

BENTHIC NUTRIENT RECYCLING IN THE NORTHEASTERN SHELF OF THE GULF  
OF CÁDIZ (SW IBERIAN PENINSULA)

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1 ABSTRACT

2 Benthic fluxes of nutrients and dissolved nitrous oxide (N<sub>2</sub>O) were determined by benthic  
3 chamber incubations in two regions on the northeastern near-shore continental shelf of the  
4 Gulf of Cádiz (depth range: 8 - 34 m), one off the Guadalquivir River mouth and the other in  
5 the Bay of Cádiz and its neighboring shelf. A total of 25 *in situ* benthic chamber incubations  
6 were performed during June 2006, November 2006 and February 2007 in order to investigate  
7 the main factors controlling benthic nutrient recycling and its significance in the study site.  
8 Nutrient benthic fluxes varied between -0.9-1.0 mmol NO<sub>3</sub><sup>-</sup> m<sup>-2</sup> d<sup>-1</sup>, -0.3-0.3 mmol NO<sub>2</sub><sup>-</sup> m<sup>-2</sup> d<sup>-1</sup>,  
9 <sup>1</sup>, -1.2-3.5 mmol NH<sub>4</sub><sup>+</sup> m<sup>-2</sup> d<sup>-1</sup>, -0.04-0.22 mmol HPO<sub>4</sub><sup>2-</sup> m<sup>-2</sup> d<sup>-1</sup> and 0.2-2.9 mmol Si(OH)<sub>4</sub> m<sup>-2</sup>  
10 d<sup>-1</sup>. Benthic fluxes of N<sub>2</sub>O, ranging from -1.2 to 10.4 μmol N-N<sub>2</sub>O m<sup>-2</sup> d<sup>-1</sup>, accounted on  
11 average for less than 1% of total inorganic nitrogen fluxes. The regeneration of NH<sub>4</sub><sup>+</sup> and  
12 Si(OH)<sub>4</sub> was mainly influenced by organic carbon oxidation rates and bulk organic carbon in  
13 surface sediments, whereas HPO<sub>4</sub><sup>2-</sup> regeneration was mostly influenced by bottom water  
14 oxygen concentration and water depth. Denitrification was estimated to account for between 9  
15 and 13% of organic matter remineralization and for a loss of between 57 and 67% of  
16 potentially recyclable nitrogen. Overall, benthic remineralization was estimated to account  
17 for about 47% of overlying primary production, supplying about 15 and 12% of the  
18 phytoplankton N and P requirements, respectively.

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20 Keywords: benthic fluxes, nutrient regeneration, denitrification, nitrous oxide, macrofauna,  
21 coastal sediments, Gulf of Cádiz.

## 1 INTRODUCTION

2 Continental shelf sediments are important sites for organic matter remineralization and  
3 nutrient recycling to the water column and, therefore, play a key role in controlling the  
4 biogeochemistry of these systems (e.g. Berelson et al. 1998, 2003, Hopkinson et al. 2001). In  
5 spite of their modest surface area, continental shelves are biogeochemically very active sites,  
6 receive large amounts of dissolved and particulate terrestrial matter, and serve as a connection  
7 between the continents and the open ocean. About 25% of total oceanic primary production  
8 occurs in the continental shelves (Wollast 2002). Due to their shallowness, a large proportion  
9 of the autochthonous and allochthonous organic matter reaches the sediments, where it suffers  
10 a vertical sequence of fermentative and respiratory microbial processes that progressively use  
11 the oxidants that yield the greatest free energy ( $O_2$ ,  $Mn^{4+}$ ,  $NO_3^-$ ,  $Fe^{3+}$ ,  $SO_4^-$ ,  $HCO_3^-$ ). The  
12 presence of benthic fauna deeply impacts the spatial distribution of microbial biogeochemical  
13 zones, altering the physical and chemical properties of marine sediments and enhancing  
14 benthic remineralization processes (Aller & Aller 1998, Mortimer et al. 1999, Wenzhofer &  
15 Glud 2004). Organic matter degradation in coastal sediments and the associated release of  
16 nutrients often provide a considerable fraction of phosphorus and nitrogen requirements for  
17 phytoplankton and can stimulate pelagic primary production (Nixon 1981, Cowan & Boynton  
18 1996, Herbert 1999, Gibbs et al. 2005).

19 Nitrogen cycling is especially critical in marine sediments due to denitrification, the anaerobic  
20 microbial reduction of nitrate ( $NO_3^-$ ) to nitrous oxide ( $N_2O$ ) and dinitrogen gas ( $N_2$ ). More  
21 than 50% of nitrogen inputs to the ocean may be removed by benthic denitrification in  
22 continental margins (Christensen 1994). Nitrate for denitrification can either be supplied  
23 directly from the overlying water column or through sedimentary aerobic nitrification of  
24 ammonium (coupled nitrification/denitrification) (Seitzinger 1988).  $N_2O$ , a potent  
25 atmospheric greenhouse gas (Rodhe 1990) which is also involved in the depletion of

