Available online at www.sciencedirect.com

ScienceDirect

Continental Shelf Research 28 (2008) 458–469

CONTINENTAL SHELF RESEARCH

www.elsevier.com/locate/csr

Benthic fluxes of dissolved inorganic carbon in the Tinto–Odiel system (SW of Spain)

T. Ortega*, R. Ponce, J. Forja, A. Gómez-Parra

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

Received 8 September 2006; received in revised form 28 September 2007; accepted 15 October 2007
Available online 22 October 2007

Abstract

The benthic fluxes (diffusive and with chambers) of dissolved inorganic carbon (DIC), dissolved oxygen (DO) and total alkalinity (TA) have been calculated in summertime in the estuary system formed by the mouths of the Tinto and Odiel rivers (SW of Spain). An increase of DIC in interstitial water with depth was found for all stations showing values of up to 28 mM at a depth of 5 cm. The diffusive fluxes of DIC and TA obtained ranging between 1.8–7.8 and 1.5–7.3 mmol $m^{-2} d^{-1}$, respectively. These intervals are in agreement with those found for other coastal systems. Considering the plots of DIC vs. alkalinity ($\Delta DIC/\Delta TA$) in the first 30 cm of interstitial water, it was deduced that sulphate reduction and the oxidation of sulphides seem to have special relevance in the sediments of the stations studied. The benthic fluxes of inorganic carbon and DO measured by benthic chambers were variable, presenting elevated values (309–433 mmol DIC $m^{-2} d^{-1}$ and 50–120 mmol DO $m^{-2} d^{-1}$). The most elevated fluxes of DIC were seen at the stations with high anthropogenic influence (close to populated areas and industrial discharges). A great proportion of these fluxes are due to $CaCO_3$ dissolution processes, which constitute an estimated 49% of total DIC flux. DIC and DO benthic flux quotients were far in excess of unity, indicating the significance processes of anaerobic degradation of organic material at the stations studied.

Keywords: Benthic fluxes; Dissolved inorganic carbon; Alkalinity; Dissolved oxygen; Carbonate dissolution; Estuary

1. Introduction

The gradual increase in atmospheric CO_2 concentration along with the significant changes the earth's climate is experiencing has brought about the intensification of study in recent years on the global carbon cycle. Coastal zones are an area of special interest in this regard. In order to comprehend the global carbon balance the processes occurring must be understood along with the fluxes generated in these areas (Walsh, 1991).

Coastal zones are comprised of a wide range of ecosystems and geomorphological forms (bays, lagoons, estuaries, wetlands and beaches) each of whose physical and biogeochemical characteristics are greatly varied while each being strongly affected by the three major surrounding bodies: continents, oceans and the atmosphere. They are characterised as being places for the deposition and regeneration of organic carbon (OC) as well as in situ production of biogenic calcium carbonate (Mackenzie et al., 1998). Coastal areas store 30–50% of biogenic calcium carbonate and 80% of oceans' OC (Wollast and Mackenzie, 1989; Milliman, 1993; Smith and Hollibaugh, 1993; Wollast, 1998). As connecting zones, they act as filters, trapping organic material of natural and anthropogenic origin, which is transported from continents and reaches the ocean.

Rivers are the greatest contributors of organic material received by coastal areas since 70–75% of their suspended load is deposited there (Milliman, 1993) with a small proportion flowing toward the ocean. This organic material is highly reactive and is rapidly consumed by benthic organisms. Part of the dissolved organic carbon (DOC) that exports seaward is degraded in transit. Raymond and Bauer (2000), for example, observed that approximately 10% of the DOC from the York river was

---

*Corresponding author. Tel.: +34 956 016164; fax: +34 956 016040.
E-mail address: teodora.ortega@uca.es (T. Ortega).

0278-4343/$ - see front matter
doi:10.1016/j.csr.2007.10.004

degraded by bacteria during estuarine transport and that the degradation process is conditioned by temperature.

Coastal systems have significant anthropogenic influences, with 50% of the world's population settled there (a figure that grows 1.5% each year; Golberg, 1994), supporting more than 60% of the world's commercial fishing activities (World Resources Institute, 1996, cited in Ver et al., 1999). Discharge of anthropogenic material is provoking an increase in nutrient (Sabine and Mackenzie, 1991) and organic and inorganic carbon (Wollast and Mackenzie, 1989) inputs to coastal areas via rivers.

This input of organic material, both allochthonous and autochthonous, received in estuarine systems, gives rise to considerable benthic regeneration of organic material. The benthic regeneration is the result of an elevated number of physical, chemical and biological processes, which take place in the sediment causing remineralisation of the organic material and diffusion of degradation products to the overlying water, where they may be used by phytoplankton. As a consequence of benthic regeneration of organic material, net inorganic carbon and nutrient production occurs within sediments. In this sense, benthic degradation of organic matter affects the water column oxygen levels and provokes an increase in inorganic carbon concentration in the water column which is highly important for coastal ecosystems (e.g., Andersen and Hargrave, 1984; Mackin and Swider, 1989; Forja et al., 1994; López et al., 1995; Cai and Wang, 1998; Cai et al., 1999), in fact contributing to these systems acting as suppliers of CO_2 to the atmosphere, despite the fact that on a global level oceans are the main sink for this greenhouse gas.

The Tinto–Odiel estuary is one of the areas most polluted by heavy metals in Western Europe. Many studies have therefore been carried out relating to heavy metals, yet few works have focussed on the carbon cycle. In order to learn more about the carbon cycle in this system and evaluate the influence of this pollution in the benthic fluxes of dissolved inorganic carbon (DIC) in the Tinto–Odiel estuary, the diffusive and the benthic fluxes of DIC, dissolved oxygen (DO) and total alkalinity (TA) have been measured.

2. Material and methods

2.1. Description of sampling stations

The Tinto and Odiel rivers are located in the northwest coast of the Gulf of Cádiz at the confluence of the Atlantic Ocean and the Mediterranean Sea. The Odiel river is 140 km long and has an average flux of 460 $hm^3\,y^{-1}$. The Odiel's wetlands constitute the most significant group of estuarine wetlands of the Iberian Peninsula being one of the most productive areas in Europe. The Tinto river is an extreme environment with an extremely low pH (mean 2.3) along the entire river (~95 km), high concentrations of heavy metals and a remarkable level of microbial diversity (González-Toril et al., 2003a). Its hydrology is highly seasonal due to the semi-arid nature of the region. The extreme conditions found in the Tinto ecosystem are the direct consequence of the active metabolism of chemolithotrophic microorganisms thriving in the rich polymetalic sulphides present in high concentrations in the Iberian Pyrite Belt (González-Toril et al., 2003b). The basins of the Tinto and Odiel rivers occupy an extension of 2300 and 720 km^2, respectively. This estuary is on a mesotidal (mean tidal range of 2.10 m) mixed-energy coast (Borrego, 1992). The volume of water that flows between the estuary and the open sea (tidal prism) during a tidal half-cycle (6 h) ranges from 37.34 hm^3 during a mean neap tide (1 m tidal range) to 81.76 hm^3 in a mean spring tide (3 m of tidal range). Meanwhile the volume of fresh water inflow from the Tinto and Odiel river to the inner zone of the estuary reflects a significant seasonal and year-to-year variation.

Sediment distribution is directly controlled by: the direction of fluvial contribution, the tidal stream and the location of discharges to the estuary. These elements give rise to a spatial variation in the geochemical characteristics of estuarine sediments (Borrego et al., 2002). The surficial sediments are mainly silt-clay and sand, and with a C/N ratio that vary between 10 and 28 (Saenz, 1998). The most abundant species of macrofauna in this system are annelids (37.3–99.6%) and crustaceans (0.4–50.1%) (Drake et al., 1999).

