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Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (north of Spain)

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Abstract

The diffusive and in situ fluxes of dissolved inorganic carbon (DIC) and total alkalinity (TA) have been measured and an estimation has been made of the water–atmosphere fluxes of CO_2 in three estuarine systems of the Cantabrian Sea during the spring of 1998. Each of these systems undergoes a different anthropogenic influence. The diffusive fluxes of dissolved inorganic carbon and total alkalinity obtained present values ranging between 0.54–2.65 and 0.0–2.4 mmol m^{-2} day^{-1}, respectively. These ranges are in agreement with those of other coastal systems. The in situ fluxes are high and extremely variable (35–284 mmol TA m^{-2} day^{-1}, 43–554 mmol DIC m^{-2} day^{-1} and 22–261 mmol dissolved oxygen (DO) m^{-2} day^{-1}), because the systems studied are very heterogeneous. The values of the ratio of the in situ fluxes of TA and DIC show on average that the rate of dissolution of $CaCO_3$ is 0.37 times that of organic carbon oxidation. Equally, the interval of variation of the relationship between the benthic fluxes of inorganic carbon and oxygen (F_{DIC}/F_{DO}) is very wide (0.3–13.9), which demonstrates the different contributions made by the processes of aerobic and anaerobic degradation of the organic matter, as well as by the dissolution–precipitation of $CaCO_3$. The water–atmosphere fluxes of CO_2 present a clear dependence on the salinity. The brackish water of these systems (salinity<20), where maximum fluxes of 989 mmol m^{-2} day^{-1} have been estimated, act as a source of CO_2 to the atmosphere. The more saline zones of the estuary (salinity>30) act as a sink of CO_2, with fluxes between −5 and −10 mmol m^{-2} day^{-1}.

Keywords: Dissolved inorganic carbon; Benthic fluxes; Dissolved oxygen; Alkalinity; Cantabrian estuaries; Carbonate dissolution; Water–atmosphere CO_2 fluxes

1. Introduction

Estuaries receive inorganic nutrients and organic matter from the land and represent important systems where terrestrial nutrients and organic matter are processed before entering the ocean. These systems

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are extremely dynamic, and usually characterised by strong physicochemical gradients, enhanced biological activity, and intense sedimentation and resuspension.

The supplies of carbon by estuaries present considerable seasonal variations (Gattuso et al., 1998) and depend on diverse factors, such as the flow rate and the section of the river, and the quantity of carbon dissolved in their waters. The origin of this carbon is principally the basin of the river itself, the atmosphere, and the continents. Continents provide carbon to their rivers from the chemical erosion of rocks, which is facilitated by reaction with the atmospheric CO_2. Chemical weathering and the subsequent export of inorganic carbon from soils to rivers account for significant amounts of terrestrially sequestered atmospheric CO_2 (Raymond and Cole, 2003). In fact, it has been estimated that, currently, the rate of sedimentation in coastal zones is probably twice that of the preindustrial era due to increased continental erosion resulting from deforestation and the changes that agricultural practices have undergone (Wollast, 1991). Raymond and Cole (2003) have estimated that cultivated land has riverine alkalinity concentrations that are five to six times higher than noncultivated land cover, for the upper Mississippi and Ohio basins, respectively.

A large part of the organic carbon deposited as sediment in estuaries is degraded by various metabolic routes, giving rise to significant benthic fluxes of inorganic carbon (Forja and Gómez-Parra, 1998). This inorganic carbon entering the estuaries can be transported by various means; a part will be exported to nearby marine zones, some will be emitted to the atmosphere in the form of CO_2, and part will remain in the water column, and in the sediment. The flux and/or residence of the inorganic carbon in each of these compartments will depend on the characteristics of each estuary, as well as on the season of the year and time of day when the study is carried out. For example, in the estuary of the Scheldt (North Sea), approximately 60% of the respiratory CO_2 is released to the atmosphere, 26% is transferred to the sediment and only 14% remains in the water column (Gattuso et al., 1998). The fluxes, sources, and mechanisms of CO_2 transport and transformation are among the most important current issues in marine and freshwater geochemistry (Cai and Wang, 1998).

The benthic fluxes of inorganic carbon are the result of a balance between the release of inorganic carbon to pore waters through the oxidation of organic carbon by the various aerobic and anaerobic mechanisms and the dissolution–precipitation of calcium carbonate. Until a few years ago, the contribution of the dissolution of $CaCO_3$ in the benthic flux of inorganic carbon was not considered significant. However, over the past decade, many researchers have come to attribute a large part of the benthic flux of inorganic carbon to processes of dissolution of $CaCO_3$ (Jahnke and Jahnke, 2000; Mucci et al., 2000; Cermelj et al., 2001).

In several studies, it has been proved that estuaries present a certain oversaturation of CO_2 with respect to the atmosphere, with partial pressures that vary between 500 and 9500 μatm. (Raymond et al., 1997; Frankignoulle et al., 1998). This extreme variability of CO_2 is significantly greater in space and time than is typically observed in open ocean environments. It has been found that CO_2 can present considerable spatial and temporal variations within the same estuary (Frankignoulle et al., 1998; Abril et al., 2000), due to the hydrodynamic and geomorphological complexity of these littoral zones. On this point, Frankignoulle et al. (1998) observed that the more fluvial part of the Scheldt estuary can act as a source of CO_2 to the atmosphere, while the more saline part, where primary production is usually very intense due to the availability of nutrients, can behave like a sink for atmospheric CO_2.

In this paper, we examine results of in situ benthic fluxes of inorganic carbon and dissolved oxygen (DO), diffusive inorganic carbon fluxes and pore water analyses, from three estuarine systems located in the north of Spain. Each of these systems undergoes a different anthropogenic influence; the estuary most affected by human activity is the Saja–Besaya estuary, followed by the Asón and the Urdaibai estuaries. It has been demonstrated how in these systems the dissolution of calcium carbonate makes an important contribution to benthic fluxes of inorganic carbon. To complete the characterisation of the vertical fluxes of inorganic carbon in the zones studied, an estimate has been made of the water–atmosphere fluxes of CO_2.

2. Materials and methods

2.1. Description of sampling station

This study was carried out in June 1998, in three estuarine systems of the Cantabrian Sea (north of Spain), along which five sampling stations were established. These systems are shown from east to west, in Fig. 1: the Urdaibai Estuary is in the northeast of the Basque Country, on the Gulf of Vizcaya. It is a shallow macrotidal estuary that extends for 12.5 km to its mouth and occupies an area of more than 1.89 km^2, with a maximum width of 1.2 km near Mundaka. It is bordered by relatively