1 stratospheric ozone (Cruzten & Schmailzl 1983), is mainly produced in aquatic environments  
2 as an obligate intermediate during denitrification and as a by-product in the first step of  
3 nitrification. Several authors have pointed out the importance of sediments as a major source  
4 of N<sub>2</sub>O in coastal systems (Robinson et al. 1998, Seitzinger et al. 2000, Bange 2006). About  
5 13% of global N<sub>2</sub>O emission to the atmosphere occurs in the oceans (Khalil & Ramussen  
6 1992), of which 35% to 60% is attributed to estuaries and near-shore coastal environments.  
7 This work reports the results derived from *in situ* benthic chamber incubations performed in  
8 near-shore sediments of the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula),  
9 during three periods of the year, corresponding to summer, autumn and winter. Documented  
10 nutrient benthic flux measurements in this region have only been performed in shallower  
11 littoral sediments such as the inner Bay of Cádiz (Gómez-Parra & Forja 1993, Forja et al.  
12 1994, Ferrón et al. 2009) where nutrient benthic fluxes were in the range of: 3-24 mmol NH<sub>4</sub><sup>+</sup>  
13 m<sup>-2</sup>d<sup>-1</sup>, 0.2-7.8 mmol HPO<sub>4</sub><sup>2-</sup> m<sup>-2</sup>d<sup>-1</sup> and 1-28 mmol Si(OH)<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>. The main goals of this  
14 research are to analyze the main factors controlling benthic organic matter decomposition and  
15 nutrient recycling in continental shelf sediments of the Gulf of Cádiz and to examine the  
16 significance of benthic nutrient regeneration in this system.

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## 1 MATERIAL AND METHODS

### 2 **Study site**

3 The study was performed in the near-shore northeastern shelf of the Gulf of Cádiz (SW  
4 Iberian Peninsula), which is a wide basin between the Iberian Peninsula and the African  
5 continent where the North Atlantic Ocean and the Mediterranean Sea meet through the Strait  
6 of Gibraltar (Fig. 1). In particular, the northeastern shelf of the gulf receives freshwater inputs  
7 from several rivers (such as Guadiana, Guadalquivir, Tinto and Odiel), and its circulation is  
8 mainly controlled by the North Atlantic Surface Water (NASW), which flows towards the  
9 east and southeast to the Strait of Gibraltar, as well as by an intermittent counter current  
10 system which seems to be closely linked to the wind regime (Lobo et al. 2004).

11 Phytoplankton distribution is tightly coupled to meteorological and hydrodynamic conditions  
12 in this sector of the gulf, which presents the highest primary production within the basin  
13 (Navarro & Ruiz 2006). Predominance of westerly winds favors the generation of upwelling  
14 events and therefore an increase in primary production, whereas easterlies lead to a decrease  
15 in phytoplankton (Navarro & Ruiz 2006).

16 Nine sites were selected in near-shore waters close to the mouth of the Guadalquivir River  
17 (GL1-GL4) and the Bay of Cádiz (BC1-BC5) (Fig. 1). The Guadalquivir River is the main  
18 fluvial source draining into the Gulf of Cádiz, with an annual water discharge of  $160 \text{ m}^3 \text{ s}^{-1}$   
19 (Van Geen et al. 1977). The river is 560 km long and its drainage basin covers an area of  
20 approximately  $58000 \text{ km}^2$ . The estuary is characterized by an irregular river discharge, which  
21 is relatively low for most of the year and considerably higher during the rainy season  
22 (February–March) (de la Paz et al. 2007). The hydrodynamics in the estuary is mainly  
23 controlled by the tidal regime. On the other hand, the Bay of Cádiz is a shallow environment  
24 divided into two basins: the southern and shallower inner bay, and the northern and deeper  
25 external bay ( $88 \text{ km}^2$ ), which is connected to the gulf through a 13.5 km-long mouth. The bay

1 is surrounded by an extensive salt marsh area and several towns and cities, with a total  
2 population of about 700000 inhabitants. The 157-km long Guadalete River, which receives  
3 the effluent of the wastewater treatment plant of Jerez de la Frontera (200000 inhabitants) and  
4 the drainage from agricultural cultivations, flows into the external bay. Nearby, a shallow  
5 tidal creek (Río San Pedro), affected by the discharges from surrounding aquaculture  
6 installations (Tovar et al. 2000), also flows into the bay.

7 The data reported in this work were collected during 3 cruises on board R/V *Mytilus*, covering  
8 three seasonal periods: June 2006, November 2006 and February 2007. At each site, CTD  
9 casts were performed at the beginning of the chamber incubations in order to obtain the  
10 vertical profiles of temperature, salinity, pressure, dissolved oxygen and fluorescence, by  
11 means of a Seabird CTD probe coupled to a Seatech fluorometer and a Seabird 43 (SBE-43)  
12 dissolved oxygen sensor. Surface and bottom waters were sampled for analysis of nutrients,  
13 chlorophyll a and nitrous oxide. The surface sediment was sampled at the beginning of each  
14 incubation by means of a box-corer (15x10 cm) to measure total C and N composition and  
15 organic carbon content in the top centimeter, and with a Van Veen drag to measure grain size  
16 distribution.

### 17 ***In situ* benthic flux measurements**

18 The fluxes of nutrients and nitrous oxide were measured by *in situ* benthic chamber  
19 incubations, using an opaque cylindrical stirred chamber (0.8 m inner diameter, 0.28 m  
20 height) that covers 0.50 m<sup>2</sup> of sea-bottom and approximately 140 L of overlying water (Ferrón  
21 et al. 2008). Stirring of the water phase is achieved by means of three centrifugal pumps.  
22 Inside the chamber, sensors for temperature (SBE-39), pH (SBE-18), oxygen (SBE-43) and  
23 turbidity (Seapoint Turbidity Meter) give a continuous recording of these variables during the  
24 incubations. Real time monitoring and data acquisition is achieved by means of a two-way  
25 radio communication system (SATELLINE-3AS, SATEL). A multiple water sampler

1 provided with 12 syringes (KC-Denmark) collects discrete 50 mL samples at pre-set time  
2 intervals. The chamber was slowly lowered to the bottom from the ship with a crane. The  
3 incubations were performed during the day and lasted for approximately 8 hours. Nutrient  
4 samples were filtered (Polycarbonate, 0.45  $\mu\text{m}$ ) and kept frozen until subsequent analysis.  
5 Samples for  $\text{N}_2\text{O}$  measurements were carefully drawn in 25 mL air-tight glass bottles,  
6 preserved with saturated mercuric chloride and sealed with Apiezon® grease and stored in the  
7 dark until analysis in the laboratory.

