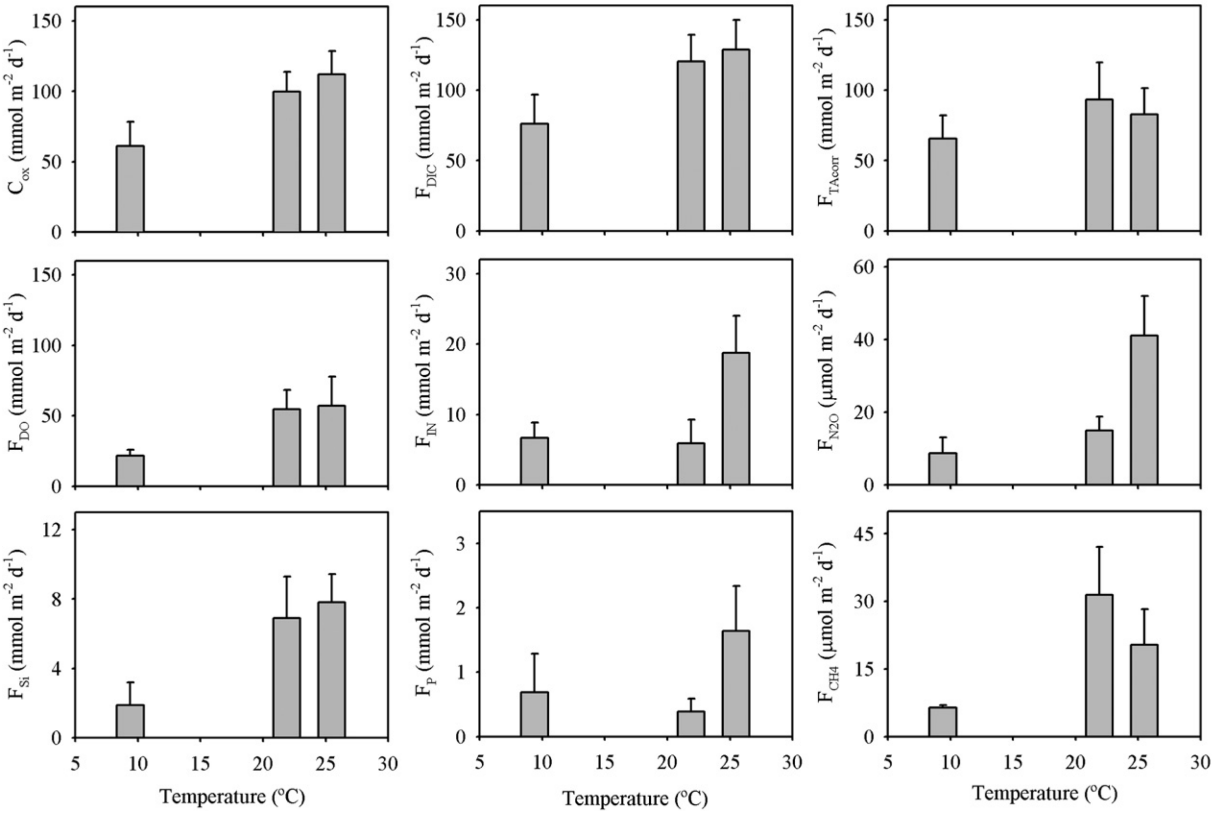

Fig. 5. Average carbon mineralization rates (C_{ox}) and fluxes of dissolved inorganic carbon (F_{DIC}), corrected total alkalinity (F_{TAcorr}), dissolved oxygen (F_{DO}), dissolved inorganic nitrogen ($NO_3^-+NO_2^-+NH_4^+$) (F_{IN}), dissolved nitrous oxide (F_{N2O}), silicate (F_{Si}), phosphate (F_P) and dissolved methane (F_{CH4}) for each season plotted versus temperature. Error bars represent the standard deviations.

the main mechanisms for the degradation of organic carbon in coastal sediments (e.g., Andersen and Hargrave, 1984; Canfield, 1993; Thamdrup and Canfield, 2000) and results in a decrease of SO_4^- and an increase of DIC, TA, NH_4^+ and HPO_4^-. Given the SO_4^- concentration gradients, sulfate reduction seemed to be an important mineralization pathway in this system. This is further corroborated by the high negative linear correlations observed between pore water sulfate concentrations with both pore water DIC ($r^2=0.75$, $r^2=0.82$ and $r^2=0.73$ for stations1, 2 and 3, respectively) and NH_4^+ ($r^2=0.69$, $r^2=0.81$ and $r^2=0.81$ for stations 1, 2 and 3, respectively). Furthermore, the plots of pore water DIC variations vs. TA variations (ΔDIC/ΔTA) can be used to investigate the end-member reactions for organic matter degradation through sulfate reduction (Hammond et al., 1999). The pore water data showed very consistent slopes at the three stations, with an average reaction stoichiometry of ΔDIC/ΔTA = 0.97 ± 0.01. Taking into account that the sediment C_{org}:N ratio ranged from 10 to 20, the ΔDIC/ΔTA ratios expected for the reaction of sulfate reduction in the presence of iron-oxyhydroxides, based on the degradation of organic matter with an average oxidation state of zero, would range from 0.86 to 0.90, being only 7 or 11% lower than observed.