Measurements were carried out during September 1998. The sampled areas were chosen to represent the distinct environments at the estuary limits such as: salt marsh, industrial areas and urban nucleus. Four sampling stations at depths between 2 and 5 m were chosen (Fig. 1): HU1 was located close to the merging point of the Odiel and Tinto rivers, HU2 was near the mouth of the Odiel, adjacent to an industrial area, HU3 was situated in the main channel of the Odiel on the opposite bank to the city of Huelva, surrounded by extensive wetlands and salt marshes and lastly, HU4 was situated in a secondary channel of the estuary, near the town Punta Umbria. In this city there is intensive tourist activity in summer.

Table 1 shows the various characteristics of water and sediments of the sampling stations.

2.2. Interstitial water: diffusive fluxes

The sediment samples were taken by scuba divers, using 60 mm i.d. gravity cores which were refrigerated and transported to the laboratory within 4 h of sampling. The cores were cut in "slices" of 1 cm at the following intervals: 0–6, 7–8, 10–11, 15–16, 19–20, 24–25 and 29–30 cm. The sections obtained were centrifuged at 15,000*g* for 30 min at 4 °C (SIGMA 3K 30). The handling of the samples in the laboratory and the subsequent analysis of the interstitial water were performed in a nitrogen atmosphere. The sediment was dried at 80 °C, gently homogenised and sieved using a 63 μm sieve, prior to OC analysis.

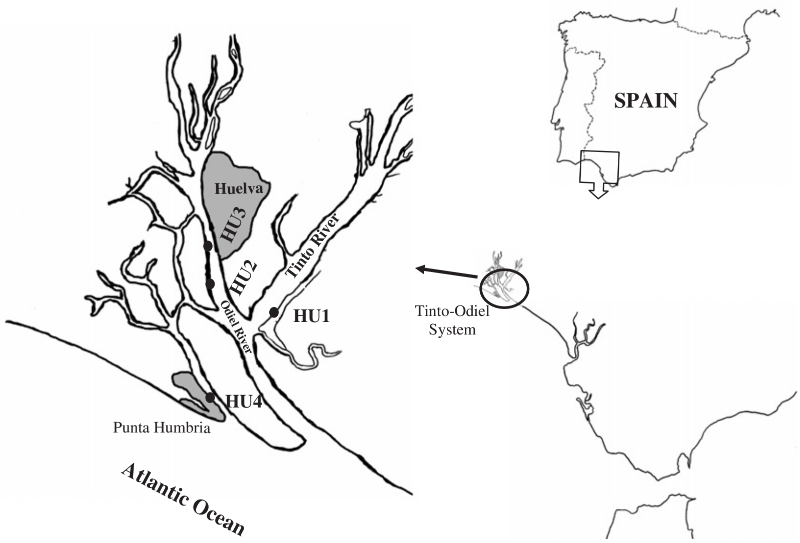

Fig. 1. Localisation of the sampling stations and the main centres of population.

Table 1

Characteristics of water and sediments of four stations during sampling: water temperature, salinity and porosity, organic carbon content and granulometry in surface sediments

Station	Temperature (°C)	Salinity	Porosity	Organic carbon (%)	Granulometry (mm)
HU1	23.9	37.33	0.62	2.4	0.13 ± 0.22
HU2	22.0	36.59	–	2.1	0.08 ± 0.07
HU3	23.8	38.41	0.57	2.3	0.03 ± 0.02
HU4	19.5	36.26	0.40	1.1	0.18 ± 0.09

The DIC diffusive fluxes were determined from the sum of bicarbonate, carbonate and CO_2 fluxes across the sediment–water interface (Cai et al., 2000), according to Fick's first law:

$$F = \phi D_S \left(\frac{\partial C}{\partial z}\right)_{z=0},$$

where F is the flux across the sediment–water interface, ϕ is the sediment porosity, D_S is the coefficient of diffusion in the sediment, $\partial C/\partial z$ represents the concentration gradient and z is the depth referring to the water–sediment interface. For the calculation of the diffusion coefficient in the sediment (D_S), we used the equation proposed by Sweerts et al. (1991), the porosity of the sediment and the diffusion coefficients for infinite dilution (D^0) for the individual carbonic acid species at 20 °C reported by Broecker and Peng (1974) and Li and Gregory (1974). The concentration gradient for each carbonate species was calculated from linear fits in the top few centimetres of the sediments.

The TA diffusive flux was calculated from the sum of the fluxes of bicarbonate and carbonate ($F(\mathrm{TA}) = F(\mathrm{HCO_3^-}) + 2F(\mathrm{CO_3^{2-}})$). In this work, we did not consider the contribution of the fluxes across the sediment–water of $B(OH)_4^-$, NO_3^- and HPO_4^{2-} to the TA diffusive flux since, in most cases, these fluxes are relatively small compared to the carbonate alkalinity fluxes. The saturation state of the porewater with respect to calcite (Ω_C) were obtained from the ratio of the $[Ca^{2+}]$ $[CO_3^{2-}]$ concentration product to the stoichiometric solubility constants of calcite (K^*_c) proposed by Mucci (1983).

2.3. In situ flux measurements

The in situ fluxes of DIC, DO and TA were obtained using two benthic chambers placed on the bottom simultaneously with the help of divers. The chambers are identical to those described by Forja and Gómez-Parra (1998). Briefly, the chambers are constructed in opaque plexiglass and are ellipsoid in shape, covering an area of sediment of $0.385\,m^2$ and containing volumes between 70 and 90 L depending on the eccentricity of the ellipsoid. The chamber has a recirculation pump to avoid stratification inside, allowing current simulation in a velocity range between 5 and $30\,cm\,s^{-1}$ near the bottom. Each chamber was sampled at pre-set intervals of 30 min during deployments from 3 to 5 h. The oxygen content in the benthic chamber that was monitored during the sampling exceeded 60% of the initial concentration at all times.

The benthic fluxes across the sediment–water interface were calculated by fitting the variations of concentration with time to linear or exponential equations (Forja et al., 1994; Forja and Gómez-Parra, 1998). No flux was reported if fewer than four data points were available. In Table 2, the type of fit is shown along with the number of data

Table 2
Linear or exponential fitted used in the DIC, TA and DO benthic fluxes calculation in the Tinto–Odiel system

Station	F_{DIC}			F_{TA}			F_{DO}		
	n	Fit	r^2	*n*	Fit	r^2	*n*	Fit	r^2
HU1	7	Exponential	0.996	6	Exponential	0.972	6	Linear	0.926
HU2	6	Exponential	0.988	6	Exponential	0.975	6	Linear	0.993
HU3	5	Exponential	0.994	4	Exponential	0.970	5	Linear	0.951
HU4	4	Exponential	0.998	4	Exponential	0.967	5	Linear	0.937

Regression coefficient and number of sampling (*n*) for each station are included.

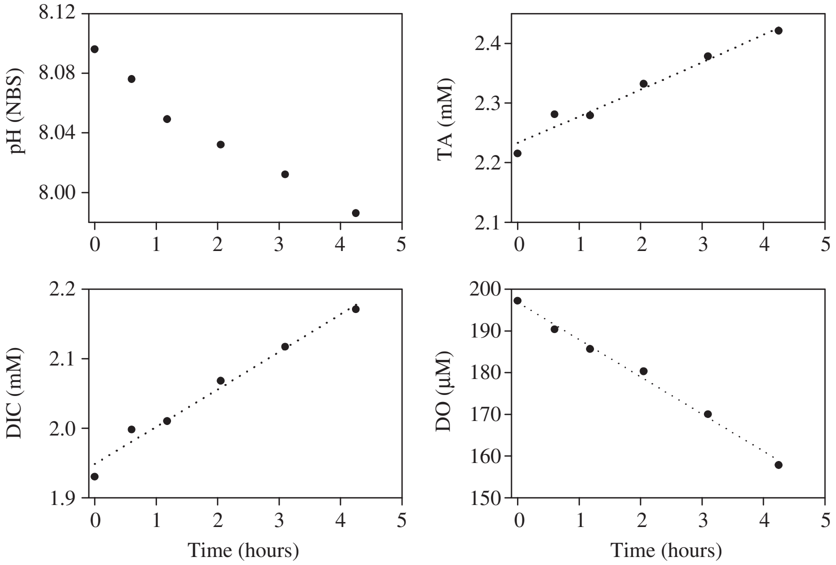

Fig. 2. Variations of the total alkalinity (TA), pH values and the concentrations of dissolved inorganic carbon (DIC) and oxygen (DO) inside the benthic chamber in the station HU2.

points (*n*) and the correlation coefficient obtained (r^2) for the calculation of the distinct benthic fluxes. The analytical precision of concentration measurements, the uncertainty associated with the lineal or exponential regression and the uncertainty in the determination of the benthic chamber volume all contribute to the uncertainty in the values of flux. Fig. 2 represents the evolution of the TA, pH and concentrations of in OC and DO in the interior of a benthic chamber in the station HU2.