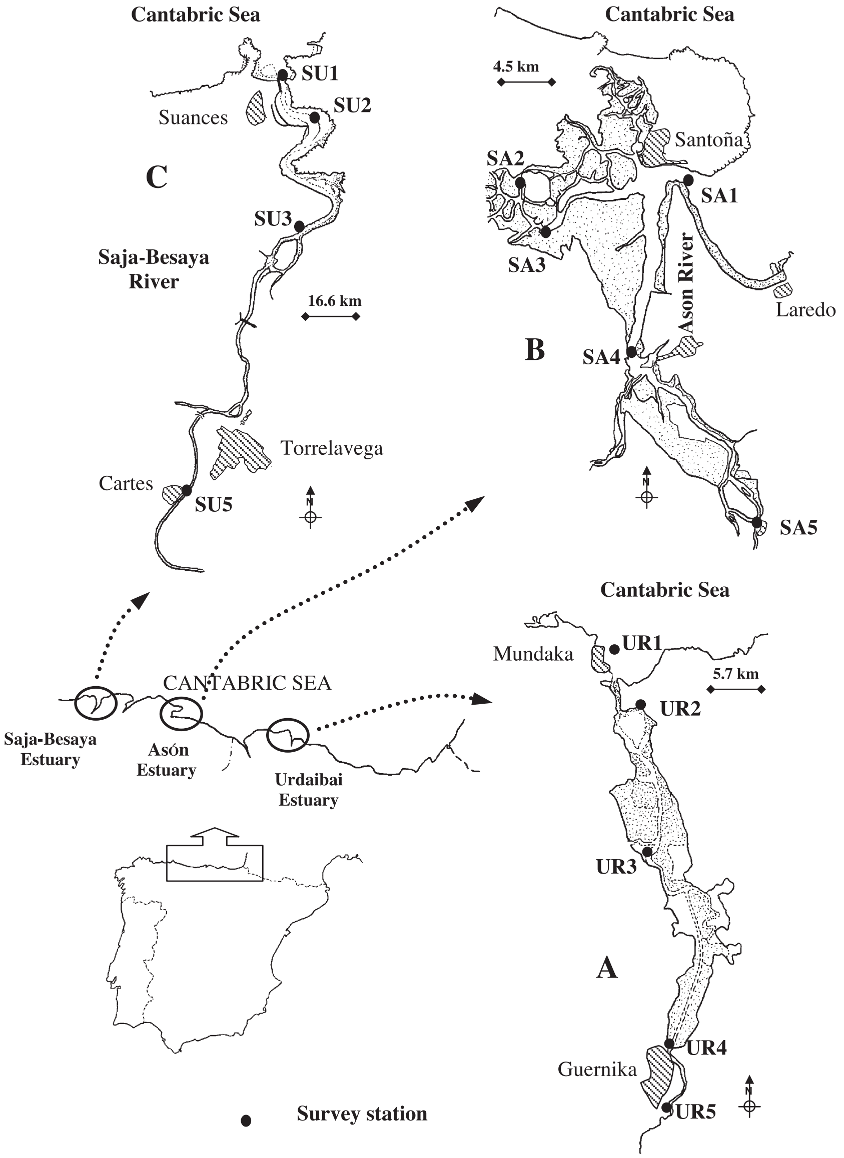

Fig. 1. Maps of the Urdaibai (A), Asón (B), and Saja–Besaya (C) estuaries, indicating the locations selected for the sampling stations, and the main centers of population.

extensive tidal flats along its lower reaches and by salt marshes in the middle section. As a result of its geomorphology, this estuarine system can vary considerably in its volume and flushing rates, and this has a considerable effect on its biological and chemical properties. It was designated a Biosphere Reserve by UNESCO in 1984. The estuary is considered nonpolluted and only some minor industrial and fishing activities take place in the estuary; most of the human activities in the area are agriculture and forestry, with some tourism in summer. Only discrete events of increased metals' bioavailability have been recorded (Soto et al., 1996). The second zone of study is the estuary of the Asón; it is characterised by tides that produce differences in water level of up to 4.5 m, causing currents that change in direction. This estuary is situated in the eastern part of Cantabria, and is of great interest because there is an area of 3.5 km^2 of salt marshes within the estuary that constitutes, together with the Urdaibai Estuary, the most important wetland area along the northern Cantabrian and Atlantic coastline of the Iberian Peninsula. Running through these littoral salt marshes are channels that supply the estuary with organic matter and sediments originating from the terrestrial zone; because the area is so flat, sediments are deposited relatively rapidly. It is a system with a high biological productivity (~200 kcal mol^{-1} year^{-1}) and a very low biodiversity. Due to the pressure from tourism development, some of the salt marsh areas are drying up. In addition, the zone is subjected to continuous discharges of wastewaters from marine aquaculture, urban and industrial areas. The input from rainwater in this system is around 1200 l m^{-2} year^{-1}, providing just over 42 Hm^3. This system has an extremely varied fauna of molluscs, crustaceans, fish, and birds. The third zone of study is the estuary formed by two rivers draining relatively small basins, the Saja and the Besaya. The two rivers join close to the town of Torrelavega, to flow into the Sea of Cantabria through the estuary of San Martín de la Arena or of Suances. During the last century, this estuarine zone has been affected by major industrial developments that have been carried out without any kind of environmental consideration. As a result of this, there currently exists a high degree of contamination of both industrial and urban origin. At Torrelavega, the river receives such a heavy volume of discharges, principally from mining and paper manufacturing, and of carbonates, inter alia, that from this point, it is classified as "extremely contaminated". The resulting contamination affects not only the estuary but also the continental shelf adjoining this coastal zone. In the final part of the estuary, due to the levels of contamination, hardly any fauna exists and the riverbank vegetation also is practically nonexistent. Although station SU4 was one of the zones preselected (Fig. 1) due to the rocky character of the bottom, it was impossible to take samples.

Table 1 presents the different characteristics of the ecosystems studied: water depth, flow volume, length, basin area, and granulometry of the superficial sediment.

2.2. Interstitial water: diffusive fluxes

The sediment samples were taken by gravity cores of 60 mm internal diameter and were transported refrigerated to the laboratory within 3 h of sampling. The cores were cut at intervals of 1 cm and the sections obtained were centrifuged at 15000×*g* for 30 min (SIGMA 3K 30). This process extracted 70–80% of the total water content of the samples, depending on the granulometry. The handling of the samples in the laboratory and the subsequent analysis of the interstitial water were performed under an inert atmosphere. The sediment was dried at 80 °C, gently homogenised and sieved using a 63-μm sieve, prior to organic carbon analysis.

The dissolved inorganic carbon (DIC) diffusive fluxes were determined from the sum of the fluxes of

Table 1
General characteristics of three systems studied: water depth at the stations studied, flow volume, length, and basin area

Site	Water depth (m)	Flow volume (m^3 s^{-1})	Length (km)	Basin area (km^2)	Granulometry (mm)
Urdaibai estuary	1–6	3.6	12.5	132	0.01–0.40
Asón estuary	2–4	0.813	~40	562	0.04–0.40
Saja–Besaya estuary	1–3	25.4[a]	~60	465	0.03–0.54

The granulometry distribution of the surface sediments is also included.

[a] Values at the proximities of the mouth of each river.

the individual carbonic acid species across the sediment–water interface, 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 porosity, D_s is the coefficient of diffusion in the sediment, $\partial C/\partial z$ is the concentration gradient and z is the depth referring to the water–sediment interface. For the calculation of the coefficient of diffusion in the sediment (D_s), we have employed the expression proposed by Sweerts et al. (1991), the porosity in the surface layer of the sediment and the diffusive coefficients for finite 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 total alkalinity (TA) diffusive flux was calculated from the sum of the fluxes of bicarbonate and carbonate ($F(\text{TA}){=}F(\text{HCO}_3^-){+}2\,F(\text{CO}_3^{2-})$). Other species, such as $B(OH)_4^-$, HPO_4^{2-}, and NO_3^-, also contribute to the alkalinity flux, but in most cases, their diffusive fluxes are relatively small compared to the total alkalinity flux. For this reason, in the following discussion, we consider that the carbonate alkalinity diffusive flux can be represented by the total alkalinity diffusive flux.

The saturation grade of the pore waters with respect to calcite (Ω_C) or aragonite (Ω_A) were obtained from the stoicheiometric solubility constants of calcite and aragonite proposed by Mucci (1983).

2.3. In situ flux measurements

The in situ fluxes of DIC, dissolved oxygen (DO) and TA were obtained using two benthic chambers placed on the bottom simultaneously with the help of divers. The chambers are constructed of opaque plexiglass and are ellipsoid in shape, covering an area of sediment of 0.385 m^2 and containing volumes between 78 and 90 l depending on the eccentricity of the ellipsoid. The chamber design included a recirculation pump to avoid stratification inside the chamber (Forja et al., 1994). At preset intervals of time (30 min), a fraction collector took the sample from the outflow for analysis. The total time during which the chamber was employed varied between 3 and 5 h, based on the oxygen consumption inside the chambers.