On the other hand, denitrification, the microbial organic carbon oxidation via nitrate reduction to nitrogen gas, results in an increase of DIC, TA, and HPO_4^{2-}. N_2O can either be produced or consumed during denitrification (Knowles, 1982). Apart from nitrate reduction, N_2O can also be formed during autotrophic nitrification by ammonia-oxidizing bacteria, either as a by-product during ammonium oxidation to nitrite or as an intermediate via nitrifier-denitrification (Wrage et al., 2001).

4.2. Carbon mineralization

In marine sediments, oxygen uptake rates and DIC fluxes are the most widely used measures of benthic organic carbon degradation. The relative benthic fluxes of DO, TA, DIC, nitrate, nitrite and ammonia give an insight into the different pathways taking place in the sediment column during organic matter mineralization. The flux of alkalinity can be affected by the dissolution of $CaCO_3$ and several organic matter mineralization processes, such as the liberation of ammonium, net denitrification, net sulfate reduction and manganese and iron reduction/oxidation processes. As proposed by Berelson et al. (1998), alkalinity fluxes were corrected for the contribution of ammonium and net denitrification by adding the fluxes of nitrite and nitrate and subtracting the flux of ammonium (Table 2). The magnitude of this correction was in all cases less than 25% of alkalinity fluxes. With this adjustment, corrected alkalinity fluxes (TA_{corr}) can be attributable to the dissolution of $CaCO_3$, net sulfate reduction and metal reduction. The fluxes of TA_{corr} were correlated with DIC fluxes ($r^2=0.52$) and the average F_{TAcorr}:F_{DIC} ratio was 0.67 ± 0.16, consistent with F_{TA}:F_{DIC} ratios measured previously in other sites of the Bay of Cádiz (0.69; Forja et al., 2004). Maximum $CaCO_3$ dissolution rates were calculated as 1/2 of the TA_{corr} flux, given that two equivalents of total alkalinity are produced per mole of $CaCO_3$ dissolved (Mucci et al., 2000) (Table 2), and ranged from 15 to 59 mmol $m^{-2}d^{-1}$. These values do not take into account the contribution of sulfate or metal reduction to the alkalinity fluxes. The lower limit of organic carbon oxidation rate (C_{ox}) was hence estimated by subtracting the maximum dissolution rates from the measured DIC fluxes. In this way, maximum $CaCO_3$ dissolution rate in the study site would account on average for 33% of DIC fluxes. The importance of $CaCO_3$ dissolution varies substantially in different coastal environments. For example, between 25 and 52% of DIC fluxes were due to $CaCO_3$ dissolution in several coastal ecosystems of the Iberian Peninsula (Forja et al., 2004; Ortega et al., 2005), and Cermelj et al. (2001) calculated a contribution of 40% in the Gulf of Trieste. On the other hand, $CaCO_3$ dissolution only contributed with about 2% to benthic DIC fluxes in the Gullmar Fjord (Skagerrak/North Sea coast) (Anderson et al., 1986). The other extreme situation to infer carbon mineralization rates would be to consider that $CaCO_3$ dissolution was negligible. In that case TA_{corr} fluxes would be due to sulfate reduction and metal reduction/oxidation, and carbon oxidation rates would equal measured DIC fluxes. An upper limit for sulfate reduction, assuming the reaction in the presence of iron-oxyhydroxides and based on the degradation of organic matter with an average oxidation state of zero would be given by $0.86 \times TA_{corr}$ (Hammond et al., 1999), considering a C_{org}:N ratio of 10 (Table 2). Maximum sulfate reduction rates ranged between 27 and 102 mmol C $m^{-2}d^{-1}$, accounting on average for 57% of benthic DIC fluxes.

Given the upper and lower limits of C_{ox}, we assume the average as the most likely value of total organic carbon oxidation rate in the study site (Table 2). Average C_{ox} rates were in all cases within ±25% of the upper and lower limit estimates of organic carbon oxidation.

