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Tidal and seasonal carbon and nutrients dynamics of the Guadalquivir Estuary and the Bay of Cádiz (SW Iberian Peninsula)

M. Ribas-Ribas[1,*], **L. I. Carracedo**[2], **E. Anfuso**[1], **and J. M. Forja**[1]

[1]Departamento de Química-Física. Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, Campus Río San Pedro, s/n, Puerto Real, Cádiz, 11510, Spain
[2]Instituto de Investigaciones Marinas, Consejo Superior de Investigaciones Científicas, Eduardo Cabello 6, Vigo, Pontevedra, 36208, Spain
[*]now at: School of Ocean and Earth Science, National Oceanography Centre, Southampton, University of Southampton, Waterfront Campus, European Way, Southampton SO14 3ZH, UK

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Correspondence to: M. Ribas-Ribas (mariana.ribas@uca.es, m.ribas-ribas@soton.ac.uk)

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Abstract

To study the effects of the physical environment on carbon and nutrients cycles dynamics in the north eastern shelf of the Gulf of Cádiz, changes in currents, tides, salinity, temperature, carbon system parameters (fugacity of CO_2 (fCO_2), dissolved organic carbon, dissolved inorganic carbon and pH) and others related (dissolved oxygen, total dissolved nitrogen, nutrients and suspended particulate matter) were measured in transects across the Guadalquivir Estuary and Bay of Cádiz mouths. Thus, the main objective of this study is to investigate the influence of these inner ecosystems on the carbon and nutrient distributions in the adjacent continental shelf. Three cruises have been undertaken in June 2006, November 2006 and February 2007, each one covering one complete tidal cycle during June, both systems were exporting components to the adjacent continental shelf of the Gulf of Cádiz. In an annual scale, Guadalquivir Estuary exported components while Bay of Cádiz imported them. Diurnal variability of fCO_2 could have a potentially important implication on the estimate of air–sea CO_2 fluxes. Monthly studies should be undertaken to completely understand this dynamic system.

1 Introduction

Coastal and marginal seas play a key role in the global carbon cycle by linking terrestrial, oceanic, and atmospheric reservoirs (Walsh, 1991). It is not clear how much of the carbon transported to the coastal seas by rivers and new production on the continental shelves is permanently sequestered by export to the deep oceans or to sediments on the shelves and shallow marginal seas (Chen and Borges, 2009). Furthermore, the importance of quantifying the transport of nutritive substances to the coastal zone has been highlighted by the Intenational Geospher-Biosphere Programme-Land-Ocean Interactions in the Coastal Zone (IGBP-LOICZ) (Gordon et al., 1996).

A number of studies have focused on estuaries and bays transport but mainly along the river course and anchor station (Borges and Frankignoulle, 2002; Dale and Prego, 2003; Goñi et al., 2009). This study provides insight into the fluxes along a perpendicular axis of the mouth of the inner ecosystems.

Previous studies have pointed out the importance of the inner ecosystems into the north eastern shelf of the Gulf of Cádiz (Ribas-Ribas et al., 2011a,b,c; de la Paz et al., 2007; Navarro and Ruiz, 2006). Ribas-Ribas et al. (2011a) found out that the Guadalquivir River is a significant source of inorganic carbon to the adjacent zone of the Atlantic Ocean. Ribas-Ribas et al. (2011b) found a strong negative correlation between salinity and $f\mathrm{CO}_2$. Ribas-Ribas et al. (2011c) found also a strong inverse linear correlation between salinity and total dissolved nitrogen (TDN) and suggested that the Guadalquivir River was a major source of dissolved organic matter for offshore sites in the surface waters of the north eastern shelf of the Gulf of Cádiz.

Thus, these studies emphasized the importance to better know the transport from/to the Guadalquivir Estuary and the Bay of Cádiz. To this end, we present high-frequency fugacity of CO_2 ($f\mathrm{CO}_2$), dissolved oxygen, dissolved organic carbon, total dissolved nitrogen, dissolved inorganic carbon (DIC), pH, nutrients, suspended particulate material and ancillary data recorded for three cruises off the Guadalquivir Estuary and the Bay of Cádiz. We firstly discuss the diurnal carbon and nutrients dynamics in both systems. We then discuss the fluxes of the Guadalquivir Estuary and the Bay of Cádiz on the continental shelf of the Gulf of Cádiz.