## 8 **Analytical methods**

9 Nitrate, nitrite, ammonium, phosphate and silicate were determined by segmented flow  
10 analysis with Alpkem autoanalyzers following Hansen & Grassoff (1983), with some  
11 improvements (Mouriño & Fraga 1985). The storage of silicate samples by freezing is  
12 satisfactory for samples with a silicate content below 50  $\mu\text{mol/L}$  (Koroleff 1983). Silicon  
13 tends to polymerize when stored frozen and hence samples must be allowed to stand for at  
14 least 3 hours after thawing, and were shaken vigorously before analysis. The analytical errors  
15 were  $\pm 0.05 \mu\text{mol kg}^{-1}$  for nitrate, ammonium and silicate,  $\pm 0.02 \mu\text{mol kg}^{-1}$  for nitrite and  $\pm$   
16  $0.01 \mu\text{mol kg}^{-1}$  for phosphate.

17 Dissolved  $\text{N}_2\text{O}$  concentrations were determined with a gas chromatograph (Varian CX 3600).  
18 In-syringe head space equilibration was used to extract the dissolved gas from the water  
19 samples. The temperature of equilibration ( $\pm 0.1 \text{ }^\circ\text{C}$ ) was registered by a thermometer (P500  
20 Dostman electronic). A mixture of  $\text{Ar}/\text{CH}_4$  (95% / 5%) was used as carrier gas ( $30 \text{ mL min}^{-1}$ ),  
21 gases were separated by a 2.5 x 1/8-in stainless steel Porapak N column (80/10), and  $\text{N}_2\text{O}$   
22 was detected by a  $^{63}\text{Ni}$  Electron Capture Detector (ECD), operated at  $300^\circ\text{C}$ . The detector was  
23 calibrated using three standard gas mixtures distributed and certified by Air Liquide (France),  
24 with certified  $\text{N}_2\text{O}$  concentrations of 0.264, 0.840 and 1.55 ppmv. The precision of the  
25 method, including the equilibration step was 6.6%, expressed as the variation coefficient of

1 based on replicate analysis ( $n = 25$ ) of a seawater sample saturated with  $N_2O$ . The  
2 concentration of  $N_2O$  in the water samples was calculated from the concentration measured in  
3 the head space, using Bunsen solubility equations given by Weiss & Price (1980).  
4 Chlorophyll a concentrations in water column samples were measured by fluorimetry, using  
5 90% acetone extracts at dark after filtration through Whatman GF/F filters ( $0.45 \mu m$ ).  
6 Total C and N were measured in dried sediment (first cm) on a CHNS-932-LECO Element  
7 Analyzer after  $Cr_2O_3$  and  $AgCO_3O_4$  catalyzed oxidation and segregation on a Haysep-Q-  
8 column. The organic C content in surface sediments was determined by chemical oxidation  
9 (Gaudette et al. 1974, El Rayis 1985) with a standard deviation of  $\pm 0.25\%$ .  
10 Grain size distribution in surface sediments was measured by sieving, except for the fraction  
11 smaller than  $63 \mu m$  which was determined with a laser diffraction analyzer. Analysis of grain  
12 size statistics was carried out using the software GRADISTAT (Blott & Pye 2001).

### 13 **Macrofauna**

14 During the survey in November 2006, macrofaunal samples were collected at each station  
15 with a Van Veen grab (sampling area:  $0.1 m^2$ ), and sieved over a 1 mm mesh-sized sieve.  
16 Recovered material was preserved in 4% buffered formaldehyde. The preserved samples were  
17 sorted and identified. Abundance of each taxonomic group was recorded and wet weight of  
18 each species from each station was calculated. Wet weights were transformed to ash-free dry  
19 weights (AFDW) using published conversion factors for major taxa (Ricciardi & Bourget  
20 1998). Trophic guilds of the sampled macrofaunal species were determined from Parada  
21 (2005), based on Pearson (1971), Fauchald & Jumars (1979) and other different works.

### 22 **Benthic flux and rate calculations**

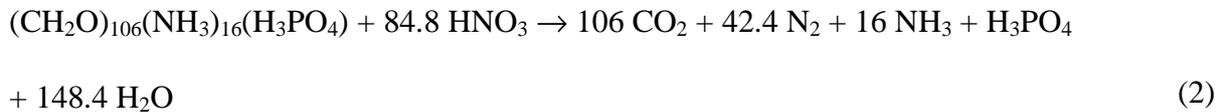
23 Fluxes across the sediment-water interface were calculated as the product of the chamber  
24 height and the slope of the linear regression of the time series concentration evolution. Errors  
25 in benthic fluxes were derived from the error of the slope resulting from the data fit.

1 *Denitrification rates*

2 Total denitrification rates ( $F_{\text{denit}}$ ) were estimated, assuming that nitrate reduction is the  
3 dominant  $\text{N}_2$ -producing process in the sediments, following the equation:

$$F_{\text{denit}} = (1/\text{C:N}) * C_{\text{ox}} - F_{\text{IN}} \quad (1)$$

4 where  $C_{\text{ox}}$  is the carbon mineralization rate, which were taken from a parallel study (Ferrón et  
5 al. submitted) and  $F_{\text{IN}}$  is the measured flux of dissolved inorganic nitrogen ( $\text{NO}_3^- + \text{NO}_2^- +$   
6  $\text{NH}_4^+$ ). Associated carbon mineralized via denitrification was estimated from the  
7 stoichiometry of the reaction (Froelich et al. 1979):