Calculated C_{ox} rates varied seasonally, showing a high linear positive correlation with temperature ($r^2=0.72$). This pattern has been reported in many other systems (e.g., Hopkinson et al., 1999; Forja et al., 2004) and reflects the diminution of reaction rates, diffusion rates and faunal activity with decreasing temperature. Moreover, Tovar et al. (2000) measured the input of particulate organic matter being discharged from the fish farm to the creek, showing

Table 2
Alkalinity and corrected alkalinity fluxes and estimations of maximum $CaCO_3$ dissolution rates, maximum carbon oxidation rates due to sulfate reduction, minimum and maximum carbon oxidation rates, average carbon oxidation rates, Community Respiration Quotient (CRQ) and percentage of remineralized N removed by denitrification

	F_{TA}	F_{TAcorr}	Max DIS	Max C_{ox} by SO_4	Min C_{ox}	Max C_{ox}	Average C_{ox}	CRQ	% N removal
Summer 04									
Stn 1	87.5	66.2	33.1	57.0	104.5	137.6	121.0	1.52	−8.5
Stn 2	62.4	50.2	25.1	43.2	79.5	104.6	92.1	2.35	16.9
Stn 3	98.5	87.5	43.9	75.5	100.0	143.9	121.9	2.31	−8.3
Mean ± SD	83 ± 19	68 ± 19	34 ± 9	59 ± 16	95 ± 13	129 ± 21	112 ± 17	2.06 ± 0.47	0 ± 15
Winter 05									
Stn 1	76.7	73.7	36.8	63.4	59.4	96.2	77.8	2.93	76.5
Stn 2	40.7	31.9	15.9	27.4	32.3	48.2	40.2	1.76	20.7
Stn 2	70.0	61.6	30.8	53.0	56.2	87.0	71.6	3.54	39.7
Stn 3	74.1	68.3	34.1	58.7	38.2	72.3	55.2	3.37	46.1
Mean ± SD	65 ± 17	59 ± 19	29 ± 9	51 ± 16	47 ± 13	76 ± 21	61 ± 17	2.90 ± 0.80	46 ± 23
Spring 06									
Stn 1	96.7	86.6	43.3	74.5	78.6	121.9	100.3	1.95	73.6
Stn 1	125.5	118.1	59.0	101.5	87.0	146.0	116.5	2.65	84.7
Stn 2	89.3	76.7	38.4	66.0	63.8	102.2	83.0	1.28	82.3
Stn 2	61.5	48.4	24.2	41.6	86.3	110.5	98.4	1.36	60.4
Stn 3	–	–	–	–	–	–	–	–	–
Mean ± SD	93 ± 26	82 ± 29	41 ± 14	71 ± 25	79 ± 11	120 ± 19	100 ± 14	1.81 ± 0.64	75 ± 11

Rate units are in mmol m^{-2} d^{-1}.

maximum values during the summer months and minimum values during the winter, which could also contribute to the seasonal variability observed.

There was a fairly good linear correlation between C_{ox} and oxygen uptake (r^2=0.58). The ratio between the fluxes of DIC and oxygen uptake (Community Respiration Quotient, CRQ) is often used to characterize benthic metabolism and to assess the relative intensity of the processes of aerobic and anaerobic respiration (Hargrave and Phillips, 1981; Andersen and Hargrave, 1984; Anderson et al., 1986). Benthic fluxes of both oxygen and inorganic carbon are affected by aerobic and anaerobic processes. Oxygen uptake results from aerobic respiration and from the re-oxidation of products generated during anaerobic respiration (Mn^{2+}, Fe^{2+}, H_2S, NH_4^+, CH_4), whereas the flux of inorganic carbon is a consequence of aerobic and anaerobic respiration processes as well as the dissolution or precipitation of $CaCO_3$. In order to take into account only the biological production of inorganic carbon, CRQ values were calculated as the ratio between average C_{ox} and oxygen uptake (Table 2). CRQ values in the creek were substantially above 1 (average 2.3±0.7, range 1.4–3.6), suggesting the importance of anaerobic respiration processes to the decomposition of organic matter, as well as the storage of reduced compounds within the sediment and/or their escape to the water column before being re-oxidized. These values are in line with those reported previously for other coastal environments (Hargrave and Phillips, 1981; Andersen and Hargrave, 1984; Anderson et al., 1986; Forja et al., 2004; Stahl et al., 2004; Ortega et al., 2005).