2 Material and methods

2.1 Study area

This study investigates tidal and seasonal fate and fluxes of carbon and nutrient from temperate estuary and bay to the coastal zone. The study was carried out over the north eastern shelf of the Gulf of Cádiz, which is located in the south western coast of the Iberian Peninsula (Fig. 1). The basin receives significant fluvial inputs associated with the discharge of large rivers such as the Guadiana, Guadalquivir, Guadalete and Tinto-Odiel. The Guadalquivir River is the main fluvial source draining into the Gulf of Cádiz margin. Coastal waters near the mouth of the Guadalquivir River and in the Bay of Cádiz present the highest primary production within the Gulf of Cádiz (Navarro and Ruiz, 2006). The coastal fringe of the Gulf of Cádiz is also characterized by the presence of waters warmer and colder than those detected in the rest of the basin during early summer and winter, respectively (Vargas et al., 2003; Navarro and Ruiz, 2006) and by a strong meteorological forcing caused by quasi-permanent episodes of winds (Ribas-Ribas et al., 2011b).

2.2 Field sampling

The data reported in this work were collected during 3 cruises that took place from 21/22 and 28/29 June 2006, from 23/24 and 29/30 November 2006 and from 4/5 and 7 February 2007 on board of the R/V *Mytilus*. Surveys consisted of repeated transects in along-shore direction, covering the mouth of Guadalquivir Estuary and the Bay of Cádiz (Fig. 1; Table 1). The chosen transect off Guadalquivir Estuary had 9 km and water depth varied from 5 to 12 m. The chosen transect off Bay of Cádiz had 6 km and water depth varied from 14 to 18 m. Each transect took about 2 h go and return. Surveys were carried out continuously during 24 h (as long as weather conditions permitted). We registered continuously currents with Acoustic Doppler Current Profiler (ADCP), temperature, salinity and fugacity of CO_2 (fCO_2). In addition, in every forward transect we stopped in three station to collect discrete samples. At each station, near-surface (~ 3 m below the sea surface) water samples were collected with Niskin bottles. Additional water samples were collected at near-bottom (~ 5 m above the seafloor) in the deepest station (southern in the Bay of Cádiz and middle in the Guadalquivir Estuary) (Fig. 1).

2.3 Inorganic carbon system determinations

At each station samples were collected to analyze total alkalinity (TA) and pH. Analyses of the filtered samples were carried out on board. The pH was measured with a glass combined electrode (Methrom) calibrated using the buffer Tris/Tris-HCl (ionic strength 0.7 M) in the total pH scale with an accuracy of ±0.003. TA was measured in 100 ml samples using an automatic potentiometric titrator "Metrohm 794 analyzer", with a combination glass electrode, calibrated following the protocol described by Del Valls and Dickson (1998). TA computation was made applying the Gran Function to the titration curve. The method has an accuracy of ±2 µmol kg^{-1}. In order to check the accuracy of the pH and TA measurements, samples of CO_2 reference material (CRM, distributed by A. G. Dickson from Scripps Institution of Oceanography) were analyzed during the cruises.

Dissolved inorganic carbon was calculated from pH and TA using thermodynamic equations in seawater and the constants described by Mehrbach et al. (1973) refitted by Dickson and Millero (1987) for carbonate and Dickson (1990) for sulphate. The calculated error for DIC was ±2.6 µmol kg^{-1}.

Fugacity of CO_2 measurements were described in detail in Ribas-Ribas et al. (2011b). The continuous data were averaged in the times the ship stopped for stations. The atmospheric $f\mathrm{CO}_2$ data were obtained from the monthly data at Tercerira Island station (Azores, Portugal), taken from National Oceanic and Atmospheric Administration (NOAA/CMDL/CCGG air sampling network) (data available online at: http://esrl.noaa.gov/dmd/dv/ftpdata.html).

2.4 DOC and TDN measurements

Samples were collected in 10 ml pre-combusted ampoules and were filtered through pre-combusted Whatman GF/F filters of 47 mm diameter (0.7 µm nominal pore size). Samples were taken in duplicate, acidified by addition of 85 % H_3PO_4 (pH < 2), sealed and stored in the dark at 4 °C in the laboratory. The Shimadzu instrument used in this study was the commercially available Model TOC-5000 analyzer with quartz combustion column in the vertical position filled with 1.2 % Pt silica pillow. In addition, system performance was verified daily using standards produced by the Hansell Certified Reference Material (CRM) program. Three seawater CRM and three low carbon water (LCW) analyses were performed each analytical day. The nominal values provided by the Hansell Laboratory were 41–44 µM and 33 µM for DOC and total dissolved nitrogen (TDN), respectively. The measured values were 42.5 ± 0.9 µM and 32.8 ± 0.3 µM. LCW values measured were 1.9 ± 1.3 µM (nominal 1–2 µM) and 0.3 ± 0.1 µM (nominal 0 µM) for DOC and TDN, respectively.

2.5 DO, SPM and nutrient measurements

Dissolved oxygen samples were fixed in oceanographic Winkler bottles and stored in darkness for 24 h, as described by Grasshoff et al. (1983), for later analysis by potentiometric titration (Metrohm 670 Titroprocessor).