2.4. Analytical methods

DIC was calculated from TA, in situ temperature-corrected pH (NBS) and salinity using the apparent dissociation constant reported by Mehrbach et al. (1973). TA and pH (NBS) were measured using a titrator (Metrohm 670) with glass combination electrodes (Metrohm, ref. 6.0210.100). The precision of the measurement of pH (NBS) of the sample was ±0.003. TA was obtained from the second point of inflection with an iterative programmme using the Gran functions (Forja et al., 2001) with a accuracy of ±0.003 mM. The titration was carried out at constant temperature with 0.1 M HCl dissolved in pure water. During the titration of samples, the dilution effect on the ionic strength was taken into account. The sample quantities analysed were 100 g (±0.001 g) for the benthic chamber and 2 mL for the interstitial water.

The DO concentration inside the chambers was measured by the Winkler method in discrete samples (to an accuracy of ±0.1 µM) and continuously monitored with polarographic electrodes (YSI, mod. 57; WTW, CellOx 325). The calcium concentration in porewaters was measured using a titrator (Metrohm 670) with an ion-selective electrode of calcium (Metrohm, ref. 6.1241.050) and a reference electrode (Metrohm, ref. 6.0726.100). EGTA 0.005 M was employed as titrant. The samples were buffered to a pH close to 9 by adding 10 mL of borax 0.1 M. Sulphate concentration was measured by gravimetry (Grasshoff et al., 1983); this method has an accuracy of ±0.02 mM. The salinity was measured using a salinometer (Beckman, Mod. RS-10) with an accuracy of ±0.001. The OC concentrations in surface sediments were determined by chemical oxidation (Gaudette et al., 1974; El Rayis, 1985) with a standard deviation of ±0.25%. Porosity was calculated from water loss after drying at 80 °C until the sediment weights were constant. In order to measure total sulphide contained in the sediment (Ortega, 2001) between 1 and 5 g of frozen sediment was taken to which 200 mL of MilliQ water and 25 mL of concentrated HCl were added. These operations were carried out in a round bottom flask, fitted with an inlet and outlet. Via the inlet, a continual flow of N_2 was introduced to avoid the sulphide oxidation and act as the gas transport medium. Through the outlet, the hydrogen sulphide formed is transported by the N_2 to the titration flask. Upon acidifying and shaking the sample, all sulphur species present in the interstitial water and sediment are converted to hydrogen sulphide, which has limited solubility and is readily separated from the sample via a stream of N_2. Following this, the gas stream is directed to the titration flask which contains a 50 mL buffer solution with a pH of around 9.5 (consisting of 0.2 M $Na_2HPO_4 \cdot 2H_2O$, 0.1 M NaOH and 0.45 M $NaNO_3$). The titration flask is kept at 10 °C. The H_2S formed is initially dissolved at low temperature and is retained in the solution as sulphide. Following a 10 min stabilisation period, a potentiometric titration is carried out with 10 mM $AgNO_3$ (Metrohm, 670). The measurements of potentials are carried out with a sulphide-specific electrode (Radiometer, F1212S) and a reference electrode with a double saline bridge (Metrohm, 6.0726.100). The precision of this method was $\pm 0.05\,\mu g\,g^{-1}$.

3. Results

3.1. Interstitial water

The depth profiles of OC, pH, saturation state of calcite and the concentrations of DIC, TA, Ca^{2+}, SO_4^{2-} and S^{2-} at the HU1, HU3 and HU4 stations of the Tinto–Odiel estuary (interstitial water data for HU2 station were not available) are presented in Fig. 3. The pH of porewater presents a decrease in the top layer of the sediment. From a depth of 2–3 cm the pH values are constant. DIC concentration increased with depth in porewaters especially at the station HU1 where values of 28 mM at a depth of 5 cm were reached. Nevertheless, from a depth of 25 cm the DIC decreased, coinciding with a drop in calcium concentration. At the HU3 station DIC increased over the first 2 cm and thereafter dropped with depth from 5 cm. At station HU4 the DIC increased continually with depth, reaching a maximum at a depth of 30 cm. This behaviour is common in coastal ecosystems (Hammond et al., 1985; Andersen and Kristensen, 1988; Alperin et al., 1999).

Contrary to expectations, OC increased with depth in all stations (Fig. 3). Calcium concentration varied between 3 and 12 mM at the three stations. (HU1, HU3 and HU4). An increase in Ω with depth at the three stations studied has been observed, especially at HU1 and HU4, where $\Omega > 1$ throughout the entire profile. The diffusive fluxes of DIC ($F_{\mathrm{dif\ DIC}}$) and TA obtained were very similar and ranged between 1.8–7.8 $\mathrm{mmol\,m^{-2}\,d^{-1}}$ and 1.5–7.3 $\mathrm{meq\,m^{-2}\,d^{-1}}$, respectively (Table 3).

3.2. In situ flux measurements

The sediments represent a sink for DO and source of DIC and depending on the station can act as a source (HU2 and HU3) or a sink (HU1 and HU4) for TA. The benthic fluxes of DIC (F_{DIC}) and oxygen (F_{DO}) are variable, presenting very high values (309–433 and 50–120 $\mathrm{mmol\,m^{-2}\,d^{-1}}$, respectively). TA benthic fluxes presented a higher interval of variation between −274.1 and 345.2 $\mathrm{meq\,m^{-2}\,d^{-1}}$.

4. Discussion

4.1. Interstitial water

The initial decrease of pH in porewaters is in response to the aerobic oxidation of organic matter and the re-oxidation of dissolved reduced species (Cai and Reimers, 1993; Canfield, 1993; Cai et al., 2000; Mucci et al., 2000). DIC concentration in porewater is the result of degradation of labile sedimentary OC and the process of dissolution–precipitation of calcium carbonate. The profile in interstitial water of DIC at the HU3 station (dropped in the first 5 cm layer increasing with depth), has been observed in other regions with shallow water (Hammond et al., 1985; Kristensen et al., 1991). At station HU4 the DIC increases continually with depth, reaching a maximum at a depth of 30 cm. This behaviour is common in coastal ecosystems (Hammond et al., 1985; Andersen and Kristensen, 1988; Alperin et al., 1999).

The increase of OC with depth in all stations (Fig. 3) may be due to a change in the hydrodynamics of the zone or a change in the organic matter inputs velocity to the sediments. In this sense, Ponce (2002) in the Tinto–Odiel sediments observed similar behaviour for the content of total phosphorous and iron due to the progressive diminution of the contaminant load into the system. It is also possible that this OC is refractory in nature and not readily degradable.

The increase in Ω with depth at the three stations studied indicates supersaturation conditions. These conditions are able to provoke precipitation of $CaCO_3$. This behaviour has been described in other systems (Kempe and Kazmierczak, 1994; Hammond et al., 1999; Mucci et al., 2000). At HU3, in contrast, there is evidence of undersaturation conditions ($\Omega < 1$) at shallow depths. The increase of Ω with depth may be due to the increase in alkalinity in the interstitial water (Fig. 3) produced by anaerobic degradation of OC.