Oxygen penetration depths were estimated from benthic oxygen fluxes and bottom water oxygen concentration, by applying the relationship proposed by Cai and Sayles (1996):

$$L = 2\phi D_s [O_2] / F_{DO} \qquad (1)$$

where L is the oxygen penetration depth, ϕ is the porosity, D_s is the diffusivity of oxygen in the sediment, $[O_2]$ is the concentration of oxygen in the water column and F_{DO} is the oxygen uptake. The diffusion coefficient (D_s) was calculated using the expression provided by Sweerts et al. (1991), and applying the diffusive coefficients for finite dilution (D^0) reported by Broecker and Peng (1974). In the study site, estimated oxygen penetration depths were relatively shallow and ranged between 0.3 and 1.4 mm, which are among the values reported in other coastal systems (e.g., Revsbech et al., 1980; Glud et al., 2003, 2005). Maximum penetration depths were obtained in the winter (average 1.1 mm), whereas in summer and spring oxygen penetration was significantly shallower (average 0.4 mm). It should be noted that the equation proposed by Cai and Sayles (1996) assumes that oxygen penetration depth is only a function of diffusion and, therefore, it does not take into account the effect of irrigation, in contrast to measured oxygen fluxes with the chamber. If irrigation was important, measured oxygen fluxes would be enhanced without resulting in a lower oxygen penetration depth (as expected by the model) and, hence, calculated L would be underestimated.

4.3. Dissolved methane fluxes

In marine sediments, methane is produced via microbial methanogenesis below the sulfate reduction zone, as sulfate reducing bacteria compete with methanogens for common substrates (Martens and Berner, 1974). In organically rich sediments the zone of sulfate to methane transition is shallower, so methane production occurs nearer to the sediment-water interface than in sediments with a low content of organic matter (Valentine, 2002). Benthic fluxes of CH_4 are then controlled by its transport to the sediment surface, which can be through molecular diffusion and/or bubble ebullition, as well as by its consumption within the sediment by anaerobic and aerobic oxidation. Although the processes of CH_4 production and consumption within the sediment are well understood (e.g., Martens and Berner, 1974; Martens and Klump, 1980; Valentine, 2002), little is known about the amount released to the water column and the role of sediments in CH_4 emissions to the atmosphere from coastal systems.

Bubble transport across the sediment-water interface was not visually observed at the study site, so it was assumed that methane benthic exchange occurs only through diffusion and macrofaunal enhancement. Methane benthic fluxes were always positive and ranged from 6 to 47 μmol $m^{-2}d^{-1}$, representing in all cases less than 0.03% of organic matter oxidation. Values were among the highly variable range of methane fluxes reported for other coastal environments (Table 3). Annually averaged, benthic fluxes of CH_4 accounted for approximately 30% of estimated CH_4 fluxes to the atmosphere (Ferrón et al., 2007), which indicates that there must be other significant sources to the creek apart from sediment production, such as the production inside the fish farm ponds and in the water column, and lateral inputs. Nevertheless, it must be taken into account that the estimation of air–water fluxes were subjected to very large uncertainties and values varied significantly depending on the parameterization used to calculate the gas transfer velocity (Ferrón et al., 2007).

4.4. Nitrogen fluxes

Solute flux molar ratios can be used as indicators to examine the preferential pathways of organic matter mineralization. As particulate organic matter reaching the bottom comes to a large extent from the residual fish food and excreta being discharged by the fish farms (Tovar et al., 2000), settling organic matter probably deviates from Redfield stoichiometry (C:N:P=106:16:1). The molar C_{org}:N ratios of

Table 3
Methane fluxes from coastal marine sediments

Location	Date	Method	CH_4 flux	Reference
Cape Lookout Bay	Oct, Nov, 76, Mar–Nov 77	In situ chamber incubation Diffusive fluxes	720–9432[a] 624–3840	Martens & Klump (1980)
Gullmar Fjord (under trout cage farm)	Dec 84, May, Sep 85, Jun 86	In situ chamber incubation	3–6266 0–978000[b]	Hall et al. (1990)
Plum Island Sound estuary	May 93–Sep 94	Core incubations	10–1020	Hopkinson et al. (1999)
Randers Fjord				
Brackish Stn	Mar–Dec 00	Core incubation	−19 to −359	Abril & Iversen (2002)
Saltwater Stn		Headspace core incubation	3–404	
Western Mexican Margin	Nov–Dec 01	Diffusive fluxes	0.2–5.5	Sansonse et al. (2004)
Mangrove forest *kandelia candel,* Jiulongjiang estuary	Jul 02, Sep 03	Headspace core incubation	5–66	Alongi et al. (2005)
Wright Myo creek, mangrove forest sediment	Jan, Jul 04	In situ chamber incubation	432–840[c]	Barnes et al. (2006)[d]
Río San Pedro creek	Jun–Jul 04, Jan–Feb 05, Mar –Apr 06	In situ chamber incubation	5.7–47	This study

Units: μmol CH_4 m^{-2} d^{-1}.
[a] Measured during non-bubble periods.
[b] Gaseous methane flux.
[c] Sediment–water–air flux.
[d] These authors provide a review of CH4 fluxes from mangrove sediments measured with static chambers (range: 0–19512 μmol m^{-2} d^{-1}).