The benthic fluxes, considering the dimensions of the chambers, were calculated by fitting the variations of concentration with time to linear or exponential equations (Forja and Gómez-Parra, 1998). Fig. 2 shows the evolution of the total alkalinity, pH, and concentrations of inorganic carbon and dissolved oxygen in the interior of a benthic chamber in one of the samplings. Table 2 shows the fit (linear or exponential) made to obtain the benthic fluxes of DIC, TA, and DO measured with benthic chambers, the number of data considered (n) and the correlation coefficients obtained (r^2).

Deviations in the fluxes that vary between 4% and 84% for DIC, between 1% and 82% for TA, and between 0.3% and 14% for DO were obtained with the chambers utilised.

Giordani et al. (1992) and Hammond et al. (1996) found that deviations of benthic fluxes of DIC measured using chambers ranged between 38% and 81%. Friedl et al. (1998) attribute the differences in the measurements made with benthic chambers to the spatial variation in the density of the macrofauna, and Giordani et al. (1992) attribute these differences to the analytical precision of the measurement, to the deviation in the fit of the experimental data, and to the uncertainty that always exists regarding the true volume of the water incubated.

2.4. Water–atmosphere CO_2 fluxes

For the estimation of the water–atmosphere CO_2 fluxes, specific samplings were made on the same dates and in the same zones as those of the benthic chambers. In these samplings, water samples were taken at a depth of 1 m utilising Niskin bottles, with the help of a boat. Samples were taken as quickly as possible to avoid large variations in the tidal cycle between one station and another. The water–atmosphere fluxes of CO_2 have been estimated by the following expression:

$$F = K\alpha\Delta p\text{CO}_2$$

where K is the transfer velocity of CO_2 (cm h^{-1}), α is the solubility of CO_2 (mol l^{-1} atm^{-1}; Weiss, 1974)

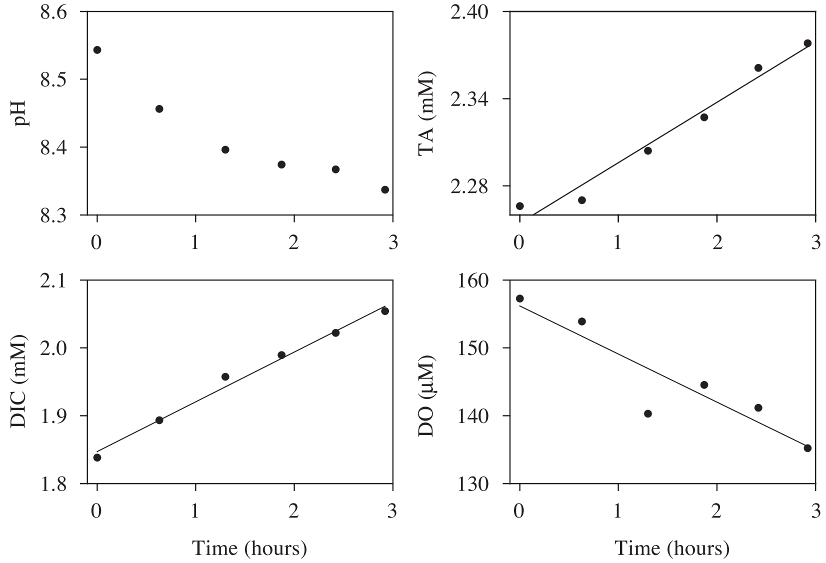

Fig. 2. Typical variations of the total alkalinity (TA), pH values, and the concentrations of dissolved inorganic carbon (DIC) and oxygen (DO) inside the benthic chamber.

and $\Delta p\mathrm{CO}_2$ (atm) is the difference of CO_2 partial pressure between the water surface and the air. In estuaries, the transfer velocity depends on the depth, mean tidal velocity, and wind regime (Raymond and Cole, 2001). For the wind speed dependence of the transfer velocity (K), we chose the parameterisation of Carini et al. (1996), based on an SF_6 release in the Parker River estuary. The use of a deliberate gas tracer for the study of K is one of the most promising techniques for estuarine studies (Raymond and Cole, 2001). These authors believe that deliberate gas tracers currently provide the best estimates of transfer velocity when estimating gas exchange for entire estuaries over long time scales.

Table 2
Type of fit: linear ($C=a+bt$) or exponential ($C=a-b\mathrm{e}^{-ct}$) made to obtain the benthic fluxes of DIC, TA, and DO measured using chambers, number of data considered (n), and coefficient of correlation (r^2) obtained

Station	F_{DIC}			F_{TA}			F_{DO}		
	n	Fit	r^2	n	Fit	r^2	n	Fit	r^2
UR1	5	Linear	0.921	5	Linear	0.863	32	Linear	0.709
UR2	5	Linear	0.900	4	Linear	0.988	20	Linear	0.848
UR3	4	Linear	0.940	3	Linear	0.999	16	Linear	0.877
UR4	3	Linear	0.974	3	Linear	0.999	14	Linear	0.948
UR5	3	Linear	0.997	3	Linear	0.930	21	Linear	0.864
SA1	5	Exponential	0.953	4	Linear	0.994	17	Linear	0.560
SA2	5	Exponential	0.960	4	Linear	0.960	15	Linear	0.906
SA3	5	Exponential	0.988	6	Linear	0.981	18	Linear	0.852
SA4	6	Exponential	0.987	6	Linear	0.969	20	Linear	0.867
SA5	5	Exponential	0.991	4	Linear	0.966	16	Linear	0.853
SU1	4	Exponential	0.994	4	Linear	0.969	12	Linear	0.836
SU2	3	Linear	0.664	3	Linear	0.789	8	Linear	0.672
SU5	4	Linear	0.781	4	Linear	0.817	17	Linear	0.867

The monthly averages provided by the Spanish National Institute of Meteorology were used for the wind speeds; these correspond to the meteorological stations close to the estuaries sampled (3.9 m s^{-1} for the Urdaibai estuary and 5.3 m s^{-1} for the Asón and Saja–Besaya estuary).

The gradient of $p\mathrm{CO}_2$ at the water–atmosphere interface was obtained as the difference between the value in each sample of surface water and the value of $p\mathrm{CO}_2$ obtained from the Mace Head station (53°33′ N 9°00′ W, southern Ireland) from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory/Carbon Cycle Greenhouse Gases Group (NOAA/CMDL/CCGG) air sampling network (available at http://www.cmdl.noaa.gov/). The Mace Head station is the nearest to the three estuaries studied available in the web page of NOAA. The $p\mathrm{CO}_2$ in the water has been calculated from the values of pH and total alkalinity utilising the constants of Mehrbach et al. (1973). A positive flux indicates a transfer of CO_2 from the surface of the water to the atmosphere.

2.4.1. Analytical methods

The dissolved inorganic carbon (DIC) concentrations in samples were determined by pH (NBS) and total alkalinity (TA) using a potentiometric analyser (Metrohm 670) with glass combination electrodes (Metrohm, ref. 6.0210.100). The total alkalinity was obtained from the second point of inflection with an iterative program using the Gran functions (Forja et al., 2001). For the DIC speciation, the acid dissociation constant of Mehrbach et al. (1973) was used. 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 about 100 g (to an accuracy of ±0.001 g) for the benthic chamber and 2 ml for the interstitial water. The accuracy of the initial measurement of the pH (NBS) of the sample is ±0.003, and of the TA is ±3 μM. The accuracy of the alkalinity determinations was checked using an inorganic carbon reference material provided by Dr. Andrew Dickson at the Scripps Institute of Oceanography (Batch #33). This accuracy and precision is good enough for the benthic flux calculation, bearing in mind that these fluxes in general result in concentration changes greater than 100 μM during the sampling by the benthic chambers.