The range of DIC diffusive fluxes ($F_{\mathrm{dif\ DIC}}$) in the Tinto–Odiel system is in agreement with those found for other coastal systems (Table 4), with maximum values of 27 and 30 $\mathrm{mmol\,m^{-2}\,d^{-1}}$ in sediments in the Northern Adriatic Sea (Hammond et al., 1999) and in coastal sediments of Georgia (Cai et al., 2000), respectively. In Fig. 4, the tendency for diffusive fluxes of DIC to increase

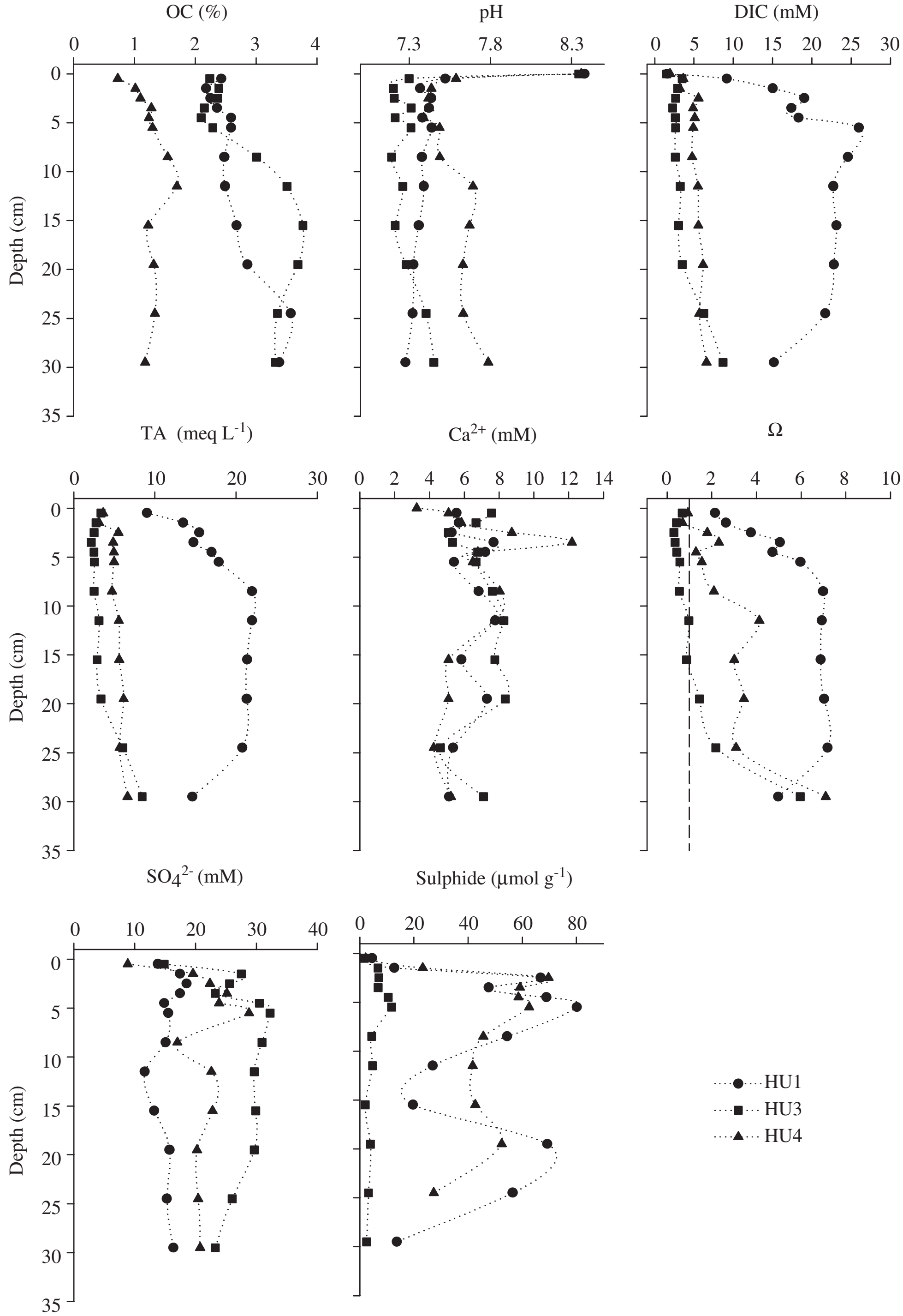

Fig. 3. Vertical variations of the organic carbon content, pH, total alkalinity, the concentration of inorganic carbon, calcium, sulphate, content of sulphur in sediment and the degree of $CaCO_3$ saturation of calcite in the Tinto–Odiel estuary: stations HU1 (●), HU3 (■) and HU4 (▲).

with temperature ($r^2 > 0.997$) and OC content ($r^2 = 0.990$) can be appreciated.

Sulphate reduction along with aerobic degradation is the principal mechanisms for the degradation of organic material in coastal systems. In this system, both sulphates and total sulphides are elevated in the first few centimetres of the sediments at the three stations, signalling the possible contribution of sulphate from the overlying water as well as diffusion of sulphide generated lower down in the sediment, having been partially oxidised. This process has been widely treated in the bibliography (Canfield et al., 1993b; Aller, 1994; Thamdrup et al., 1994). The contribution of sulphate to interstitial waters from the overlying water in the Tinto–Odiel estuary is possible, because that system receives a very high flux of sulphates (1,200,000 t/year) due to both the effluent from chemical industry and

Table 3
Benthic fluxes of dissolved inorganic carbon (F_{DIC}), alkalinity (F_{TA}) and oxygen (F_{DO}) in the four station the Tinto–Odiel estuary

Station	F_{DIC}	F_{TA}	F_{DO}	Diffusive F_{DIC}	Diffusive F_{TA}
HU1	333.4	−274.1	120	7.5	7.3
HU2	415.9	345.2	50	–	–
HU3	308.7	96.1	94	7.7	7.2
HU4	433.3	−252.9	37	9	1.5

Included the diffusive fluxes of dissolved inorganic carbon (Diffusive F_{DIC}). The benthic and diffusive fluxes of DIC and TA are expressed in mmol $\mathrm{m^{-2}\,d^{-1}}$.

Table 4
Diffusive fluxes of dissolved inorganic carbon ($F_{\mathrm{DIC\ diff}}$) in different coastal ecosystems

Site	$F_{\mathrm{DIC\ diff}}$	References
Northern Adriatic Sea	4–27	Hammond et al. (1999)
Coastal sediments of Georgia	16–30	Cai et al. (2000)
Iberian Peninsula	2–12	Forja et al. (2004)
Estuaries of the Cantabrian Sea	0.5–7	Ortega et al. (2005)

The diffusive fluxes are expressed in mmol $\mathrm{m^{-2}\,d^{-1}}$.