particulate matter in the water column, which were measured in a seasonal study during 2004 (Forja et al., in preparation), presented a high variability with the tides. Assuming that the settling of particulate matter mainly occurs at low current velocities (during low and high tide), we considered the average C_{org}:N molar ratios over entire tidal cycles as representative of the particulate organic matter reaching the bottom. In this way, C_{org}:N molar ratios varied seasonally and presented average values of 6.0 in summer, 5.4 in spring and 4.8 in winter. The comparison of these ratios with the molar ratios of benthic organic carbon oxidized and total inorganic flux (ammonia + nitrate + nitrite) (C_{ox}:F_{IN}) provides an insight into dissolved inorganic nitrogen reactions within the pore water. During the summer, measured F_{IN} did not deviate significantly from predictable remineralized nitrogen, which would equal C_{ox}/(C_{org}:N) (Fig. 6a), although during the winter and spring F_{IN} were typically lower than expected from organic matter mineralization. These deviations are normally explained as a loss of fixed nitrogen as nitrogen gas or nitrous oxide, assuming that the flux of dissolved organic nitrogen is negligible. Considering that denitrification is the main N_2-producing process, the percentage of remineralized N removed by denitrification can be estimated as:

$$\%\ \mathrm{N\ removal} = 100 * \{1 - [F_{IN} * (C_{org} : N) / C_{ox}]\} \qquad (2)$$

However, recent observations indicate that there may be other processes apart from traditional denitrification involved in the production of N_2, such as the anaerobic ammonium oxidation (anammox), in which NH_4^+ is converted to N_2 without the simultaneous production of N_2O, although this route is generally less favored compared to denitrification in reactive sediments with elevated access to reduced compounds (Hulth et al., 2005).

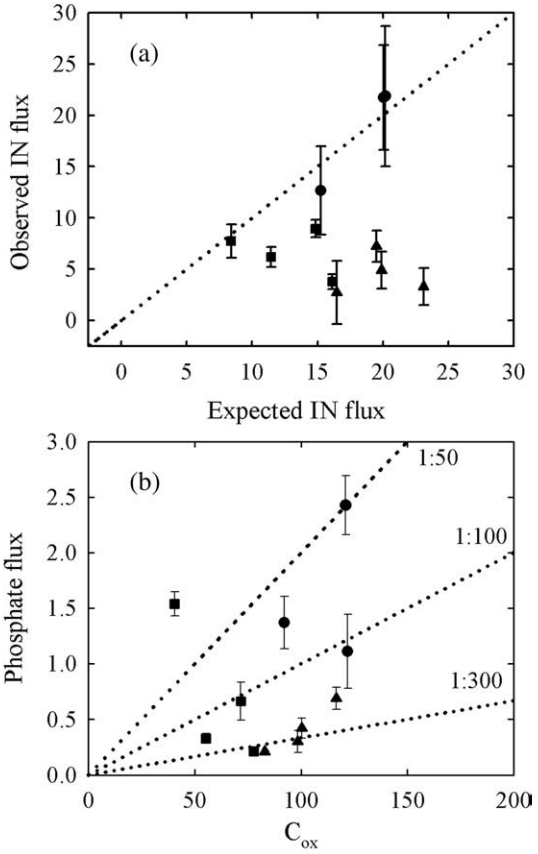

Fig. 6. (a) Observed vs. expected N flux relationships. The dotted lines represent 1:1 agreement (b) Benthic phosphate fluxes vs. sediment carbon oxidation rates. The dotted lines represent the indicated P:C molar ratios of remineralized organic matter. Circles: summer 2004; squares: winter 2005; triangles: spring 2006.