For the assessment of the Suspended Particulate Matter (SPM) and the Particulate Organic Carbon (POC) 500 ml samples were filtered on board onto precombusted GF/F filters that were immediately frozen at −20 °C. Once at the laboratory, they were dried out in an oven and weighted to calculate total SPM. Filters were completely rinsed of residual salt prior to drying. Subsequently they were ashed at 450 °C in a muffle furnace for 4 h and once again weighted to calculate the inorganic particulates (Loring and Rantala, 1991).

Samples for nutrients (nitrate, silicate and nitrite) were filtered onboard through 0.45 µm Millipore filters, immediately frozen at −20 °C, and analyzed in the laboratory. Nutrients were determined by segmented flow analysis with Alpkem autoanalyzers, following Grasshoff et al. (1983).

2.6 ADCP

Velocity measurements between 4 m and bottom were obtained along the route by the R/V *Mytilus*'s RD Broad Band Instrument at 300 kHz. Raw data were post-processed by CASCADE 6.1 software (LeBot et al., 2011), that includes ship velocity removal, quality flag assignment and data filtering. Orthogonal velocities to the sections were estimated and punctual data extracted at those locations where chemical samples were acquired.

2.7 Flux calculation and estimations of uncertainty

The instantaneous flux across the section of one constituent is computed with velocity and concentrations taken every 2 h and is defined as:

$$F_c = c \cdot u \tag{1}$$

Where c represents the constituent concentration, u is the punctual current velocity. A similar approach has also been used by Goñi et al. (2009).

The sections have been calculated for every sampling taking into account the bathymetry and the tide height. It could be integrated for the day to have the diurnal flux. Then, we extrapolated first to the seasonal flux and then to the annual flux, taking into account the associated uncertainties.

Estimating the transport uncertainties is important, since it conditions the influence of the velocity data on the final results. The uncertainties have two sources: one is due to the instrumental error, and the other is due to the physical environment, i.e. fine-scale currents, for instance, which scaling is assumed to be smaller than a few kilometers. The between-station route is divided into N independent x-meters segments. The velocity standard deviations (std) are calculated between 2 depths for all the segments, representing the contributions of the two uncertainty sources. The velocity uncertainty is then deduced from the vertical and horizontal averages of the std values divided by N. Uncertainties are found between 0.01 and 0.06 $\mathrm{m\,s^{-1}}$ for the whole section. The concentration variables have also associated a vertical and horizontal uncertainty.

3 Results and discussion

3.1 Tide and current velocity

Figure 2 shows the diurnal evolution of surface velocity from transect off the Bay of Cádiz (Fig. 2a) and off the Guadalquivir Estuary (Fig. 2b) in the three different surface stations (Fig. 1) and tidal amplitude in Cádiz and Rota, respectively. Positive velocity values indicate onshore, while negative values represent offshore flux. The general trend was that velocity varied with tidal influence. However, we observed the north station of Guadalquivir had less tidal influence and more coastal current influence, which small onshore velocity during the three seasons.

3.2 Physicochemical measurements during tidal cycle

Figure 3 shows the diurnal evolution of salinity, temperature, fCO_2 and percentage of oxygen saturation (% O_2) from transect off the Bay of Cádiz (Fig. 3a) and off the Guadalquivir Estuary (Fig. 3b) in the three different surface stations (Fig. 1). The general trend was that salinity, temperature, fCO_2 and % O_2 varied with tidal influence. Other cases did not show clearly tidal variations because of biological influence. Litt et al. (2010) also found at some cruises that variability of pCO_2 has tidal influence. They showed this relationship by a significant negative correlation with salinity and high temperature dependence.

Both the Guadalquivir Estuary and the Gulf of Cádiz acted as a source of CO_2 to the atmosphere in early summer and fall (fCO_2 above atmospheric value (fCO_2^{atm} summer = 383 µatm and fCO_2^{atm} fall = 382 µatm) in Fig. 3) while as a sink of CO_2 in winter (fCO_2 below atmospheric value(fCO_2^{atm} winter = 387 µatm) in Fig. 3). Diurnal variability of fCO_2 could have a potentially important implication on the estimate of air–sea CO_2 fluxes. The Bay of Cádiz, during the whole tidal cycle sampling, behaves as a source (June and November) or as a sink (February) (Fig. 3a). In contrast, source/sink behavior was fluctuating in the same tidal cycle in the Guadalquivir Estuary during June and

November, depending on (Fig. 3b). This fact highlighted the dynamic of this coastal area and emphasized the importance of incresing the sampling frequency and/or the presence of mooring buoys with physicohemical sensors. In an annual scale, the global behaviour was a net source in agreement with Chen and Borges (2009) who distinguished between inner ecosystems as a source and continental shelf as a sink.