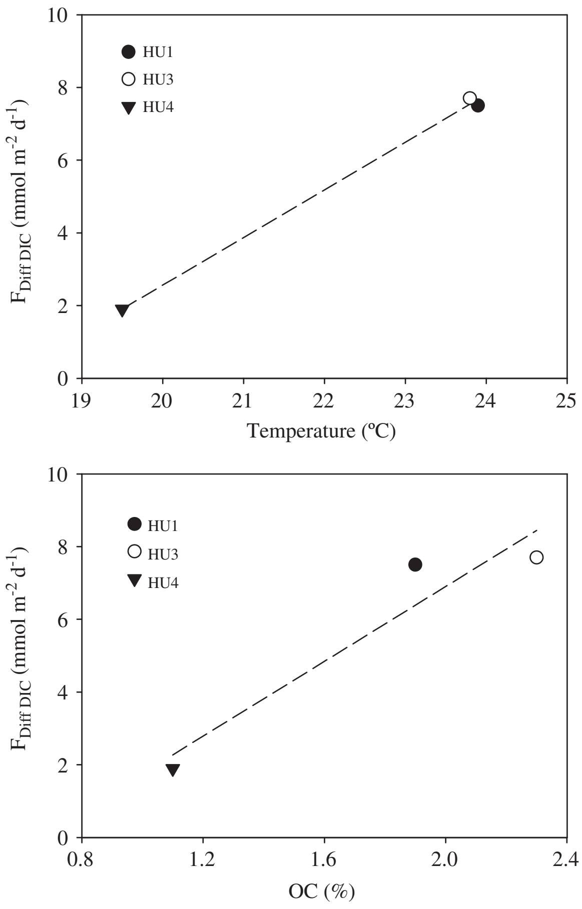

Fig. 4. Variation of the diffusive fluxes of dissolved inorganic carbon with the temperature and with the organic carbon content in surface sediments in the station HU1, HU3 and HU4 of the Tinto–Odiel estuary.

the contributions from the river itself (Sainz et al., 2003). Sulphate reduction mechanisms in the estuary cannot be determined from the vertical profiles of sulphate and sulphide alone. For this reason, a similar treatment has been carried out to that proposed by Hammond et al. (1999) for the sediments of the Northern Adriatic Sea. In this work, the authors used the DIC changes vs. alkalinity changes observed in porewaters, the ratio C/N of the organic matter and four reaction equations (Table 7 in Hammond et al., 1999) to determine the end-member reactions for organic matter degradation through sulphate reduction. Thus, plots of DIC variations vs. alkalinity (ΔDIC/ΔTA) over the first 30 cm of interstitial water have been made (Fig. 5). A high linearity between DIC changes and TA changes is observed at HU3 and HU4, with slopes of 1.00 ($r^2 = 0.969$) for HU3 and 0.94 ($r^2 = 0.962$) for HU4. At HU1, the linearity was reduced ($r^2 = 0.560$) while the slope was similarly close to unity (0.97). The similarities of the slopes across all stations suggest that the processes involved in the degradation of organic matter by sulphate reduction may be similar, despite the heterogeneity of the system. Considering that the C/N ratio in surface sediments of the stations studied of the Tinto–Odiel system has an approximate average value of 16 (Saenz, 1998), a slope of 0.94 would be expected for the degradation of organic matter based on sulphate reduction with an average oxidation state of zero, while a slope of 1.12 would be expected upon oxidation of sulphides to elemental sulphur present in the sediments at shallow depths, in the presence of oxygen. According to this description of the system, the prior mentioned mechanisms (sulphate reduction and oxidation of reduced sulphides) appear to be particularly relevant in the sediments of the stations studied.

4.2. *In situ DIC fluxes*

The benthic fluxes of inorganic carbon (309–433 mmol $\mathrm{m^{-2}\,d^{-1}}$) are higher than those observed from other coastal ecosystems around the world (Table 5). One exception is the DIC fluxes found at Albufera de Majorca (López et al., 1995) and at the Ria of Vigo (Forja et al., 2004) with maximum values of 732 and 224.5 mmol $\mathrm{m^{-2}\,d^{-1}}$, respectively. The elevated bottom water temperature observed (between 19 and 24 °C) in the four stations is a factor to be considered. A temperature increase generally produces an higher microbial activity and a greater benthic regeneration. The dissolution of calcium carbonate should also be taken into account when considering benthic DIC fluxes. Cermelj et al. (2001) in the Gulf of Trieste observed increased values of benthic DIC flux in summer compared to winter and estimated a contribution of carbonate dissolution to DIC benthic flux of approximately 40%.

In the station HU1 and HU4 negative benthic fluxes of TA have been measured, while TA diffusive fluxes are positive. Negative values of F_{TA} have been found in very

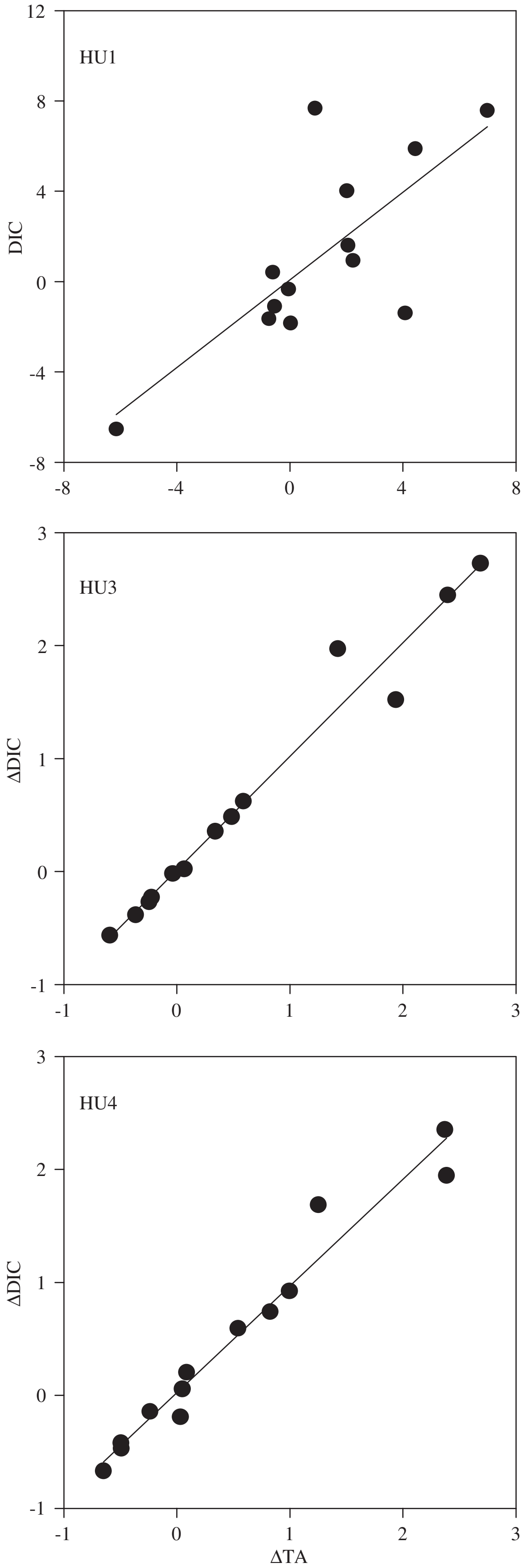

Fig. 5. DIC changes vs. alkalinity changes observed in porewaters of the Tinto–Odiel system (stations HU1, HU3 and HU4).

few coastal areas (Friedl et al., 1998; Berelson et al., 2003; Ortega et al., 2005). In the Tinto–Odiel estuary the negative TA benthic fluxes may be due to acidification occurring within the chamber, provoking a diminution in the concentration of CO_3^{2-}. HU1 and HU4 stations showed a drop in the pH of 0.4 and 0.3 units, respectively, within the 4-h bottom sampling period, resulting in a reduction of TA flux.

A direct relationship has not been found for benthic DIC fluxes, OC content (%) of superficial sediments and temperature. This may be due to the spatial heterogeneity of the estuary as well as the significant contribution of $CaCO_3$ dissolution processes to benthic DIC fluxes. Nevertheless, benthic DO fluxes are dependent on these two variables (Fig. 6). Generally, DO fluxes from bottom water toward the sediment increase as temperature and inorganic carbon content rise, as it has been shown by various authors (Glud et al., 1994; Hopkinson et al., 1999; Cermelj et al., 2001).