The percentage of total remineralized nitrogen removed by denitrification, calculated by applying Eq. (2), was highly variable among the sites and seasons (Table 2) and seemed to be significant during the winter and spring, with an average loss of mineralized N of 46 ± 23% and 75 ± 11%, respectively, whereas during the summer N regeneration was apparently more effective. Interestingly, reported benthic N_2O and NO_2^- effluxes were significantly higher during the summer compared to winter and spring. N_2O in marine sediments can be produced during denitrification, nitrification, nitrifier–denitrification and nitrate reduction to ammonium (DNRA). Denitrification can either produce or consume N_2O (Knowles, 1982). On the other hand, the relatively high benthic NO_2^- effluxes measured in this work must imply that either NO_3^- reduction occurred at a greater rate than NO_2^- reduction during the denitrification or DNRA processes, or that the oxidation of NH_4^+ was greater than that of NO_2^- during nitrification. One possibility to explain the summer situation in terms of the N cycling is that the sediment reducing conditions and the shallow oxygen penetration depth during this period could provoke an accumulation of hydrogen sulfide in the pore water, due to higher rates of sulfate reduction and possibly an incomplete re-oxidation of sulfide. This could inhibit nitrous oxide reductase in the last step of denitrification (Knowles, 1982), leading to an accumulation of N_2O. However, taking into account that N–N_2O fluxes represented a very small fraction of total inorganic N flux (0.07%–0.64%), the inhibition of N_2O reductase would only explain the higher benthic N_2O fluxes observed but not the lack of net N loss from the sediments. On the other hand, several authors have reported negligible or very low rates of denitrification in sediments subjected to waste deposition from fish farms (Blackburn et al., 1988; Kaspar et al., 1988; Hall et al., 1992), where DNRA can be stimulated (Kaspar et al., 1988; Hall et al., 1992; Christensen et al., 2000). DNRA is also thought to be favoured by a high ratio of available carbon to nitrogen (Tiedje, 1988). The absence of denitrification in sediments below fish cages is often attributed to the inhibitory effect of hydrogen sulfide on nitrification activity (Kaspar et al., 1988) plus low availability of oxygen for nitrification. Senga et al. (2006) demonstrated that the presence of H_2S in coastal sediments enhanced the accumulation of N_2O, NO_2^- and NH_4^+ and argued that the former could provoke a shift from denitrification to DNRA. Although this could be a reasonable explanation for our summer data it still does not explain why there was such a difference between summer and spring, as environmental conditions were similar during both seasons and, in contrast, denitrification in spring seemed to remove the highest percentage of potentially recyclable N. In any case, and even though that with the data available in this study it is difficult to elucidate the processes involved in the N cycling of these sediments, it is essential to note the occurrence of this apparent change in the processes involved in the removal of potentially recyclable N observed during the summer, as well as its associated environmental implications in eutrophication.

Measured nitrous oxide benthic fluxes in Río San Pedro creek were of the same order of magnitude as methane benthic fluxes and were within the range of those reported by other authors in coastal sediments (Table 4). There was a linear relationship between nitrous oxide fluxes and benthic fluxes of ammonium (r^2 = 0.64) and nitrite (r^2 = 0.44). Just as with CH_4 fluxes, annually averaged benthic fluxes of N_2O were about 4 times lower than average estimated N_2O emissions to the atmosphere (Ferrón et al., 2007). This implies that there must be other important sources of N_2O to the creek besides sediment production, such as the fish farm effluent, water column nitrification and/or denitrification and lateral inputs. Due to the conditions inside the fish ponds, it is expected that the fish farm effluent may be a significant source of CH_4 and N_2O to the creek, as sediments inside the ponds must be very favorable sites for their production.

4.5. Phosphate fluxes

The molar ratios of mineralized carbon to the flux of phosphate (C_{ox}:F_P) can also be used to examine organic matter remineralization processes, given the C:P ratio of deposited organic matter. Particulate

Table 4
Nitrous oxide fluxes from coastal marine sediments

Location	Date	Method	N_2O flux	Reference
Narragensett Bay	Jul 78, Mar, Jul, Oct, Nov 79	Headspace core incubation	0.9–44	Seitzinger et al. (1984)
Ochlockonee Bay	Mar 85	Headspace core incubation	0.5–1.2	Seitzinger (1987)
Delaware Bay	Jul 85	Headspace core incubation	0–62	Seitzinger (1988)
Wadden Sea[a]	Apr 89–Mar 90	Headspace core incubation	−.6–13	Kieskamp et al. (1991)
Scheldt estuary[a]	Sep 90–Dec 91	In situ chamber incubation	−68–205[b]	Middelburg et al. (1995)
Tokio Bay	Nov 88, Feb 89	One dimensional diffusion model	0.1–3.1	Koike & Terauchi (1996)
Mangrove forest sediments, Puerto Rico[a]	Jan–Jun 91, Jan –Dec 95, Nov –Feb 97	In situ chamber incubation	2.9–187[b]	Corredor et al. (1998)
Plum Island Sound estuary	May 93–Sep 94	Core incubations	−0.5–1.9	Hopkinson et al. (1999)
Koaziro Bay	Apr, Aug 92	Diffusive fluxes	−1.1–0.2	Usui et al. (1998)
Tama estuary	Feb, May 96	Continuous culture experiment	30–37	Usui et al. (2001)
Mangrove forest sediments, Puerto Rico[a]	No data	Chambers	1.2–34[b]	Bauza et al. (2002)
Mid-Atlantic Bight sediments	Jun, Nov 98, May, Aug 99	In situ chamber incubation	−17–97	Laursen & Seitzinger (2002)
Mangrove forest *Kandelia candel,* Jiulongjiang estuary[a]	Jul 02, Sep 03	Headspace core incubation	3.2–213	Alongi et al. (2005)
Wright Myo creek, mangrove forest sediment	Jan, Jul 04	In situ chamber incubation	2.4–31	Barnes et al. (2006)[c]
Yangzte estuary[a]	Jul 04	In situ chamber incubation	16–236[b]	Wang et al. (2007)
Río San Pedro creek	Jun–Jul 04, Jan–Feb 05, Mar –Apr 06	In situ chamber incubation	4.3–49	This study