Before being utilised for the speciation of the DIC, the pH was normalised to the temperature at time of sampling. This normalisation was performed assuming that the concentration of the DIC and the total alkalinity are independent of the temperature (Zhang, 2000). In the samples of interstitial water, the normalisation of the pH was performed considering the salinity of the overlaying water and a temperature of 20 °C, and in the samples from the chambers, the temperature and salinity of the overlaying water.

The salinity was measured using a salinometer (Beckman, Mod. RS-10) with an accuracy of ±0.001. The dissolved oxygen (DO) concentration inside the chambers was measured by the Winkler method in discrete samples (accuracy of ±0.1 μM) and continuously monitored with polarographic electrodes (YSI, mod. 57; WTW, CellOx 325). The calcium concentration was measured using a potentiometric analyser (Metrohm 670) with a selective electrode of calcium (Metrohm, ref. 6.1241.050) and a reference electrode (Metrohm, ref. 6.0726.100). EGTA 0.05 M was employed as titrant. The samples were buffered to a pH of close to 9 by adding 10 ml of borax 0.1 M. The organic carbon concentrations [OC (%)] 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 constant weight.

3. Results

3.1. Interstitial waters

Figs. 3 and 4 show the variables associated with inorganic carbon speciation versus the sediment depth for the different stations of the Urdaibai, Asón, and Saja–Besaya estuaries. The eight stations studied in the three estuarine systems show a generalised trend of diminishing OC (%) content with depth, except for SA5 where the content in organic carbon increases appreciably (Fig. 4). The pH presents the profile typical of coastal marine sediments (Cai et al., 2000), in that there is a decrease of pH in the top layer of the sediment; this may be a consequence of the processes of aerobic degradation of the organic matter and of oxidation of reduced dissolved species (Cai et al., 2000; Mucci et al., 2000).

In all the stations, a certain increase of DIC with depth is found. Unlike other coastal systems of the Iberian Peninsula (Gómez-Parra and Forja, 1994), the concentrations of dissolved inorganic carbon are small, with a maximum value at SA4 of 10 mM at 9 cm depth.

The concentration of calcium is very variable due to the estuarine character of the sampling stations. The values for this element range from 0.4 mM in SA4 to 20 mM in UR4. These high concentrations in UR4 may be due to wastewater discharges originating from the town of Guernika (Fig. 1).

In general terms, in the interstitial water of the sediments studied, an increase is found in the degree of saturation of both calcite and aragonite, with depth (Figs. 3 and 4). At stations SA2, SA4, SA5, and SU2, there is evidence of undersaturation of aragonite and/or calcite at shallow depths (at SA4 and SA5) or

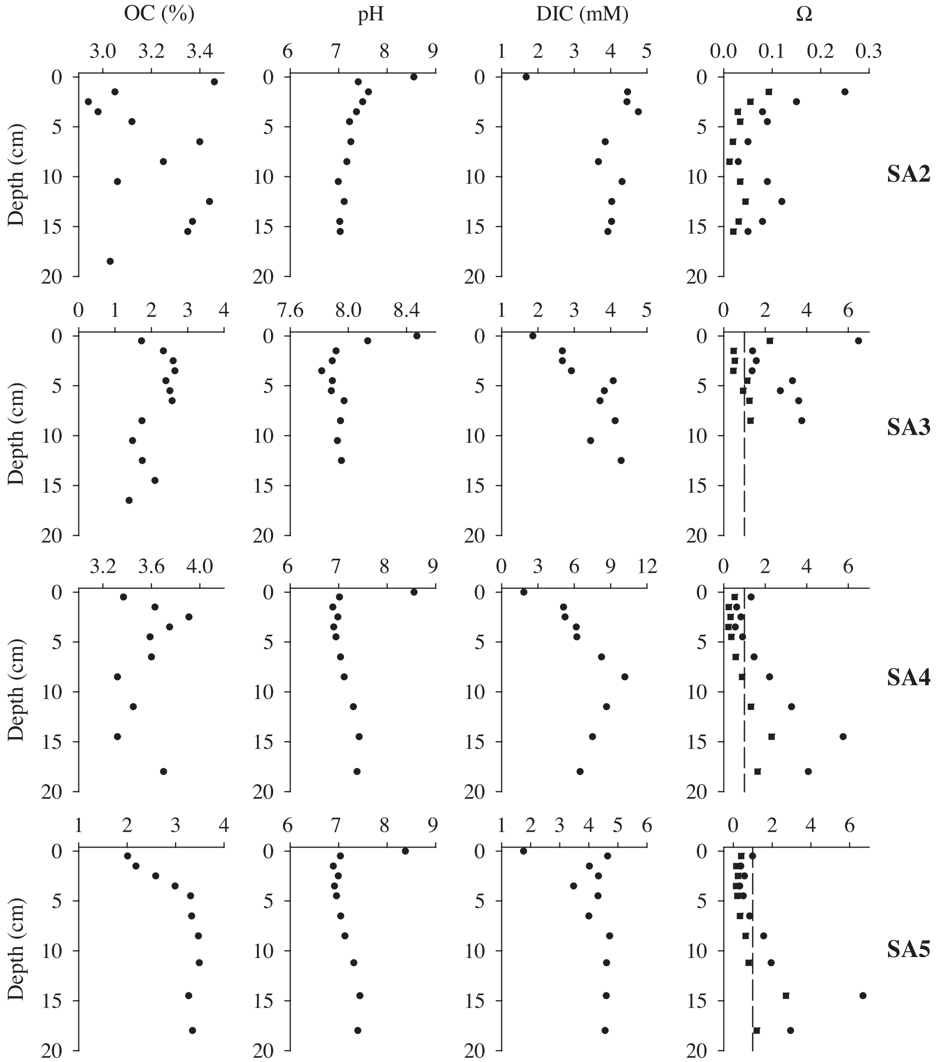

Fig. 3. Vertical variations of the organic carbon content, pH, the concentration of inorganic carbon, and the degree of $CaCO_3$ saturation of calcite (●) and aragonite (■) in the Asón estuary (stations SA2, SA3, SA4, and SA5).

throughout the entire profile (at SA2 and SU2). At most of these stations, this undersaturation coincides with a decrease in the concentration of Ca^{2+}, and at station SU2, this reaches 22%. This finding may be indicative of the precipitation of $CaCO_3$. However, at stations SU3, UR2, and UR4, values much higher than 10 are reached, especially at SU3 where Ω exceeds 100 at a depth of 6 cm. This behaviour has been described in other marine systems (Sayles, 1981; Hammond et al., 1999; Mucci et al., 2000). The high values of the degree of saturation may be caused by the absence of reactive growth surfaces (content of $CaCO_3$) and/or by the abundance of precipitation inhibitors, such as phosphate, dissolved organic carbon (Mucci et al., 2000), manganese (Sayles, 1981), or magnesium (Sholkovitz, 1973).