In order to obtain an estimation of the contribution of the $CaCO_3$ dissolution processes, the ratio of alkalinity flux (F_{TA}) to inorganic carbon flux (F_{DIC}) was applied for the Odiel stations HU2 and HU3, where the benthic fluxes of alkalinity are positive. The ratio between F_{TA} and F_{DIC} was 0.83 for HU2 and 0.31 for HU3. Jahnke and Jahnke (2000) found the ratio of the $CaCO_3$ dissolution rate to the OC oxidation rate using the quotient F_{TA}/F_{DIC}. Utilising this model, the rate of $CaCO_3$ dissolution is 0.7 times the rate of OC oxidation at HU2 and 0.2 for HU3. The two stations when considered together give an average value of 0.44. If we consider the average value of F_{DIC} to be 362 mmol m^{-2} d^{-1} for the two stations studied, the contribution of the dissolution of $CaCO_3$ to this flux would be approximately 176 mmol m^{-2} d^{-1}. This flux constitutes 49% of the total DIC flux and is greater than benthic DIC fluxes measured in other coastal zones (Table 5). Other authors have estimated the contribution of $CaCO_3$ dissolution in benthic DIC fluxes. Cai et al. (2006), for example, calculated the carbonate dissolution rate as half that of the TA generation rate (or net diffusive flux change) for northern Gulf of Mexico petroleum seep sediments, concluding that approximately 48% of DIC fluxes to overlying water are due to $CaCO_3$ dissolution.

The depth of penetration of oxygen in the sediment was estimated from the expression proposed by Cai and Sayles (1996). The results (HU1: 1.9 mm; HU3: 2.3 mm and HU4: 4.1 mm) are similar to those published for other coastal systems, where the depth of penetration of O_2 extends for only a few millimetres (Jørgensen, 1982; Forja et al., 2004). Fig. 6 shows the DO benthic fluxes with the depths of penetration of oxygen. The relationship is inverse, and may be due, at the stations with lower depth of oxygen penetration, to the oxygen from the overlying water being used to oxidise reduced species in both the first millimetres of interstitial water and within the chamber. Thus, the DO practically did not penetrate in the sediment porewater.

Table 5
Benthic fluxes of total alkalinity dissolved inorganic carbon and oxygen in several coastal marine ecosystems measured by different authors

Site	Technique	Depth (m)	Temperature (°C)	Organic carbon (%)	TA flux ($\text{mmol m}^{-2}\,\text{d}^{-1}$)	DIC flux ($\text{mmol m}^{-2}\,\text{d}^{-1}$)	DO flux ($\text{mmol m}^{-2}\,\text{d}^{-1}$)	References
Cape Lookout Bight (N Carolina)	Chambers	–	12.0–27.5	3.3–5.0	–	31.0–162.7	–	Martens and Klump (1984)
San Francisco Bay (S California)	Chambers	1.5–14	14.3–14.5	1.4	6.0–14.0	17.0–28.0	1.1–7.7	Hammond et al. (1985)
Tomales Bay (California)	Chambers	4–6	–	–	3.8–11.6	14.4–26.0	3.7–15.0	Dollar et al. (1991)
Albufera of Majorca (Mediterranean)	Chambers	–	28.5–31.9	–	–	63.4–732.0	32.4–97.2	López et al. (1995)
Boston Harbor (Massachusetts)	Core incubations	3.5–13	0.0–20.0	0.14–6.1	–	10.0–185.0	7.0–220.0	Giblin et al. (1997)
Bay of Cádiz (Spain)	Chambers	2–14	18.4±6.8	2.2–3.1	–	154.6–224.5	–	Forja and Gómez-Parra (1998)
Young Sound (Northeast Greenland)	Core incubations	36	−1.2–(−1.8)	1.3	–	5.4–9.6	5.0–13.0	Rysgaard et al. (1998)
Plum Island Sound–River Parker estuary	Core incubations	0.5–4	3.6–28.1	0.2–10.3	–	3.0–520.0	6.0–433.0	Hopkinson et al. (1999)
Gulf of Trieste (Northern Adriatic)	Core incubations	–	10.0–20.0	–	–	5.0–10.1	–	Cermelj et al. (2001)
Monterey Bay (California)	Chambers	95–100	–	0.2–0.5	−0.7–11.7	4.7–17.8	5.0–13.5	Berelson et al. (2003)
Albufera dés Grau (Minorca Island)	Core incubations	1–3	23.0–23.2	–	–	30.0–60.0	–	López (2003)
Iberian Peninsula	Chambers	2–20	11.4–27.3	0.9–7.0	22.0–206.0	135.0–447.0	98.0–199.0	Forja et al. (2004)
Makirina Bay (Croatia)	Chambers	0.2–0.8	25	6.0–7.5	–	−1.9–23.3	–	Lojen et al. (2004)
South Atlantic Bight	Core incubations	14–45	15.8–28.0	0.05	–	5.3–17.3	–	Jahnke et al. (2005)

Technique used to measure the fluxes, interval of depth variations, temperature and organic carbon content of the different studied systems are included in the table.

The quotient of benthic metabolism (CRQ)—expressed as the relationship between the in situ benthic fluxes of inorganic carbon and oxygen (HU1: 2.8, HU2: 8.3, HU3: 3.3 and HU4: 11.6) is variable and higher than 1 in all stations. These elevated values indicate the importance of metabolic anaerobic routes in the degradation of organic matter, especially at HU2 and HU4, as well as the significance of contributions from the dissolution of $CaCO_3$ to the total benthic DIC fluxes. It should be considered that sampling was carried out in summer when sulphate reduction is more intense (Nedwell and Floodgate, 1972).

DIC diffusive fluxes constituted 0.4–2.2% of benthic chamber values. The great difference found between the diffusive and in situ fluxes provides evidence that advective transport is a significant contributor to solute exchange in coastal sediments. Another factor to consider is the possible role of calcium carbonate dissolution processes in the Odiel–Tinto estuary that may produce an increase in the benthic fluxes of DIC. This variability in benthic fluxes may be due to the substantial heterogeneity in the sediment column and to the elevated spatial resolution considered in the top layer of sediment (1 cm). Large differences between the diffusive and in situ fluxes have been reported in other systems (Cermelj et al., 1997; Berelson et al., 2003). Cermelj et al. (1997) found that benthic fluxes exceeded diffusive fluxes by up to 10-fold in the Gulf of Trieste in summertime as a consequence of benthic macrofaunal bioturbation and irrigation.

It is important to consider that this study was carried out during summer months only, and that it was limited to four samplings stations located over the final stretch of the estuary. In order to obtain a better characterisation of the system, a great number of stations would be required, with measurements taken throughout the year. Prior to this, only one other study of this type had been carried out, during spring and summer of 1996 (Forja et al., 2004), where equally elevated values of benthic DIC flux (178–305 $\text{mmol m}^{-2}\,\text{d}^{-1}$) and DO (99–139 $\text{mmol m}^{-2}\,\text{d}^{-1}$) were obtained. The TA benthic fluxes were positive and elevated in all stations, with values between 61 and 192 $\text{meq m}^{-2}\,\text{d}^{-1}$.

5. Conclusions

Benthic DIC fluxes in the Tinto–Odiel estuary were relatively high (309–433 $\text{mmol m}^{-2}\,\text{d}^{-1}$) perhaps owing to the nearby industrial and mining activities carried out in the estuarine system along with the elevated water temperatures present during the sampling period. Fluxes reached