Figure 4 shows the diurnal evolution of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), dissolved inorganic carbon (DIC) and pH from transect off the Bay of Cádiz (Fig. 4a) and off the Guadalquivir Estuary (Fig. 4b) in the three different surface stations (Fig. 1). Figure 5 shows the diurnal evolution of nutrients (phosphate (PO_4), dissolved inorganic nitrogen (DIN) and silicate (SiO_2)) and suspended particulate matter, total dissolved nitrogen, dissolved inorganic carbon and pH from transect off the Bay of Cádiz (Fig. 5a) and off the Guadalquivir Estuary (Fig. 5b) in the three different surface stations (Fig. 1). In these plots, tidal influence is not as evident as for hydrographic parameters, mainly due to biological activity and daily (light/dark) variability.

3.3 Seasonal and annual fluxes

Figure 6 illustrates the trends in the instantaneous fluxes of dissolved inorganic carbon (F_{DIC}), at the four sampling position in each transect for the three different sampling periods. As was the case for current speed, positive F values indicate onshore, while negative values represent offshore flux. Several important features in the diurnal flux data are evident in Fig. 6. First, there was a marked tidal signal in the fluxes of all constituents at all stations except the north of the Guadalquivir Estuary, which normally have an offshore behaviour. Second, the fluxes were normally higher in the south station in the Guadalquivir Estuary and in the north station in the Bay of Cádiz. Finally, in both transects, there were no significant difference between the surface and the depth sample (the middle station off the Guadalquivir Estuary and the southern off the Bay of Cádiz). A similar trend was evident with other constituent fluxes (plots not shown).

Figure 7 is the absolute magnitude of instantaneous fluxes of non-conservative variable (in this case [F_{TDN}]) vs. those of salt, a predominantly conservative tracer. This plot is a way to illustrate the landward vs. seaward dominance in the fluxes. A deviation from linearity at all three seasons was observed. These deviations could be greater during positive salt flux, which means that excess TDN is introduced into the system from local sources. In contrast, greater deviations during negative salt fluxes indicates that the system export TDN to the adjacent coastal water. In general, the Guadalquivir Estuary has a greater deviation from conservative behaviour during negative salt fluxes while the Bay of Cádiz has greater deviation during positive salt fluxes. However, seasonal differences also exist. Thus, during June both systems have seaward fluxes while in February both systems have landward fluxes (Fig. 7, Table 2). Landward fluxes have been observed in the Winyah Bay by Goñi et al. (2009).

The Guadalquivir Estuary export DIC in the early-summer and fall at a rate of $-1.5\,\mathrm{Gmol\,d^{-1}}$ and $-4.1\,\mathrm{Gmol\,d^{-1}}$, respectively (Fig. 6, Table 2). In winter, the estuary imported DIC at a rate of $0.5\,\mathrm{Gmol\,d^{-1}}$. This value was unexpected and possible due to the not finished tidal cycle. The Bay of Cádiz had a different behaviour, acting as an imported in the early summer and as an exported during fall and winter (-1.0, 3.7 and $1.8\,\mathrm{Gmol\,d^{-1}}$, respectively). The same behaviour was observed for the other constituents (Table 2). The Guadalquivir Estuary has been identified as a net source of DIC, DOC, TDN and $f\mathrm{CO_2}$ (Ribas-Ribas et al., 2011a,b,c). This transport was mainly driven by tidal influence and, in the case of the Guadalquivir Estuary during fall and winter, by river discharge.

4 Conclusions

The Bay of Cádiz imported 0.1 Gmol of $\mathrm{PO_4}$, 3.2 Gmol of $\mathrm{SiO_2}$, 1.5 Gmol of DIN, 2.4 Gmol of TDN, 32.7 Gmol of DOC and 562.0 Gmol of DIC, in an annual scale while the Guadalquivir Estuary exported 0.2, 3.2, 1.5, 3.2, 31.4, 603.9 Gmol of $\mathrm{PO_4}$, $\mathrm{SiO_2}$, DIN, TDN, DOC and DIC, respectively to the adjacent coastal area. During June, both systems were exporting components to the adjacent continental shelf of the Gulf of Cádiz. Daily variability between CO_2 source/sink behaviour has been observed in the Guadalquivir Estuary in June and November. These highlight coastal zones as highly dynamic areas and further studies are needed to better understand these systems.

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Table 1. Transects in the Bay of Cádiz (BC) and the Guadalquivir Estuary (GL), date when transects were done and hours of the tidal cycle covered. In some cases (*), due to bad weather conditions, the 24 h cycle could not be completed.

Transect	Date	Hours
1BC	21–22 Jun 2006	24
1GL	28–29 Jun 2006	24
2BC	23–24 Nov 2006	16*
2GL	29–30 Nov 2006	24
3BC	04–05 Feb 2007	24
3GL	07 Feb 2007	10*

Table 2. Fluxes of phosphate (F_{PO_4}), silicate (F_{SiO_2}), dissolved inorganic carbon (F_{DIN}), total dissolved nitrogen (F_{TDN}), dissolved organic carbon (F_{DOC}) and dissolved inorganic carbon (F_{DIC}) during the three sampling periods in the two different transect (Bay of Cádiz (BC) and Guadalquivir Estuary (GL)). Extrapolate annual fluxes for every component.