8 *Nitrification rates*

9 Nitrification rates ( $F_{\text{nit}}$ ) were calculated as the difference between total organic N mineralized  
10 and ammonium flux ( $F_{\text{NH}_4}$ ) (Lehmann et al. 2004):

$$F_{\text{nit}} = (1/\text{C:N}) * C_{\text{ox}} - F_{\text{NH}_4} \quad (3)$$

11 The first term of equations (1) and (3) represents the total organic N mineralized and depends  
12 on the C/N atomic ratio of organic matter undergoing diagenesis. In the study site, the organic  
13 matter deposited into the sediments is likely influenced by the supplies of terrestrial carbon  
14 discharged by the Guadalquivir and Guadalete rivers, as well as by autochthonous  
15 phytoplankton-derived material. Therefore, the C/N ratio of degrading organic matter is  
16 expected to range from the Redfield ratio for phytoplankton (C/N = 6.6) to the C/N ratio  
17 measured in the top centimeter of sediment. Consequently, to delimit the upper and lower  
18 limits of denitrification and nitrification rates, these were calculated assuming both Redfield  
19 and sediment C/N ratios for organic matter.

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1 *P recycling efficiency*

2 P recycling efficiency was calculated as the percentage of measured phosphate fluxes ( $F_{PO_4}$ )  
3 relative to the expected  $F_{PO_4}$  from organic carbon remineralization assuming Redfield  
4 stoichiometry, by applying the expression:

$$\% \text{ P recycling} = 100 * [F_{PO_4} / (C_{ox} * 1 / C:P)]$$

In this case, calculations were only based on Redfield stoichiometry ratio (C:P =  
106:1), as the sediment C/P ratio was not available. Therefore, these estimates are likely  
a lower limit for P recycling efficiency. (4)

5 **Statistical analysis**

6 Seasonal and spatial (between GL and BC sites) differences of sediment properties and  
7 benthic fluxes were analyzed by using one-way ANOVA followed by Bonferroni post-hoc  
8 test (Statgraphics Plus 5.1). The threshold value for statistical difference was assumed to be p  
9 < 0.05.

10 Relationship between sediment and bottom water properties and sediments were assessed  
11 using Principal Components Analysis (PCA) (Statgraphics Plus 5.1).

12

## 1 RESULTS

### 2 **Water column characteristics**

3 Water temperature varied seasonally, presenting highest temperatures in the summer and  
4 lowest in the winter (Fig. 2). Temperature differences between surface and bottom waters  
5 were mainly observed at GL sites during the summer. During autumn and winter, salinity  
6 values in surface waters were generally lower than in bottom waters, due to the influence of  
7 terrestrial freshwater inputs. Bottom water oxygen concentrations ranged from 163 to 248  
8  $\mu\text{M}$ , corresponding to atmospheric saturations of 62% and 99%, respectively. Oxygen  
9 concentrations were significantly lower in the summer than in the winter ( $p < 0.05$ ). Water  
10 column nutrient concentrations (only nitrate shown) were significantly lower for the summer  
11 than the autumn and winter periods ( $p < 0.01$ ). Whereas phosphate concentrations were in  
12 most cases above  $0.05 \mu\text{M}$ , the concentration of nitrate was, during the summer and mostly in  
13 surface waters, often below  $0.5 \mu\text{M}$ , which is considered limiting to phytoplankton growth  
14 (Fasham et al. 1990). Sea surface concentrations of nitrate, nitrite, phosphate and silicate were  
15 directly influenced by freshwater supply, as a negative linear relationship with salinity pointed  
16 out ( $r^2 = 0.80$  for  $\text{NO}_3^- + \text{NO}_2^-$ ,  $r^2 = 0.61$  for  $\text{PO}_4^-$ , and  $r^2 = 0.71$  for  $\text{Si}(\text{OH})_4$ ). Nitrous oxide  
17 concentrations were significantly lower during the winter compared to autumn and summer ( $p$   
18  $< 0.01$ ). Water column was in all cases  $\text{N}_2\text{O}$  oversaturated with respect to atmosphere, with  
19 saturations ranging from 220-340%, 230-290% and 120-155% during summer, autumn and  
20 winter respectively.

### 21 **Sediment characteristics**

22 Sediment from GL stations was characterized as mud (GL4, GL2 and GL3) and sandy mud  
23 (GL1), with a mud:sand ratio higher than 8:1 and negligible gravel content. The BC sites  
24 showed a higher fraction of sand. Sediments at BC1 and BC3 were characterized as muddy  
25 sands with a sand:mud ratio close to 9:1, whereas BC2, BC4 and BC5 were muddy sands with

1 similar proportions of sand and mud but characterized by different fractions of gravel (1% in  
2 BC2 and 5% in BC4 and BC5). Coarse material was mostly calcareous shell fragments.  
3 Average organic carbon for each site ranged from 0.25 to 1.18% and was significantly higher  
4 at GL sites than at BC sites ( $p < 0.01$ ) (Table 1). Sediment nitrogen contents ranged from  
5 0.03% to 0.18%, and also showed significantly lower values ( $p < 0.01$ ) at BC stations than at  
6 GL stations. The C:N molar ratios in surface sediments ranged from 7.0 to 9.4 and were not  
7 significantly different in GL and BC sites.