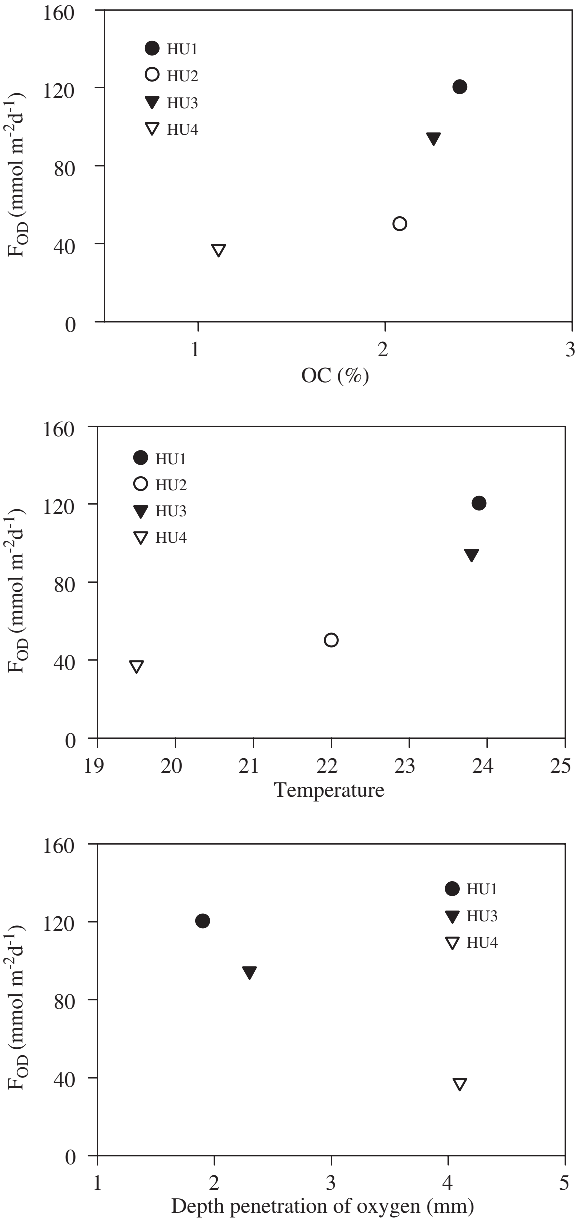

Fig. 6. Relationship between the benthic fluxes of dissolved oxygen, and the organic carbon content in surface sediments, the temperature and the depth of penetration of oxygen (estimated by Cai and Sayles, 1996).

maximum values at the HU2 and HU4 stations situated adjacent to an industrial area and to the town Punta Umbria respectively. Parallel to this, the quotient of in situ DIC and DO fluxes (CRQ) reach values in excess of unity at these two stations, indicating the importance of anaerobic degradation paths, mainly sulphate reduction, along with possible calcium carbonate dissolution. In other Spanish estuarine systems, a direct relation between CRQ and anthropogenic activity has been found (Ortega et al., 2005).

Acknowledgement

This work was supported by the Spanish CICYT (Comisión Interministerial de Ciencias y Tecnología) of the Ministerio de Educación y Ciencia under Contract REN2001-3577/MAR.

References

Aller, R.C., 1994. The sedimentary manganese cycle in Long Island Sound: its role as intermediate oxidant and the influence of bioturbation, O_2, and C_{org} flux on diagenetic reaction balances. Journal of Marine Research 52, 259–295.

Alperin, M.J., Martens, C.S., Albert, D.B., Suayah, I.B., Benninger, L.K., Blair, N.E., Jahnke, R.A., 1999. Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. Geochimica et Cosmochimica Acta 63, 427–448.

Andersen, F.O., Hargrave, B.T., 1984. Effects of Spartina detritus enrichment on aerobic/anaerobic benthic metabolism in an intertidal sediment. Marine Ecology Progress Series 16, 161–171.

Andersen, F.O., Kristensen, E., 1988. The influence of macrofauna on estuarine benthic community metabolism: a microcosm study. Marine Biology 99, 591–603.

Berelson, W.M., McManus, J., Coale, K., Johnson, K., Burdige, D., Kilgore, T., Colodner, D., Chavez, F., Kudela, R., Li, H.-C., 2003. A time series of benthic flux measurements from Monterey Bay, CA. Continental Shelf Research 23, 457–481.

Borrego, J., 1992. Sedimentología del estuario del río Odiel (Huelva, S.O., España). Ph.D. Thesis, University of Sevilla.

Borrego, J., Morales, J.A., de la Torre, M.L., Grande, J.A., 2002. Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). Environmental Geology 41, 785–796.

Broecker, W.S., Peng, T.H., 1974. Gas exchange rates between air and sea. Tellus 26, 21–35.

Cai, W.-J., Reimers, C.E., 1993. The development of pH and $p\mathrm{CO}_2$ microelectrodes for studying the carbonate chemistry of pore waters near the sediment–water interface. Limnology and Oceanography 38, 1762–1773.

Cai, W.-J., Sayles, F.L., 1996. Oxygen penetration depths and fluxes in marine sediments. Marine Chemistry 52, 123–131.

Cai, W.-J., Wang, Y., 1998. The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. Limnology and Oceanography 43, 657–668.

Cai, W.-J., Pomeroy, L.R., Moran, M.A., Wang, Y., 1999. Oxygen and carbon dioxide mass balance in the estuarine/intertidal marsh complex of five rivers in the Southeastern US. Limnology and Oceanography 44, 639–649.

Cai, W.-J., Zhao, P., Wang, Y., 2000. pH and $p\mathrm{CO}_2$ microelectrode measurements and the diffusive behaviour of carbon dioxide species in coastal marine sediments. Marine Chemistry 70, 133–148.

Cai, W.-J., Chen, F., Powell, E.N., Walker, S.E., Parsons-Hubbard, K.M., Staff, G.M., Wang, Y., Ashton-Alcox, K.M., Callender, W.R., Brett, C., 2006. Preferential dissolution of carbonate shells driven by petroleum seep activity in the Gulf of Mexico. Earth and Planetary Science Letters 248, 227–243.

Canfield, D.E., 1993. Organic matter oxidation in marine sediments. In: Wollast, R., Mackenzie F.T., Chou L. (Eds.), Interactions of C, N, P and S Biogeochemical Cycles and Global Change, NATO ASI Series. Springer, Berlin, pp. 333–363.

Canfield, D.E., Thamdrup, B., Hassen, J.W., 1993. The anaerobic degradation of organic matter in danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochimica et Cosmochimica Acta 57, 3867–3883.

Cermelj, B., Bertuzzi, A., Faganeli, J., 1997. Modelling of pore water nutrient distribution and benthic fluxes in shallow coastal waters (Gulf of Trieste, northern Adriatic). Water Air and Soil Pollution 99, 435–444.

Cermelj, B., Ogrinc, N., Faganeli, J., 2001. Anoxic mineralization of biogenic debris in near-shore marine sediments (Gulf of Trieste, northern Adriatic). Science of the Total Environment 266, 143–152.

Dollar, S.J., Smith, S.V., Vink, S.M., Obrebski, S., Hollibaugh, J.T., 1991. Annual cycle of benthic nutrient fluxes in Tomales Bay, California, and contribution of the benthos to total ecosystem metabolism. Marine Ecology Progress Series 79, 115–125.

Drake, P., Baldó, F., Sáenz, V., Arias, A.M., 1999. Macrobenthic community structure in estuarine pollution assessment on the Gulf of Cádiz (SW Spain): is the phylum-level meta-analysis approach applicable? Marine Pollution Bulletin 38, 1038–1047.

El Rayis, O.A., 1985. Re-assessment of the titration methods for determination of organic carbon in recent sediments. Rapport Commission International Mer Mediterranée 29, 45–47.

Forja, J.M., Gómez-Parra, A., 1998. Measuring nutrient fluxes across the sediment–water interface using benthic chambers. Marine Ecology Progress Series 164, 95–105.

Forja, J.M., Blasco, J., Gómez-Parra, A., 1994. Spatial and seasonal variation of "in situ" benthic fluxes in the Bay of Cádiz (SW Spain). Estuarine Coastal and Shelf Science 39, 127–141.

Forja, J.M., Ortega, T., DelValls, T.A., Gómez-Parra, A., 2001. Influence of benthic regeneration on the biogeochemical cycle of CO_2 in littoral ecosystems. Ciencias Marinas 27, 311–333.

Forja, J.M., Ortega, T., DelValls, T.A., Gómez-Parra, A., 2004. Benthic fluxes of inorganic carbon in shallow coastal ecosystems of the Iberian Peninsula. Marine Chemistry 85, 141–156.

Friedl, G., Dinkel, C., Wehrli, B., 1998. Benthic fluxes of nutrients in the northwestern Black Sea. Marine Chemistry 62, 77–88.