	F_{PO_4}		F_{SiO_2}		F_{DIN}		F_{TDN}		F_{DOC}		F_{DIC}	
(Mmol d^{-1})	BC	GL	BC	GL	BC	GL	BC	GL	BC	GL	BC	GL
Jun 06	−0.0	−0.1	−0.6	−0.2	−0.2	−0.6	−5.5	−3.3	−83.4	−61.6	−955.7	−1463.6
Nov 06	0.8*	−0.8	8.6*	−16.0	9.9*	−19.3	15.9*	−33.4	280.1*	−226.5	3747.6*	−4055.2
Feb 07	0.	*n*	18.4	*n*	2.6	*n*	9.7	10.4*	72.0	29.9*	1827.7	555.2*
Annual Flux (Gmol yr^{-1})	0.1	−0.2	3.2	−3.0	1.5	−3.6	2.4	−3.2	32.7	−31.4	562.0	−603.9

* Means that the tidal cycle was not closed and the transport could be over/underestimated.

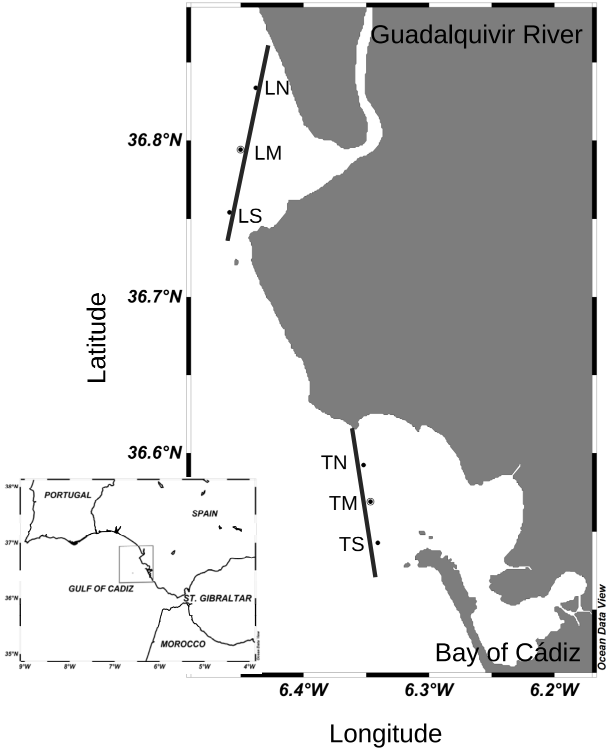

Fig. 1. Map of the north eastern shelf of the Gulf of Cádiz showing the location of sampled stations. Lines represent transects where currents and physicochemical variables were measured.

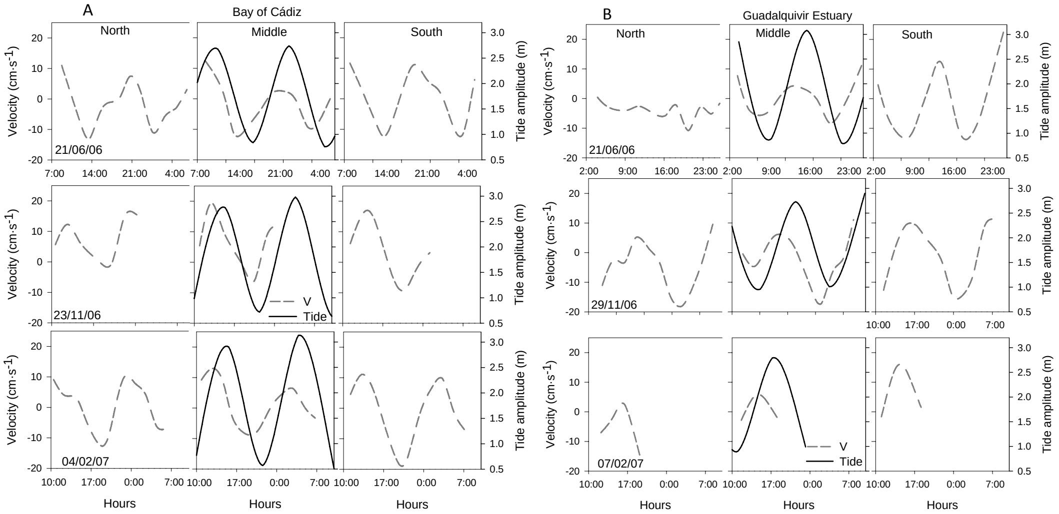

Fig. 2. One tidal cycle of surface velocity (grey dashed line) and tide amplitude (black solid line) from the transect off the Bay of Cádiz **(A)** and Guadalquivir Estuary **(B)** in the three different stations (Fig. 1). Fall cycle in the Bay of Cádiz and winter cycle in the Guadalquivir Estuary were not closed due to bad weather conditions.