## 8 **Macrofauna**

9 A total of 97 benthic macrofaunal taxa were identified in the study area in November 2006  
10 (see Appendix I). Total macrofaunal abundances and biomass ranged from 660 to 2570  
11 individuals  $m^{-2}$ , and from 0.4 to 6.9  $g\ m^{-2}$ , respectively. Polychaeta was the dominant class  
12 and accounted in all sites for more than 45% of total biomass, with the exception of BC2 and  
13 BC3 (Fig. 3a). The polychaetes population was mainly dominated by small-size opportunistic  
14 polychaetes belonging to the families Lumbrineridae, Spionidae, Paraonidae, Capitellidae,  
15 Magelonidae and *Sternaspis scutata*, or the large-size and active irrigating polychaete climax  
16 species such as *Maldane glebifex* or *Glycera unicornis* in BC4 and BC5. Molluscs were the  
17 next dominant macrofaunal class in most sites, with biomass ranging from 0.04 to 1.28  $g\ m^{-2}$ .  
18 Surface deposit feeders were the dominant macrofaunal trophic group in terms of abundance,  
19 with the exceptions of GL1 and GL4 (Fig. 3b). In most of the stations, the dominance was  
20 well distributed among different groups except for sites GL3 and BC5 and BC2 and BC4. In  
21 terms of total biomass, carnivores accounted for more than 60% of total biomass in GL3 and  
22 BC5, mainly as a result of the presence of the nemertean *Cerebratulus* sp and to the  
23 burrowing polychaete *Glycera unicornis*, respectively. On the other hand, at sites BC2 and  
24 BC4, surface deposit feeders dominated due to the presence of the urchin *Echinocardium*  
25 *cordatum* at BC2, and to the tube-dwelling of the family Maldanidae at BC4.

## 1 **Benthic fluxes**

2 Nitrate fluxes ranged from -0.9 to 1.0 mmol m<sup>-2</sup> d<sup>-1</sup> whereas nitrite fluxes varied between -  
3 0.25 and 0.26 mmol m<sup>-2</sup> d<sup>-1</sup> (Table 2). Twice in November 2006 and three times in February  
4 2007, nitrate and nitrite fluxes were directed in opposite directions. Ammonium fluxes,  
5 ranging from -0.33 to 3.10 mmol m<sup>-2</sup> d<sup>-1</sup>, were always positive except for three occasions in  
6 BC sites. Benthic fluxes of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> did not differ significantly between BC and  
7 GL regions or among seasons. Seasonally averaged NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> fluxes at each site showed  
8 a significant linear correlation with the organic carbon content of surface sediments, which  
9 was negative for the former (r<sup>2</sup> = 0.47) and positive for the latter (r<sup>2</sup> = 0.74). In contrast to  
10 nitrate fluxes, seasonally averaged NH<sub>4</sub><sup>+</sup> fluxes also correlated with average carbon oxidation  
11 rates for each site (r<sup>2</sup> = 0.72).

12 Nitrous oxide fluxes were very variable and directed out of the sediments, except for one  
13 deployment in June 2006 at BC3, which also coincided with a sediment uptake of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>  
14 and NH<sub>4</sub><sup>+</sup>. Nitrous oxide fluxes ranged from -1.2 to 10.4 μmol N-N<sub>2</sub>O m<sup>-2</sup> d<sup>-1</sup> and accounted  
15 on average for less than 1% of benthic inorganic nitrogen fluxes (NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>). The  
16 ratio of N<sub>2</sub>O fluxes to total inorganic nitrogen fluxes varied significantly between the three  
17 sampled seasons (p < 0.05), being highest in June 2006 and lowest in February 2007. Nitrous  
18 oxide fluxes were significantly smaller in February 2007 than in November 2006 (p < 0.01),  
19 and no significant differences were observed between GL and BC sites.

20 Phosphate was normally released to the water column with the exception of a few cases in  
21 which it was taken up by the sediment. Benthic phosphate fluxes, ranging from -0.04 to 0.22  
22 mmol m<sup>-2</sup> d<sup>-1</sup>, were variable and did not show any clear spatial or temporal trends.

23 Silicate fluxes ranged from 0.21 to 2.87 mmol m<sup>-2</sup> d<sup>-1</sup>, did not differ significantly between  
24 BC and GL sites or among seasons. Seasonally averaged silicate fluxes were linearly

1 correlated with average carbon oxidation rates ( $r^2 = 0.65$ ) and sediment surface organic  
2 carbon ( $r^2 = 0.65$ ).

### 3 **Factors controlling benthic organic matter mineralization and nutrient recycling**

4 The relationships among sediment and bottom water properties and benthic fluxes were  
5 analyzed using principal components analysis (PCA) in order to elucidate the primary factors  
6 driving benthic organic matter mineralization and nutrient recycling in the northeastern shelf  
7 of the Gulf of Cádiz (Table 3). Component 1 is indicative of organic matter mineralization  
8 ( $C_{ox}$ ), concomitant with ammonium and silicate effluxes, and it is significantly associated  
9 with the content of organic carbon and median grain size of surface sediments. Component 2  
10 is positively associated to benthic fluxes of phosphate, nitrate and nitrite, and negatively  
11 correlated to bottom water oxygen concentration. Component 3 indicates a negative  
12 relationship between bottom water nitrate concentrations and both temperature and salinity.  
13 Finally, component 4 is positively associated to the abundance and biomass of macrofauna,  
14 which are mostly correlated (negative) to sediment grain size. The four components explained  
15 74.5% of the data variability.