Gaudette, H.E., Flight, W.R., Torner, L., Folger, D.W., 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. Journal of Sedimentary Petrology 44, 249–253.

Giblin, A.E., Hopkinson, C.S., Tucker, J., 1997. Benthic metabolism and nutrient cycling in Boston Harbor, Massachusetts. Estuaries 20, 346–364.

Glud, R.N., Gundersen, J.K., Jørgensen, B.B., Revsbech, N.P., Shulz, H.D., 1994. Diffusive and total oxygen uptake of deep-sea sediments in the eastern South Atlantic Ocean: in situ and laboratory measurements. Deep-Sea Research I 41, 1767–1788.

González-Toril, E., Gómez, F., Rodríguez, N., Fernández-Remolar, D., Zuloaga, S., Marín, I., Amils, R., 2003a. Geomicrobiology of the Tinto river, a model of interest for biohydrometallurgy. Hydrometallurgy 71, 301–309.

González-Toril, E., Llobet-Brossa, E., Casamayor, E.O., Amann, R., Amils, R., 2003b. Microbial ecology of an extreme acidic environment, the Tinto River. Applied and Environmental Microbiology 69, 4853–4865.

Golberg, E.D., 1994. Coastal zone space. Prelude to conflict? In: Coastal Problems, Paris, UNESCO.

Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. Methods of Seawater Analysis. Verlag Chemie, R.F.A., pp. 259–260.

Hammond, D.E., Fuller, C., Harmon, D., Hartman, B., Korosec, M., Miller, L.G., Rea, R., Warren, S., Berelson, W., Hager, S.W., 1985. Benthic fluxes in San Francisco Bay. Hydrobiologia 129, 69–90.

Hammond, D.E., Giordani, P., Berelson, W.M., Poletti, R., 1999. Diagenesis of carbon and nutrients and benthic exchange in sediments of the Northern Adriatic Sea. Marine Chemistry 66, 53–79.

Hopkinson, C.S., Giblin, A.E., Tucker, J., Garrit, R.H., 1999. Benthic metabolism and nutrient cycling along an estuarine salinity gradient. Estuaries 22, 825–843.

Jahnke, R.A., Jahnke, D.B., 2000. Rates of C, N, P and Si recycling and denitrification at the US Mid-Atlantic continental slope depocenter. Deep-Sea Research I 47, 1405–1428.

Jahnke, R.A., Richards, M., Nelson, J., Robertson, C., Rao, A., Jahnke, D.B., 2005. Organic matter remineralization and porewater exchange rates in permeable South Atlantic Bight continental shelf sediments. Continental Shelf Research 25, 1433–1452.

Jørgensen, B.B., 1982. Mineralization of organic matter in the sea bed—the role of sulfate reduction. Nature 296, 643–645.

Kempe, S., Kazmierczak, J., 1994. The role of alkalinity in the evolution of ocean chemistry, organization of living systems, and biocalcification processes. Bulletin de l'Institut océanographique, Monaco no spécial 13, 61–117.

Kristensen, E., Holmer, M., Bussarawit, N., 1991. Benthic metabolism and sulfate reduction in a southeast Asian mangrove swamp. Marine Ecology Progress Series 73, 93–103.

Li, Y.H., Gregory, S., 1974. Diffusion of ions in seawater and in deep sea sediments. Geochimica et Cosmochimica Acta 40, 257–266.

López, P., 2003. Effect of changes in water salinity on ammonium, calcium, dissolved inorganic carbon and influence on water/sediment dynamics. Estuarine Coastal and Shelf Science 56, 943–956.

López, P., Vidal, M., Lluch, X., Morgue, J.A., 1995. Sediment metabolism in a transitional continental/marine area: the Albufera of Majorca (Balearic Islands, Spain). Marine and Freshwater Research 46, 45–53.

Lojen, S., Ogrinc, N., Dolenec, T., Vokal, B., Szaran, J., Mihelčić, G., Branica, M., 2004. Nutrient fluxes and sulfur cycling in the organic-rich sediment of Makirina Bay (Central Dalmatia, Croatia). Science of the Total Environment 327, 265–284.

Mackenzie, F.T., Lerman, A., Ver, L.M., 1998. Role of the continental margin in the global carbon balance during the past three centuries. Geology 26, 423–426.

Mackin, J.E., Swider, K.T., 1989. Organic matter decomposition pathways and oxygen consumption in coastal marine sediments. Journal of Marine Research 47, 681–716.

Martens, C.S., Klump, V., 1984. Biogeochemical cycling in an organic-rich coastal marine basin 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. Geochimica et Cosmochimica Acta 48, 1987–2004.

Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurement of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure. Limnology and Oceanography 18, 897–907.

Milliman, J.D., 1993. Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state. Global Biogeochemical Cycles 7, 927–957.

Mucci, A., 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. American Journal of Science 283, 780–799.

Mucci, A., Sundby, B., Gehlen, M., Arakaki, T., Zhong, S., Silverberg, N., 2000. The fate of carbon in continental shelf sediments of eastern Canada: a case study. Deep-Sea Research II 47, 733–760.

Nedwell, D.B., Floodgate, G.D., 1972. Temperature-induced changes in the formation of sulfide in a marine sediment. Marine Biology 14, 18–24.

Ortega, T., 2001. Flujos de carbono inorgánico en sistemas costeros de la península Ibérica. Ph.D. Thesis, University of Cádiz.

Ortega, T., Ponce, R., Forja, J., Gómez-Parra, A., 2005. Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (North of Spain). Journal of Marine System 53, 125–142.

Ponce, R., 2002. Importancia de la regeneración bentónica en la dinámica de nutrientes de los sistemas costeros. Ph.D. Thesis, University of Cádiz.

Raymond, P.A., Bauer, J.E., 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology 22, 1–12.

Rysgaard, S., Thamdrup, B., Risgaard-Petersen, N., Fossing, H., Berg, P., Christensen, P.B., Dalsgaard, T., 1998. Seasonal carbon and nutrient mineralization in a high-Artic coastal marine sediment, Young Sound, Northeast Greenland. Marine Ecology Progress Series 175, 261–276.

Sabine, C.L., Mackenzie, F.T., 1991. Oceanic sinks for antropogenic CO_2. International Journal of Energy Environment and Economy 1, 119–127.

Saenz, V., 1998. Distribución espacial y especiación de metales pesados en sedimentos de tres sistemas litorales del Golfo de Cádiz. Ph.D. Thesis, University of Cádiz.

Sainz, A., Grande, J.A., de la Torre, M.L., 2003. Odiel River, acid mine drainage and current characterisation by means of univariate analysis. Environmental International 29, 51–59.

Smith, S.V., Hollibaugh, J.T., 1993. Coastal metabolism and the oceanic organic carbon balance. Reviews of Geophysics 31, 75–89.

Sweerts, J.P.R.A., Baer-Gilissen, M.J., Cornelese, A.A., 1991. Oxygen-consuming processes at the profundal and littoral sediment–water interface of a small meso-eutrophic lake (Lake Vechten, The Netherlands). Limnology and Oceanography 36, 1124–1133.

Thamdrup, B., Fossing, H., Jørgensen, B.B., 1994. Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochimica et Cosmochimica Acta 58, 5115–5129.

Ver, L.M., Mackenzie, F.T., Lerman, A., 1999. Carbon cycle in the coastal zone: effects of global perturbations and change in the past three centuries. Chemical Geology 159, 283–304.

Walsh, J.J., 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. Nature 350, 53–55.

Wollast, R., 1998. Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean. In: Brink, K.H., Robinson, A.R. (Eds.), The Sea. Wiley, New York, pp. 213–252.

Wollast, R., Mackenzie, F.T., 1989. Global biogeochemical cycles and climate. In: Berger, A., Schneidder, S., Duplessy, J.-C. (Eds.), Climate and Geo-Sciences. Kluwer Academic Publishers, Dordrecht, MA, pp. 453–473.