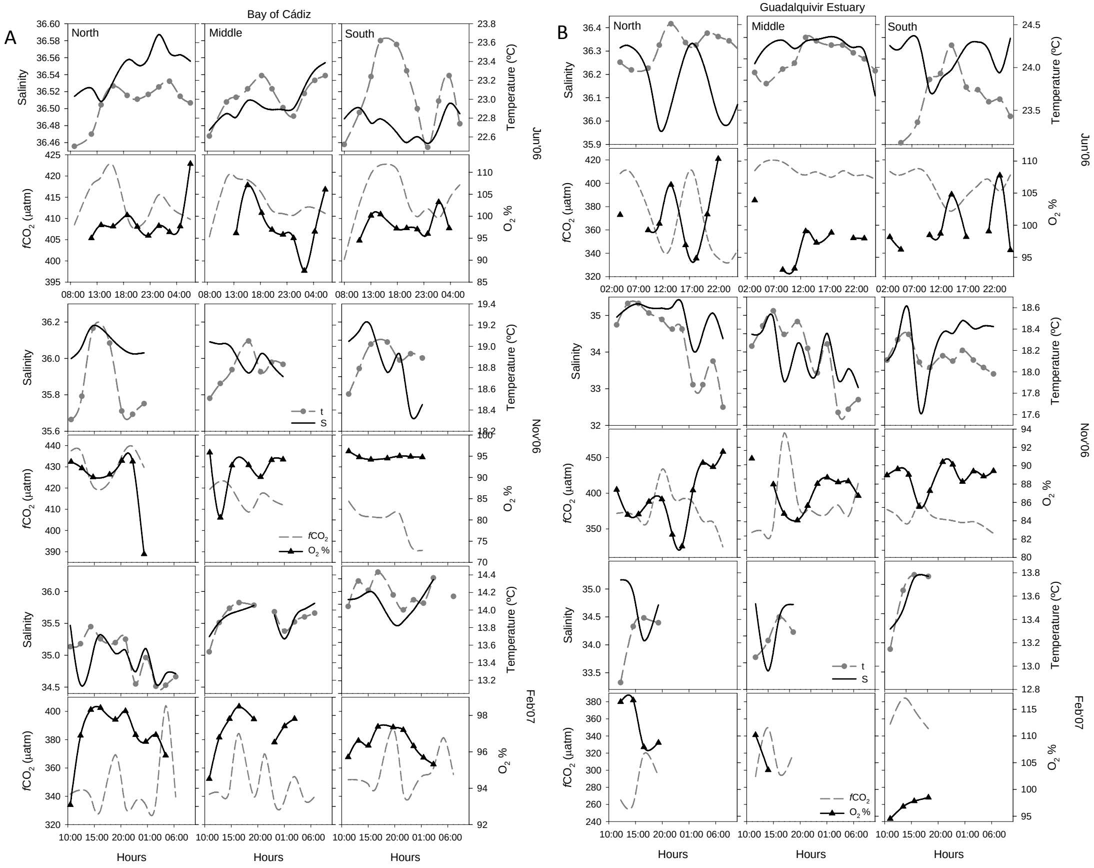

Fig. 3. Daily variations in surface seawater salinity (black solid line), temperature (grey dashed line with circle), fCO_2 (grey dashed line) and percentage of oxygen saturation (% O_2) (black solid line with triangles) from the transect off the Bay of Cádiz **(A)** and Guadalquivir Estuary **(B)** in the three different stations (Fig. 1).