### 16 **Denitrification and nitrification rates**

17 The molar ratios of mineralized carbon to the flux of inorganic nitrogen (nitrate + nitrite +  
18 ammonium) ( $C_{ox}:F_{IN}$ ) can be used to investigate the preferential pathways of organic matter  
19 remineralization, given the C/N ratio of deposited organic matter. The C:N:P Redfield ratio  
20 (106:16:1) is often applied to compare it to measured solute flux ratios, considering that only  
21 phytoplankton-derived material is undergoing diagenesis (Berelson et al. 1998, 2003, Jahnke  
22 & Jahnke 2000). However, the organic matter in the study site is likely affected by terrestrial  
23 or seagrass detritus, which are expected to have higher C/N ratios (e.g. Enriquez et al. 1993).  
24 Measured fluxes of inorganic nitrogen ( $NO_3^- + NO_2^- + NH_4^+$ ) were in general lower than those  
25 expected from benthic mineralization when assuming in one case the Redfield and in the other

1 case the sediment C/N ratios for organic matter (Fig 4a and b). Average denitrification rates  
2 for each site, calculated applying equation (1), ranged from 1.12 to 3.74 mmol N m<sup>-2</sup> d<sup>-1</sup>,  
3 assuming a Redfield stoichiometry for mineralized organic matter, and from 0.61 to 3.23  
4 mmol N m<sup>-2</sup> d<sup>-1</sup>, assuming observed sediment C:N molar ratios (Table 4). The ratio of  
5 denitrification rates based on Redfield stoichiometry to the ones based on sediment C/N ratios  
6 was on average 1.7, which demonstrates the sensitivity of these calculations to the C/N ratio  
7 of mineralized organic matter. Averaged carbon remineralization rates attributed to  
8 denitrification ranged from 8 to 15% considering Redfield stoichiometry, and from 4 to 14%  
9 considering sediment C:N ratios.

10 Average nitrification rates calculated from equation (3) ranged from 1.79 to 3.90 mmol N m<sup>-2</sup>  
11 d<sup>-1</sup> and from 1.27 to 3.42 mmol N m<sup>-2</sup> d<sup>-1</sup>, applying Redfield and observed sediment C:N ratio,  
12 respectively (Table 4). These rates were on average between 1.2 and 1.5 times higher than  
13 denitrification rates. The ratio of nitrification rates based on Redfield stoichiometry to the  
14 ones based on sediment C/N ratios was on average 1.5. Estimated denitrification and  
15 nitrification rates did not vary significantly among the seasons or between BC and GL  
16 regions, although they were considerably smaller in BC1 compared to the rest of stations.

### 17 **P recycling efficiency**

18 Averaged for each site, P recycling efficiencies, which account for the average fraction of  
19 remineralized P that is recycled to the water column, were very variable and ranged from -8%  
20 (net uptake) at GL4 to 72% at BC1. Average P recycling efficiencies were found to be  
21 negatively correlated to the water depth, with the best fit being logarithmic (%P = -37.4\*Ln(z)  
22 + 137.2; r<sup>2</sup> = 0.65).

23

## 1 DISCUSSION

### 2 **N regeneration**

3 In marine sediments there are three principle microbial processes that affect N regeneration:  
4 denitrification, nitrification and ammonification, i.e. the release of  $\text{NH}_4^+$  from organic matter  
5 (Bronk & Steinberg 2008). Denitrification is of particular interest in coastal systems because  
6 it represents a net loss of N (as  $\text{N}_2$ ) and, therefore, reduces the N-enrichment in these  
7 environments (Devol 2008). Apart from the classical denitrification process, the recently  
8 discovered anaerobic ammonium oxidation with nitrite (anammox) can also be involved in  
9 benthic production of  $\text{N}_2$  (Thamdrup & Dalsgaard 2002). The most important drivers  
10 controlling the relative importance of anammox in sediment  $\text{N}_2$  production are water depth  
11 (and hence benthic mineralization rates) and  $\text{NO}_3^-$  availability (Thamdrup & Dalsgaard 2002,  
12 Dalsgaard et al. 2005). According to these authors, the relative contribution of this route to  $\text{N}_2$   
13 production is often less than 20% in shallow sediments (<50 m) with the highest  $\text{N}_2$   
14 production in environments with high  $\text{NO}_3^-$  availability. Thus, given the shallowness and very  
15 low nitrate levels of the study site, we have assumed that denitrification is the main  $\text{N}_2$ -  
16 producing process. In addition, the anaerobic dissimilatory nitrate reduction to ammonium  
17 (DNRA) can also be involved in the sedimentary N cycle, although this route is generally  
18 only significant in organic rich sediments with high free sulfide concentrations, such as  
19 estuarine sediments (Rysgaard et al. 1996) and under fish culture net pens (Christensen et al.  
20 2000).

21 Benthic  $\text{NH}_4^+$  fluxes measured in the northeastern shelf of the Gulf of Cádiz were within the  
22 range reported for coastal environments (Berelson et al. 1998, 2003, Hopkinson et al. 2001,  
23 Bronk & Steinberg 2008 and references therein). The regeneration of  $\text{NH}_4^+$  was related to  
24 benthic organic matter remineralization, which in the study site was found to be mainly  
25 controlled by the organic matter content in surface sediments. (Table 3, Ferrón et al.

1 submitted). Although this pattern has been previously observed (e.g. Forja et al. 2004,  
2 Lansard et al. 2008), other authors have found that benthic remineralization is mainly  
3 controlled by the quality, rather than the quantity, of sedimentary organic matter (Arnosti &  
4 Holmer 2003, Ståhl et al. 2004). Although not significantly, component 1 of the PCA was  
5 negatively associated to surface sediment C/N ratios, which are considered to be indicative of  
6 organic matter quality. However, the stronger contribution of bulk sediment organic carbon to  
7 component 1, together with the significant relationships observed between silicate benthic  
8 fluxes and both organic carbon oxidation rates and organic carbon content in surface  
9 sediments, seemed to indicate that a considerable fraction of the latter must be labile (e.g.  
10 fresh diatoms).