The diffusive fluxes of DIC and TA obtained present values ranging between 0.54–2.65 and 0.0–1.0 mmol m^{-2} day^{-1}, respectively (Table 3). These ranges have the same order of magnitude but are lower than those found for other coastal ecosystems (Hammond et al., 1999; Cai et al., 2000). For

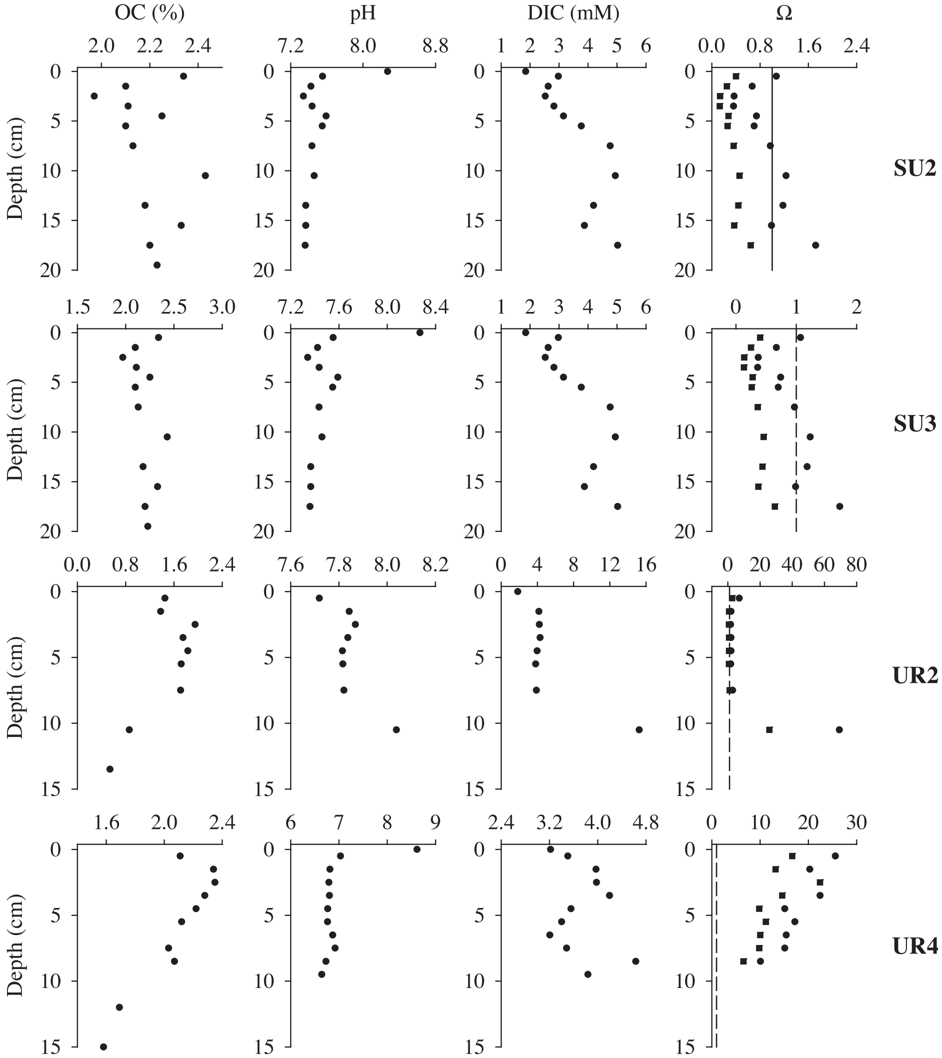

Fig. 4. Vertical variations of the organic carbon content, pH, the concentration of inorganic carbon, and the degree of $CaCO_3$ saturation of calcite (●) and aragonite (■) in the Urdaibai and Saja–Besaya estuaries (stations UR2, UR4, and SU2, SU3, respectively).

example, Cai et al. (2000) measured diffusive fluxes of DIC in coastal sediments of Georgia with values between 15.5 and 29.9 mmol m^{-2} day^{-1}, and in different coastal systems of the Iberian Peninsula. Forja et al. (2004) obtained diffusive fluxes of DIC that vary between 2 and 12 mmol m^{-2} day^{-1}. The relatively small fluxes obtained may be due to the existence in these estuaries of sediments deposited by significant advective transport, caused by bio-irrigation that is not considered in these fluxes. On this point, Jahnke et al. (2003) consider that advective transport of pore waters may be a major input pathway of nutrients into the Satilla River Estuary.

3.2. Benthic fluxes

Table 3 shows the values of the benthic fluxes of total alkalinity, inorganic carbon, and dissolved oxygen at the various stations of the zones studied. The data of the fluxes obtained with benthic chambers at station SU3 of the Saja–Besaya estuary are not available. The fluxes of TA, DIC, and DO measured

Table 3
Benthic fluxes of inorganic carbon (F_{DIC}), alkalinity (F_{TA}), and oxygen (F_{DO}) in the three estuaries studied in the north of Spain

System	Station	Temperature (°C)	Salinity	F_{DIC}	F_{TA}	F_{DO}	Diffusive F_{DIC}	Diffusive F_{TA}	Porosity	Organic carbon (%)
Urdaibai estuary	UR1	18.0	34.9	134.3	−216.4	46.2	–	–	–	1.40
	UR2	17.7	33.7	415.6	231.0	181.3	1.3	0.8	0.35	1.68
	UR3	17.6	34.0	375.1	284.4	121.1	–	–	–	1.18
	UR4	18.2	0.7	554.2	162.8	261.5	0.7	0.0	0.41	2.24
	UR5	15.1	0.2	235.1	71.3	134.2	–	–	–	0.38
Asón estuary	SA1	19.3	33.4	104.2	77.7	46.0	–	–	–	0.23
	SA2	21.1	33.1	128.5	34.7	41.6	2.7	2.4	0.53	3.11
	SA3	20.8	32.2	384.2	−87.3	62.2	0.6	0.5	0.42	2.37
	SA4	20.3	25.4	344.0	232.2	68.5	1.5	1.0	0.51	3.65
	SA5	20.5	23.7	300.1	66.6	117.9	0.7	0.6	0.33	2.62
Saja–Besaya estuary	SU1	17.3	28.1	501.6	172.5	36.0	–	–	–	0.73
	SU2	18.8	33.5	43.0	99.0	141.2	0.5	0.4	0.41	2.14
	SU3	19.2	11.4	–	–	–	1.1	1.2	0.45	3.62
	SU5	18.0	0.2	107.4	88.5	43.6	–	–	–	0.38

Included are the range of variation for the temperature and salinity, the diffusive fluxes of inorganic carbon (diffusive F_{DIC}), the porosity, and the organic carbon concentration in surface sediments. The benthic and diffusive fluxes are expressed in mmol m^{-2} day^{-1}.

vary between 35 and 284, between 43 and 554, and between 22 and 261 mmol m^{-2} day^{-1}, respectively, and can be considered relatively high if they are compared with the benthic fluxes of TA, DIC, and DO of other coastal ecosystems (Table 4). It will be noted that a wide range of variation is found in the benthic fluxes of the coastal zones presented in Table 4, due to the considerable spatial heterogeneity they present, as can be observed from the interval of variation measured in each zone; there also exists a wide variety in the design of benthic chambers, which implies equipment with different

Table 4
Benthic fluxes of total alkalinity, dissolved inorganic carbon, and oxygen in several coastal marine ecosystems measured with benthic chambers

Site	Depth (m)	Temperature (°C)	Organic carbon (%)	TA flux (mmol m^{-2} day^{-1})	DIC flux (mmol m^{-2} day^{-1})	DO flux (mmol m^{-2} day^{-1})	Reference
Halifax Harbour (Canada)	~2		0.1–1.1	–	28.6–95.7	8.3–41.1	Hargrave and Phillips (1981)
Cape Lookout Bight (N Carolina)	–	12.0–27.5	3.3–5.0	–	31.0–162.7	–	Martens and Klump (1984)
San Francisco Bay (S California)	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)	4–6	–	–	3.8–11.6	14.4–26.0	3.7–15.0	Dollar et al. (1991)
Northern Adriatic Sea	~40	18.0–22.0	0.5–1.3	0.9–10.4	12.2–25.2	5.3–19.9	Giordani et al. (1992)
Albufera of Majorca (Mediterranean)	–	28.5–31.9	–	–	63.4–732.0	32.4–97.2	López et al. (1995)
Port Phillip Bay (Australia)	14	10.0–13.0	–	6.0–56.0	23.0–103.0	23.0–102.0	Berelson et al. (1998)
Bay of Cádiz (Spain)	2–14	18.4±6.8	2.2–3.1	–	154.6–224.5	–	Forja and Gómez-Parra (1998)
San Pedro Shelf	63–67	–	–	15.0–33.0	14.0–55.0	14.0–42.0	Berelson et al. (2002)
Monterey Bay (California)	95–100	–	0.2–0.5	−0.7–11.7	4.7–17.8	5.0–13.5	Berelson et al. (2003)
Iberian Peninsula	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)