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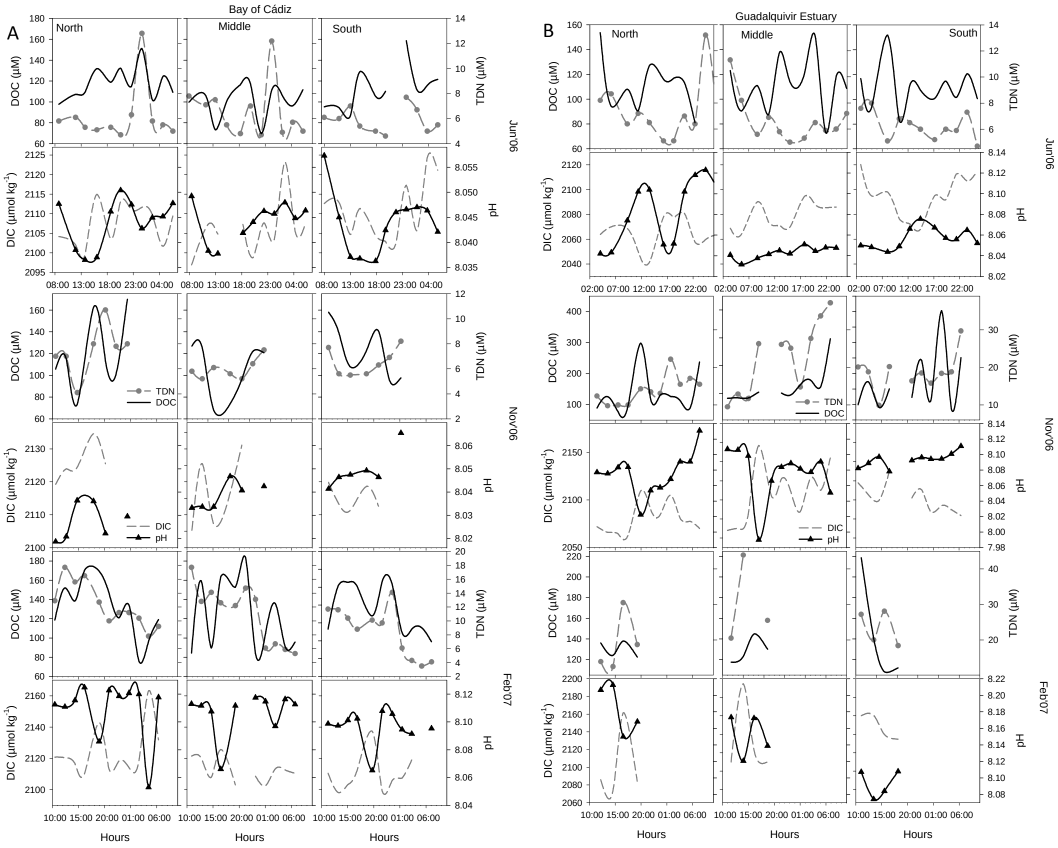

Fig. 4. Daily variations in surface seawater dissolved organic carbon (DOC) (black solid line), total dissolved nitrogen (TDN) (grey dashed line with circle), dissolved inorganic carbon (DIC) (grey dashed line) and pH (black solid line with triangles) from the transect off the Bay of Cádiz **(A)** and Guadalquivir Estuary **(B)** in the three different stations (Fig. 1).

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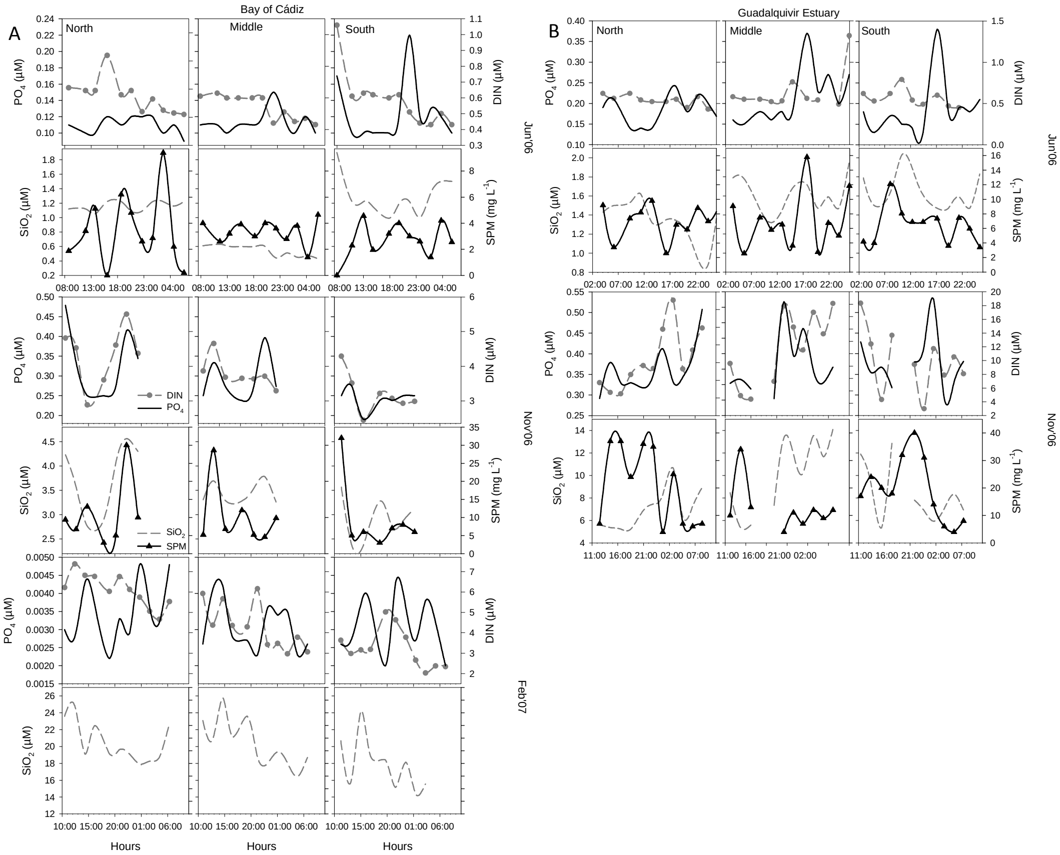