11 Contrary to  $\text{NH}_4^+$  fluxes,  $\text{NO}_3^-$  fluxes were negatively correlated to component 1. In addition,  
12 benthic fluxes of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , which were within the range reported for other coastal  
13 environments (Berelson et al. 1998,2003, Hopkinson et al. 2001, Bronks & Steinberg 2008  
14 and references therein), were negatively correlated to bottom water oxygen concentration  
15 (component 2). In fact, oxygen strongly affects most of the processes involved in the N cycle,  
16 with the exception of organic N mineralization or  $\text{NH}_4^+$  regeneration, which occurs under  
17 both oxic and anoxic conditions (Joye & Anderson 2008). The lower and upper limits for  
18 denitrification rates estimated for the study site, assuming that denitrification was the main  
19  $\text{N}_2$ -producing process, indicated that on average between 60% and 68% of the nitrogen  
20 mineralized was denitrified, respectively. This is in good agreement with other values  
21 reported in the literature for marine sediments (Seitzinger et al. 1988, Seitzinger & Giblin  
22 1996, Berelson et al. 1998, Jahnke & Jahnke 2000, Hopkinson et al. 2001, Laursen &  
23 Seitzinger 2002). Average denitrification rates for each sampling site were linearly correlated  
24 to surface sediment organic carbon and carbon oxidation rates. Taking into account the lower  
25 and upper limits calculated for denitrification rates, it was estimated that this process

1 contributed between 9 and 13% to total organic matter oxidation. Laursen & Setzinger (2002)  
2 found a similar contribution in continental shelf sediments of the Mid-Atlantic Bight, where  
3 denitrification accounted for 13% of total benthic remineralization.  
4 In general, sediments acted as a source of N<sub>2</sub>O to the water column and measured fluxes were  
5 in the range of those reported in other coastal environments (Seitzinger 1988, Hopkinson et al.  
6 2001, Laursen & Seitzinger 2002). In marine sediments, N<sub>2</sub>O is mainly produced by  
7 denitrification, nitrification, nitrifier-denitrification and DNRA. Although N<sub>2</sub>O benthic fluxes  
8 were negligible in terms of mineralized N, representing on average less than 1% of measured  
9 inorganic N fluxes (NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup>), they may represent a significant source of N<sub>2</sub>O to  
10 the water column. In this sense, averaged for each season and region (BC and GL), bottom  
11 water N<sub>2</sub>O concentrations significantly correlated with N<sub>2</sub>O benthic fluxes, with the best fit  
12 being a second order polynomial ( $r^2 = 0.83$ ).

### 13 **P regeneration**

14 Phosphate fluxes were in good agreement with those measured in other coastal environments  
15 (Berelson et al. 1998, 2003, Hopkinson et al. 2001) and were poorly correlated with carbon  
16 remineralization rates, indicating that there must be other sources and sinks for P (Fig. 5).  
17 Flux ratio lines of 1:106 (Redfield ratio), 1:50 and 1:300 (F<sub>P</sub>:C<sub>Ox</sub>) are plotted in figure 6 as a  
18 reference, as P:C ratios of mineralized organic matter may deviate from Redfield  
19 stoichiometry. Measured benthic phosphate fluxes were in all cases lower than expected from  
20 carbon mineralization rates and Redfield stoichiometry, and also often lower than expected  
21 from organic matter with lower P:C ratios. On the other hand, the PCA showed a significant  
22 negative relationship between benthic phosphate fluxes and bottom water oxygen  
23 concentrations (component 2). In this context, lower F<sub>P</sub>:C<sub>Ox</sub> ratios are often reported in  
24 literature for oxic environments, whereas higher ratios are found in areas with oxygen  
25 depleted bottom waters (e.g. Ingall & Jahnke 1997, McManus et al. 1997). This is further

1 corroborated by the negative linear relationship found between estimated P recycling  
2 efficiencies and oxygen concentrations in bottom water ( $r^2 = 0.51$ ; only efficiencies  $> 0\%$   
3 considered in the fit). The efflux of remineralized phosphate may be controlled in the surface  
4 oxidized layer by sorption with iron oxyhydroxides (Patrick & Khalid 1974). In a nearby  
5 shallow tidal creek located within the saltmarsh area of the Bay of Cádiz (Río San Pedro),  
6 Ferrón et al. (2009) reported phosphate benthic fluxes ranging from 0.2 to 2.4  $\text{mmol m}^{-2} \text{d}^{-1}$ ,  
7 and they associated the high P recycling efficiencies observed (mostly in the summer) to the  
8 low oxygen concentrations in the water column, as well to the release of inorganic mineral P  
9 adsorbed into the sediments. In the study site, where relatively high bottom water oxygen  
10 concentrations were observed, and taking into account the low ( $F_P:C_{OX}$ ) ratios found, a  
11 considerable fraction of the P mineralized is likely being retained in the sediments by  
12 adsorption or mineral precipitation. In addition, the magnitude of P regenerated to the water  
13 column seemed to be mainly driven by bottom water oxygen concentration and water column  
14 depth, rather than by the total rate of organic matter mineralization.

#### 15 **Influence of macrofauna on nutrient regeneration**

16 It is well documented that the presence of meio- and macrofauna impacts benthic  
17 mineralization and nutrient recycling through feeding, burrowing and irrigation (Aller 1982,  
18 Aller & Aller 1998). Due to the large sediment surface covered by the chamber used in this  
19 study, measured benthic fluxes already integrate the influence of macrofauna on benthic  
20 carbon remineralization and nutrient regeneration. Sediment bioturbation, burrowing and  
21 irrigation affect the vertical distribution of organic matter within sediments, increase exposure  
22 of sediment to oxygen, enhance the exchange of solutes between sediment and overlying  
23 water and, therefore, influence a variety of aerobic and anaerobic microbial processes (Aller  
24 1982, Aller & Aller 1998). In shallow nearby sediments of the Bay of Cádiz, Forja & Gómez-  
25 Parra (1998) found that macrofauna affected the top 10 to 15 cm of sediment, significantly