Table 5
Wind velocities (m s^{-1}) and range of variation of the salinity, $p\mathrm{CO}_2$ (ppm), and water–atmosphere fluxes of CO_2, in the three estuaries studied in the north of the Iberian Peninsula

Station	Wind velocity	Salinity	$p\mathrm{CO}_2$	CO_2 flux
Urdaibai estuary	3.9	17.0–33.3	256–1569	(−5.5)–63.3
Asón estuary	5.3	18.3–34.4	246–436	(−10.8)–6.3
Saja–Besaya estuary	5.3	0.85–34.6	264–9728	(−9.2)–988.0

The fluxes are expressed in mmol m^{-2} day^{-1}.

characteristics. These differences affect the calculations of the benthic fluxes, and for this reason, they should be considered when making comparisons of benthic fluxes between coastal systems. Variability in chamber fluxes may be attributable to a number of factors: uncertainties in the flux determinations, heterogeneity in the scale of separation between chambers, and temporal variability in fluxes.

At some of the stations (UR1 and SA3), the variations of the total alkalinity, pH, and inorganic carbon inside the chambers are contrary, thus giving rise to negative benthic fluxes of TA at different stations. This behaviour has been described very infrequently in the bibliography (Friedl et al., 1998; Berelson et al., 2003) and may be due to an acidification of the incubated water that produces an increase in the concentration of CO_2 to the detriment of the concentration of CO_3^{2-}. In fact, at stations UR1 and SA3, the pH decreases by more than 0.2 units in 3 h.

3.3. Fluxes with the atmosphere

Table 5 gives the range of variation of the salinity, $p\mathrm{CO}_2$, and the fluxes of CO_2 obtained in each of the estuarine systems studied. If the mean values are considered, in the estuaries of the Urdaibai and Saja–Besaya, a transfer of CO_2 takes place from the water to the atmosphere, which means that these estuaries act as sources of CO_2. The mean fluxes estimated vary between −3 and 446 mmol m^{-2} day^{-1} (for the Asón and Saja–Besaya estuaries, respectively). This range of variation is less than that obtained by Frankignoulle et al. (1998) in several different European estuaries (between 50 and 760 mmol m^{-2} day^{-1}).

In the estuary of the Asón, because the samples were taken at high tide when the marine influence was strong, very low values of CO_2 flux were obtained, meaning that overall the system behaves as a sink of CO_2.

4. Discussion

4.1. Diffusive and in situ benthic fluxes

Fig. 5 shows the relationship of the diffusive fluxes of DIC with the organic carbon content of the superficial sediments and with the temperature. Although a significant correlation between these variables is not found [r^2=0.188 for diffusive fluxes of DIC versus OC (%) and r^2=0.130 for diffusive fluxes of DIC versus temperature (°C)], a certain tendency towards an increase can be observed. This is due to the systems being very heterogeneous, and to the fact that all the samplings were made in spring, with very small variations in temperature. In many other systems, it has been observed that the temperature and the supply of organic carbon both influence the intensity with which the diagenetic

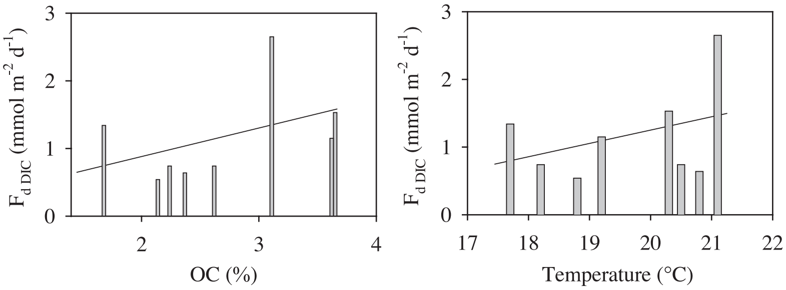

Fig. 5. Relationship between the diffusive fluxes of inorganic carbon and the organic carbon content in surface sediments and with the temperature.

processes take place (Thamdrup et al., 1998; Kostka et al., 1999).

It should be noted that at station UR4, the diffusive flux of TA is 0; the possible reason for this is that in the surface layer of sediment the flux of HCO_3^- produced by the degradation of organic matter is compensated by the precipitation of $CaCO_3$. Although there is no direct evidence of this precipitation, the degree of saturation of the calcite and aragonite at this station is high (Fig. 4), possibly induced by the high concentration of calcium.

The depth of penetration of oxygen in the sediment has been estimated from the expression proposed by Cai and Sayles (1996):

$$L = 2\phi D_S [O_2]_{BW} / F_{DO}$$

where L is the depth of penetration of oxygen, ϕ is the porosity, D_S is the diffusion coefficient of oxygen in the sediment, $[O_2]_{BW}$ is the bottom water oxygen concentration and F_{DO} is the benthic oxygen flux. For the calculation of the coefficient of diffusion in the sediment (D_s), we have employed the same expression used for diffusive fluxes (Sweerts et al., 1991) and the diffusive coefficients for finite dilution (D^0) reported by Broecker and Peng (1974). In these stations, the depth of penetration of oxygen varies between 0.1 mm (SU3) and 3.6 mm (SA2). Despite the error implicit in this estimation, the results obtained are consistent with those of other coastal systems, where the depth of penetration of O_2 extends for only a few millimetres, and aerobic oxidation is one of the most important mechanisms in the degradation of organic matter (Jørgensen, 1982).

Figs. 6 and 7 show the dependence of the benthic fluxes of DIC and DO measured at each of the stations studied on the OC content of the superficial sediments, and on the temperature. In no case were significant correlations found between the fluxes and these variables (r^2<0.5); however, certain trends can be appreciated. In the estuaries of Urdaibai and Asón,

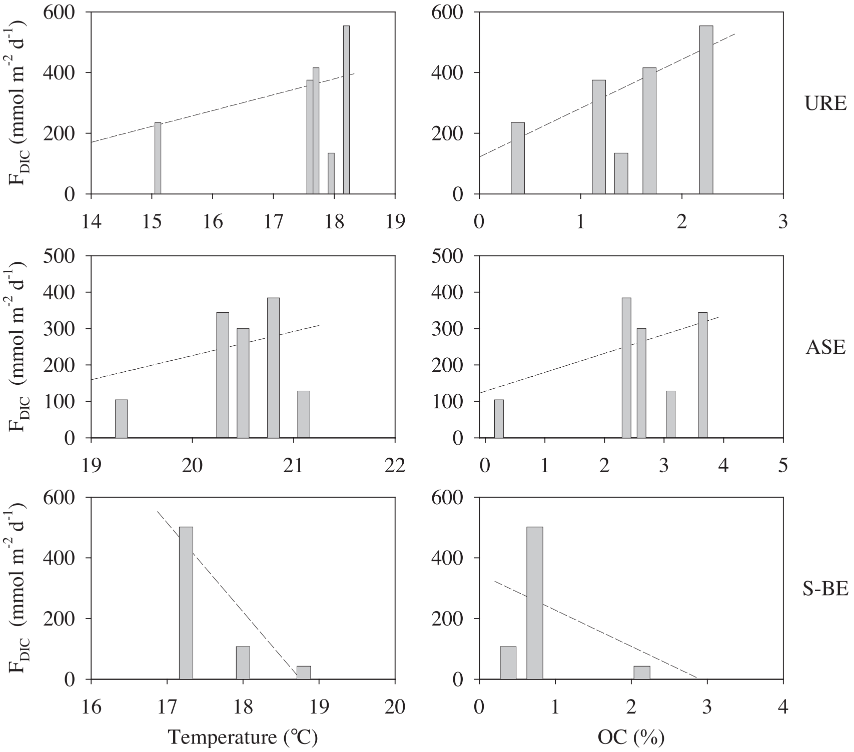

Fig. 6. Variation of dissolved inorganic carbon benthic fluxes (F_{DIC}) versus the organic carbon content in surface sediments and the temperature of the Urdaibai (URE), Ason (ASE), and Saja–Besaya (S–BE) estuaries.