Units: µmol N_2O–N m^{-2} d^{-1}.
[a] Intertidal sediments.
[b] Sediment–atmosphere fluxes.
[c] These authors provide a review of N_2O fluxes from mangrove sediments measured with static chambers (range: −2.4–4800 µmol m^{-2} d^{-1}).

organic matter reaching the bottom in the study site is expected, due to the high content of phosphorus of fish farm food, to have lower C:P molar ratios than the Redfield ratio of 106, unless the inputs from the surrounding salt marshes are significant. Tovar (2000) studied the solid-phase content of phosphorus in surface sediments of the creek and found that it was significantly higher in the upper part of the channel, corresponding to our Stn 1 and Stn 2. The average content of total sediment phosphorus varied between 517 µg/g in Stn 3 and 687 µg/g in Stn 1, from which 53–81% was inorganic. Tovar (2000) observed that, although the sediment content of organic phosphorus was relatively homogeneous along the creek, higher contents of inorganic solid-phase phosphorus were associated with the sediments of the upper creek, suggesting the fish farm as the main source. In our study, benthic phosphate fluxes were poorly correlated with carbon mineralization rates, indicating that there must be other sources or sinks for P. Although measured C_{ox}:F_P ratios showed a high variability (Fig. 6b), during summer and spring they were found to correlate linearly with water column oxygen concentration ($r^2=0.94$), which is consistent with the findings of Ingall and Jahnke (1997), who concluded that P regeneration relative to carbon oxidation was higher at low water column oxygen concentrations. However, during the winter, C_{ox}:F_P ratios showed the highest variability and did not follow the former relationship. So even though the concentration of oxygen in the water column was significantly higher during the winter ($p<0.001$), measured C_{ox}:F_P ratios were not statistically different from those observed in summer and spring. The higher P recycling efficiencies observed during the summer seemed to be related to the low oxygen concentrations in the water column. In addition to the phosphate coming from organic matter mineralization, phosphate fluxes could also be affected by the release of inorganic mineral phosphorus adsorbed in the sediments, given the relatively high solid-phase content of inorganic phosphorus in these sediments, which seem to be associated to the fish farm discharge (Tovar, 2000).

4.6. Silicate fluxes

Benthic silicate fluxes were linearly correlated with carbon oxidation rates ($r^2=0.58$) and temperature ($r^2=0.71$). Temperature is considered as one of the main factors controlling the dissolution of biogenic silica in marine sediments (Cermelj et al., 2001) and, possibly, the relationship between F_{Si} and C_{ox} is just a consequence of their own seasonal variability. However, Bidle and Azam (1999) showed a potential linkage between the oxidation of organic matter and the regeneration of silica and established the role of bacterial activity in increasing biogenic silica dissolution by degrading the organic matrix that protects diatom frustules against dissolution. Diatoms are the main group of phytoplankton in the Bay of Cádiz (Establier et al., 1986) and probably represent the main source of biogenic silica in these sediments. Measured molar ratios of F_{Si} to C_{ox} in the study site were relatively low, ranging from 0.01 to 0.09 (average ± SD; 0.06 ± 0.03). Average Si:C ratio reported for pelagic diatoms is 0.13 (Brzezinski, 1985), whereas benthic diatoms are considered to have significantly higher ratios (Sigmon and Cahoon, 1997). However, the low F_{Si} to C_{ox} ratios observed in the study site are not surprising, as organic matter is recycled more rapidly than biogenic silica (Ragueneau et al., 2000) and, furthermore, the particulate organic matter that reaches the sediments, which to a large extent comes from the fish farm inputs in this upper part of the creek (Tovar et al., 2000), may have low contents of silica.

4.7. Role of benthic mineralization and nutrient recycling

Assuming that sediment carbon oxidation rates do not vary significantly along the creek, the mean C_{ox} derived from this study −89 ± 29 mmol C m^{-2} d^{-1} — can be extrapolated to the entire sediment surface of the creek (~ 1.3 km^2). With this approximation, about 515 10^3 kg of organic C are annually being degraded in the sediments of Río San Pedro creek, accounting for approximately 60% of total particulate organic matter being discharged by the fish farm (843 10^3 kg yr^{-1};Tovar et al., 2000). Similarly, the average measured benthic DIC flux, which was 106 ± 30 mmol C m^{-2} d^{-1}, would result in an annual release of approximately 613 10^3 kg of inorganic C, if integrated for the entire sediment surface of the creek. About 43% of benthic DIC fluxes to the water column are subsequently emitted to the atmosphere as CO_2 (22 10^6 mol CO_2 yr^{-1}; De la Paz et al., 2008a). However, sediments seem to play only a minor role (~ 6%) in the net export of DIC to the Bay of Cádiz, which was estimated to be 1.05 10^7 kg DIC yr^{-1} (De la Paz et al., 2008b), meaning that there must be other important sources of DIC to the creek. De la Paz et al. (2008b) hypothesized that the high amounts of DIC exported to the Bay of Cádiz were related to the direct inputs from the fish farm effluent. In this sense, sediments in the fish farm ponds comprise a similar surface as sediments in the creek itself, but the water height is considerably smaller and they presumably receive larger amounts of organic matter. Therefore, it is very likely that the remineralization of organic matter inside fish farm results in large quantities of DIC, which are subsequently discharged into the creek. In addition, given the large amounts of dissolved organic matter discharged into the creek (Tovar et al., 2000), water column respiration may be quantitatively important, influencing not only DIC but also the concentrations of dissolved oxygen and nutrients.