Fig. 5. Daily variations in surface seawater phosphate (PO_4) (black solid line), dissolved inorganic nitrogen (DIN) (grey dashed line with circle), silicate (SiO_2) (grey dashed line) and suspended particulate matter (black solid line with triangles) from the transect off the Bay of Cádiz **(A)** and Guadalquivir Estuary **(B)** in the three different stations (Fig. 1).

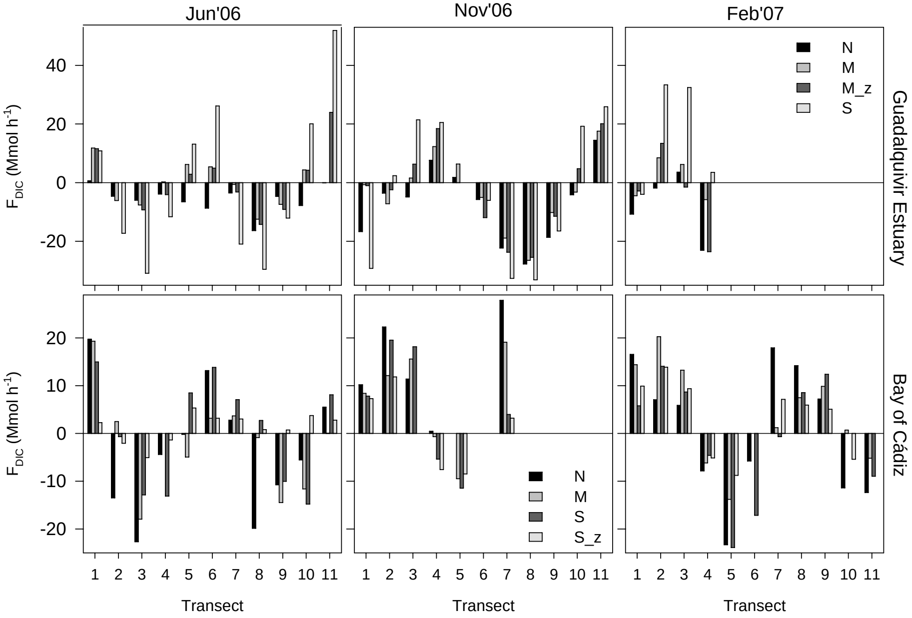

Fig. 6. Daily variations in dissolved inorganic carbon fluxes (F_{DIC}) during June, November and February in the Guadalquivir Estuary (upper panels) and the Bay of Cádiz (lower panels) in the different sampling stations.

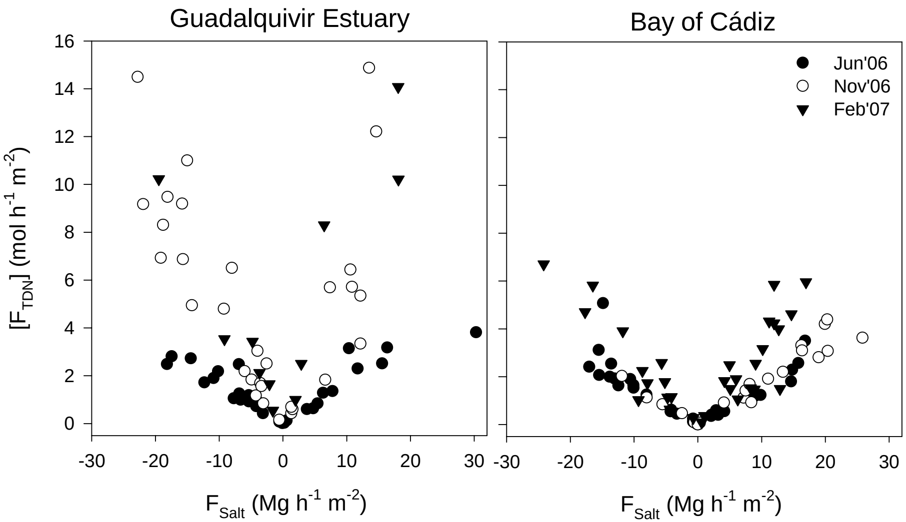

Fig. 7. Instantaneous salinity fluxes (F_{Salt}) versus the absolute magnitude of instantaneous total dissolved nitrogen fluxes (F_{TDN}) determined in the two study areas (Guadalquivir Estuary and the Bay of Cádiz) in the three different sampling periods: June 2006 (black circles), November 2006 (white circles) and February 2007 (black triangles).