there appears to be an increase of the DIC flux with the OC content and the temperature while in the Saja–Besaya estuary, a certain decrease can be appreciated (Fig. 6). Unlike the DIC fluxes, the general tendency of the dissolved oxygen fluxes is to increase with the temperature and with the organic carbon content of the superficial sediments (Fig. 7). This increase with temperature is widely recognised in the bibliography (Giordani et al., 1992; Friedl et al., 1998; Cermelj et al., 2001).

One station of particular interest is SU2 (close to the mouth of the Saja–Besaya estuary) where, despite the high content in organic carbon (2.14%) and the high DO flux (141.2 mmol m^{-2} day^{-1}), the diffusive and benthic fluxes of DIC are relatively low (0.54 and 43.0 mmol m^{-2} day^{-1}, respectively). What may occur at this station is that the organic carbon of the sediment may be more refractory, and therefore more difficult to degrade, and that a large part of the DO that is diffused into the sediment may be utilised in the oxidation of species reduced in the processes of anaerobic degradation of organic matter. This consumption of dissolved oxygen by reduced inorganic species has been found in many other coastal systems (Jørgensen, 1982; Glud et al., 1999).

If the benthic fluxes of DIC and DO of the three estuarine systems are compared, it is observed that the highest values are obtained in the Urdaibai estuary (134–554 mmol DIC m^{-2} day^{-1}; 46–261 mmol DO m^{-2} day^{-1}), followed by the Asón estuary (104–384 mmol DIC m^{-2} day^{-1}; 42–118 mmol DO m^{-2} day^{-1}) and the Saja–Besaya estuary (43–502 mmol DIC m^{-2} day^{-1}; 36–141 mmol DO m^{-2} day^{-1}). It can be appreciated how the benthic fluxes of DIC present an inverse relationship with the degree of anthropogenic alteration of the system.

Benthic fluxes of dissolved inorganic carbon and total alkalinity are the result of the sum of the release of inorganic carbon to the pore waters from organic matter oxidation and calcium carbonate dissolution

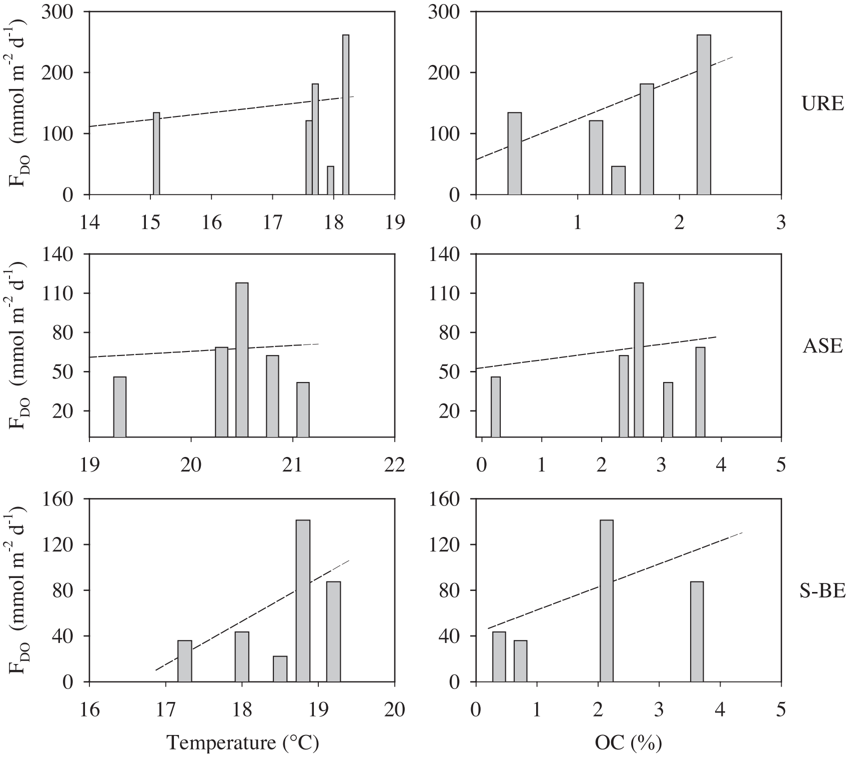

Fig. 7. Variation of dissolved oxygen benthic fluxes (F_{DO}) versus the organic carbon content in surface sediments and the temperature of the Urdaibai (URE), Asón (ASE), and Saja–Besaya (S–BE) estuaries.

and, possibly, the removal by calcium carbonate precipitation. To estimate the relative importance of these processes in the benthic fluxes, the ratio between the fluxes of alkalinity (F_{TA}) and of inorganic carbon (F_{DIC}) has been employed. For the stations taken together, a well-defined trend between the variations of F_{TA} and F_{DIC} has not been found, largely due to the heterogeneity of the systems considered. The ratio between F_{TA} and F_{DIC} presents an average value of 0.70. The Urdaibai and Asón estuaries present the same average value of 0.48, whereas the Saja–Besaya estuary presents the much higher ratio of 1.15. From F_{TA}/F_{DIC}, Jahnke and Jahnke (2000) estimate the ratio of the $CaCO_3$ dissolution rate to the organic carbon oxidation rate. Utilising the simple model that they propose, the rate of $CaCO_3$ dissolution is 0.32 times the rate of organic carbon oxidation in the Urdaibai and Asón estuaries, and 1.35 in the estuary of the Saja–Besaya. For all the stations taken together, an average value of 0.54 is obtained, very close to the value of 0.58 obtained by Jahnke and Jahnke (2000) on the North Carolina continental slope. From these estimations, it can be deduced that, in the Saja–Besaya estuary, the dissolution of $CaCO_3$ is the factor responsible for the greater part of the benthic fluxes of DIC. If this approach is adopted for the diffusive fluxes, it is found that the dissolution of $CaCO_3$ is 0.7, 0.8, and 0.4 times the rate of organic carbon oxidation in the estuaries of Asón, Saja–Besaya, and Urdaibai, respectively. In this latter estimation, it has to be taken into account that the number of stations considered is less than the number of benthic chambers deployed. However, again, the estuary of the Saja–Besaya is seen to be where the dissolution of $CaCO_3$ makes the most contribution to the DIC flux. Similarly, Hulth et al. (1997) estimated that the DIC fluxes originating from carbonate dissolution were 2.6 and 71% of the DIC fluxes resulting from organic carbon in the south of the Weddel Sea (Antarctica). Cermelj et al. (2001) calculated a contribution of $CaCO_3$ dissolution to DIC benthic fluxes of 40% in the Gulf of Trieste, and Giordani et al. (1992) estimated a contribution of 20% in the Northern Adriatic Sea.