Overall, the degradation of organic matter taking place in the sediments of the creek resulted in the regeneration of 9 ± 7 mmol m^{-2} d^{-1} of inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$), 0.8 ± 0.7 mmol m^{-2} d^{-1} of phosphate and 5.5 ± 3.2 mmol m^{-2} d^{-1} of silicate. To examine the role of nutrient benthic regeneration in the creek, these values were integrated annually and over the entire surface of the creek and compared to the total annual discharges calculated by Tovar et al. (2000). From these calculations it can be inferred that these sediments release about 5 times more dissolved PO_4^{3-} (13 10^3 kg N yr^{-1}) than the fish farm effluent and a similar or slightly higher amount of dissolved inorganic nitrogen (~60 10^3 kg N yr^{-1}). However, the contributions of the different species of inorganic N differed in the two sources. Sediments were a net sink of NO_3^-, taking about 7.5 10^3 kg N–NO_3^- yr^{-1} from the water column, which would almost compensate for the fish farm input (6.73 kg N–NO_3^- yr^{-1}). However, NO_2^- was released from the sediments (4.3 10^3 kg N–NO_2^- yr^{-1}) at a similar rate as that estimated for the fish farm (4.95 10^3 kg N–NO_2^- yr^{-1}), whereas the net amount of NH_4^+ liberated by benthic processes (65 10^3 kg N–NH_4^+ yr^{-1}) was about 1.8 times higher than total fish farm input (36 10^3 kg N–NH_4^+ yr^{-1}). Therefore, even though denitrification accounted for a loss from the system of 46 and 75% of fixed N as N_2 during winter and spring, respectively, the net efflux of bioavailable inorganic N to the water column was still as important as the direct discharge from the fish farm.

These results emphasize the significance of benthic organic matter remineralization as a source of nutrients to the creek. The relatively high benthic nutrient effluxes released were possibly a consequence of the high contents of P and N associated with the particulate matter being discharged from the fish farm and deposited on the sediments.

5. Conclusions

Benthic organic C oxidation in sediments of Río San Pedro creek averaged 32.5 mol C m^{-2} yr^{-1} and, integrated over the entire sediment area of the creek, accounted for the degradation of 60% of the particulate organic matter being annually discharged into the system by the main fish farm effluent. Furthermore, results showed that benthic nutrient regeneration resulting from organic matter remineralization represented a significant source of dissolved nutrients into the system. Specifically, sediments were estimated to release around 5 times more phosphate than the fish farm effluent itself, possibly as a result of both organic matter mineralization and the release of mineral P scavenged to the particulate matter deposited on the sediments. The efficiency of P regeneration was apparently enhanced by low water column oxygen concentrations. Denitrification was estimated to account for an average loss of 46% of the potentially recyclable N during the winter, whereas this value increased to 75% during the spring. However, during the summer there seemed to be a shift in the processes involved in the removal of potentially recyclable N, as there was a complete recycling of mineralized N, and benthic N_2O and NO_2^- were significantly higher. Carbon oxidation rates varied seasonally as a consequence of the enhancement of metabolic rates with temperature and the seasonal variability of the discharges from the fish farm. This highlights the importance of having a seasonal coverage when studying benthic remineralization. Sediments were in all cases a source of N_2O and CH_4 to the water column, although benthic fluxes of these gases represented a small fraction of total inorganic N and C flux.

Acknowledgements

This work was supported by the Spanish CICYT (Spanish Commission for Research and Development) of the Ministerio de Educación y Ciencia under contracts REN2001-3577/MAR and CTM2005-01364/MAR. S.F. was funded by a grant from the Spanish MECD. The authors would like to thank V. Vietez and Dr. C. G. Castro, from the Department of Oceanography of the Instituto de Investigacións Mariñas de Vigo (CSIC), for their generous assistance during the measurement of nutrients, and S. Smith for language correction. The manuscript benefited from the comments provided by two anonymous reviewers.

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