The quotient between the benthic fluxes of DIC and DO, commonly known by the initials CRQ (Community Respiration Quotient), allow the characterisation of the benthic metabolism, taking into account the relative intensity of the processes of aerobic and anaerobic respiration, together with that of chemical oxidation (Hargrave and Phillips, 1981; Andersen and Kristensen, 1988). In the three systems studied, the value of the CRQ is highly variable (1.8–13.9) and more than 1, as occurs in a large part of the coastal systems (Table 6). The highest values are found in those zones where the dissolution of $CaCO_3$ makes a significant contribution to the total benthic fluxes of DIC.

An exception is the station SU2 of the estuary of the Saja–Besaya, with a CRQ value of 0.3. Here, the degradation of organic matter takes place principally by the aerobic route, or else the fluxes of DIC could have decreased due to several very different causes. In this context, Teal and Kanwisher (1961) and Granéli (1979) measured ratios of CO_2 release to oxygen consumption of less than 1, in sediments of different marine and fresh water zones. These low values were attributed to different microbial processes that remove CO_2 from the medium, such as the production of methane, and even to the absorption of CO_2 by plant roots, or to mechanisms of lateral transport in the interstitial water (Kristensen et al., 1994).

If the mean values of the CRQ of each estuary are compared, it can be seen that the highest values correspond to the zones with the most alteration of the system due to intense anthropogenic activity, which inputs to the system organic matter that is more refractory to aerobic oxidation. Thus, the Saja–Besaya

Table 6
Ratio between benthic fluxes of dissolved inorganic carbon and dissolved oxygen (F_{DIC}/F_{DO}:CRQ) in several coastal marine ecosystems

Site	F_{DIC}/F_{DO}	Reference
Halifax Harbour (Canada)	1.8–4.0	Hargrave and Phillips (1981)
Eastern Passage (Nova Scotia)	1.0–5.0	Andersen and Hargrave (1984)
Norsminde Fjord (Denmark)	0.9–2.6	Andersen and Kristensen (1988)
Ao Nam Bor mangrove (Thailand)	1.3–1.8	Kristensen et al. (1991, 1994)
Lagoon in New Caledonia	0.9–1.2	Boucher et al. (1994)
Bangrong mangrove (Thailand)	1.4–4.1	Holmer et al. (1999)
Iberian Peninsula	1.1–3.1	Forja et al. (2004)

estuary (CRQ=5.6±7.6) is the one that receives more discharges of industrial and urban wastewaters, followed by the Asón (CRQ=3.8±1.7) and the Urdaibai (CRQ=2.4±0.5).

The values obtained for diffusive fluxes of inorganic carbon constitute from 0.1% to 2% of those measured with benthic chambers, which may to a large extent be due to the spatial resolution considered in the top layer of sediment (1 cm). The underestimation of the benthic fluxes of inorganic carbon calculated in samples of sediment has been described by Glud et al. (1998), Forja and Gómez-Parra (1998), and Cermelj et al. (2001), and generally has been related to the potentiation of the processes of transfer that are produced by the irrigation of the benthic macrofauna, as well as to the substantial heterogeneity in the sediment column. This phenomenon has also been found in the exchange of other substances, mainly nutrients (e.g. Hammond et al., 1999; Jahnke and Jahnke, 2000). The great difference found between the two fluxes may be due in part to processes of dissolution–precipitation of calcium carbonate. In this respect, different researchers have found that the contribution of the dissolution–precipitation of calcium carbonate to the benthic flux of inorganic carbon can be fairly considerable (Giordani et al., 1992; Hulth et al., 1997; Jahnke and Jahnke, 2000; Mucci et al., 2000; Cermelj et al., 2001).

4.2. Fluxes with the atmosphere

In Fig. 8, a decrease of $p\mathrm{CO}_2$ and of the CO_2 flux with the salinity is observed in the three systems studied. This behaviour has been observed in various European estuaries (the Elbe, Ems, Rhine, Scheldt, Tamar, Thames, Gironde, Douro, and Sado) by different authors (Kempe et al., 1991; Frankignoulle et al., 1998; Abril et al., 2000). In the estuaries studied, two parts can be differentiated: a brackish part, oversaturated with CO_2 with respect to the atmosphere, and another more saline part where $p\mathrm{CO}_2$ is substantially less, and in some systems, may even reach values lower than that of the atmospheric mean, as occurs in the estuaries of the Asón and Saja–Besaya (Fig. 8).

The estuary of the Saja–Besaya presents the highest values of $p\mathrm{CO}_2$ (9700 ppm at a salinity of 2.6), while its fluxes of CO_2 at low salinities reach values 120 times higher than those in the open ocean (<8.2 mmol m^{-2} day^{-1}; Smethie et al., 1985). Such high values of $p\mathrm{CO}_2$ have only been found in highly contaminated estuaries such as that of the Scheldt (Frankignoulle et al., 1998).

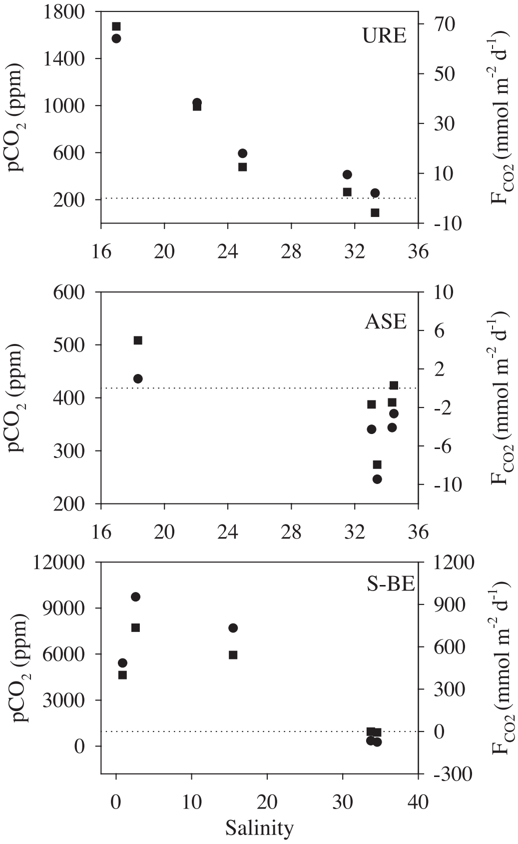

Fig. 8. Evolution of $p\mathrm{CO}_2$ (●) and of the water–atmosphere flux of CO_2 (■) with the salinity, in the Urdaibai (URE), Asón (ASE), and Saja–Besaya (S–BE) estuaries. Broken lines indicate zero flux of CO_2.

4.3. Final remarks

As well as presenting significant differences in respect of each other, the three systems studied are characterised by their considerable spatial heterogeneity. However, in all three systems, considerable benthic fluxes of DIC have been measured, resulting from the release of inorganic carbon to the pore waters from the oxidation of organic matter and the dissolution of calcium carbonate.

An inverse relationship has been observed between the benthic fluxes of DIC and the level of anthropogenic activity of the estuary. Thus, the highest values are obtained in the estuary of Urdaibai, which receives hardly any supplies of the anthropogenic type, and the lowest values in the Saja–Besaya estuary, where a high degree of contamination of both industrial and urban origin exists. However, the quotient between the benthic fluxes of DIC and DO (CRQ) presents a contrary behaviour, which reflects the greater importance of the processes of anaerobic degradation of the organic matter and of dissolution of calcium carbonate in the more contaminated systems.

It must be stressed that the water–atmosphere fluxes of CO_2 presented in this study reflect only one single sampling performed in spring, during the daytime when the sunlight was intense. Because the CO_2 fluxes vary greatly and present different patterns, according to the season, in order to determine if these systems act overall as sources or sinks of CO_2, it would be necessary to perform many more samplings over the course of a full year.

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