1 enhancing benthic fluxes of inorganic carbon and nutrients. However, the PCA failed to show  
2 any significant relationship between total macrofaunal abundance or biomass and organic  
3 matter mineralization and nutrient benthic fluxes. This was also true when separated into the  
4 different classes or the different trophic groups. The PCA showed that macrofaunal  
5 abundance and biomass correlated with component 4 (Table 3), and that both variables were  
6 negatively correlated to the median sediment grain size. No trends were observed between  
7 macrofaunal community and organic carbon content in surface sediments. Similarly, previous  
8 investigations in the northern Aegean Sea and the Skagerrak (NE North Sea) showed no  
9 correlation between macrofaunal biomass and organic carbon oxidation rates (Ståhl et al.  
10 2004 a,b). However, in Skagerrak sediments measured dissolved inorganic carbon fluxes were  
11 enhanced by 1.0 –5.4 times over diffusive fluxes, indicating that macrofauna had a significant  
12 impact on benthic exchange rates of organic carbon remineralization products (Ståhl et al.  
13 2004 a,b). The lack of correlation between macrofauna abundance or biomass and carbon  
14 oxidation rates may partly be explained by the existence of patchiness in the macrofaunal  
15 communities, as well as the complexity of assessing the species-specific traits and functional  
16 biodiversity. In this sense, the overall indirect enhancement of bacterial respiration rates by  
17 bioirrigation and bioturbation activities depends on several factors such as the structure of the  
18 macrobenthic community, the size distribution, the geometrical shape of burrows and the  
19 modes of burrow ventilation and feeding strategies (Aller & Yingst 1978). Therefore,  
20 macrofaunal biomass or abundance may not be sensitive measures of macrofaunal influence on  
21 benthic remineralization rates (Ståhl et al. 2004a). Furthermore, macrofauna in this study was  
22 only sampled in November 2006 and, hence, data may not be sufficient to establish any  
23 correlation with other parameters measured in this study.

24 In addition to macrofauna, the presence of benthic microalgae is known to have a significant  
25 impact in sediment biogeochemistry and nutrient cycling (Jahnke 2005). This has been clearly

1 demonstrated in shallow littoral sediments (< 2m) that present lower sediment-water  $\text{NH}_4^+$   
2 fluxes than deeper sediments (Joye & Anderson 2008), suggesting an autotrophic uptake at  
3 shallower depths. However, some authors have observed significant benthic primary  
4 production rates in continental shelf sediments (e.g. Hopkinson 1991, Jahnke et al. 2000). It is  
5 estimated that up to 30% of the continental shelf sea floor could receive enough light to  
6 support significant rates of benthic photosynthesis (Jahnke 2005). If that was the case, the  
7 exclusion of sunlight by the chambers would prevent benthic primary production reducing  
8 sediment oxygen penetration depth and, thereby, nitrification-denitrification potential and  
9 phosphate binding capacity. Consequently, our data would not integrate net metabolism but  
10 only respiration.

#### 11 **Role of benthic remineralization and nutrient recycling**

12 Based on net primary production measurements performed in nearby stations of the Gulf of  
13 Cádiz using the  $^{14}\text{C}$  uptake method (Huertas et al. 2005, Navarro et al. 2006), it is possible to  
14 examine the importance of benthic carbon remineralization on the fertilization of the system.  
15 An average integrated primary production value of about  $700 \text{ mg C m}^{-2} \text{ d}^{-1}$  was assumed,  
16 which is the average of the values reported by Navarro et al. (2006) for the most coastal  
17 stations. Given the annually averaged carbon oxidation rate for the study site ( $28 \pm 8 \text{ mmol C}$   
18  $\text{m}^{-2} \text{ d}^{-1}$ ), benthic remineralization degrades about 47% of net primary production (Fig. 6). The  
19 dependence of carbon remineralization rates on surface sediment organic carbon reported  
20 throughout the study site, together with the significance of sediments in degrading primary  
21 produced organic matter, seem to indicate a tight benthic-pelagic coupling in this system (Fig.  
22 6). Moreover, based on measured average fluxes of inorganic nitrogen ( $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ )  
23 and phosphate, benthic nutrient recycling supplied to the water column about 15% and 12%,  
24 respectively, of total nitrogen and phosphorus phytoplankton requirements. The remaining N  
25 and P required by phytoplankton are very likely supplied by terrestrial inputs and upwelling

1 events. The significance of benthic carbon remineralization and nutrient regeneration in these  
2 shelf sediments seems to be relatively high. For example, Hopkinson et al. (2001) found that  
3 benthic metabolism was equivalent to 20-24% and 11-14% of the primary production in  
4 Massachusetts Bay (30 m deep) and Stellwagen Bay (75 m deep), respectively. In the same  
5 study, these authors reported that benthic remineralization supplied between 3 and 8% of the  
6 N and 11 to 15% of the P required for phytoplankton primary production in those coastal  
7 systems.

8 Two different average budgets for the N cycle have been estimated for the study site  
9 depending on our assumption about the C:N of organic matter undergoing decomposition:  
10 based on Redfield ratio or based on bulk sediment C:N ratio (Fig. 6a and b, respectively). For  
11 P, only the Redfield assumption was available. Overall, between 29 and 36% of total  
12 mineralized nitrogen was released to the water column as  $\text{NH}_4^+$ , whereas a small fraction  
13 (~4%) was released as  $\text{NO}_3^-$ . Between 61 and 67% of total mineralized nitrogen was estimated  
14 to be lost via denitrification. If this fraction of mineralized N was returned to the water  
15 column as bioavailable DIN instead of lost as  $\text{N}_2$ , it could support an additional ~14-19 mmol  
16  $\text{C m}^{-2} \text{d}^{-1}$  of phytoplankton production. Therefore, even if these sediments seemed to recycle a  
17 considerable fraction of the N required by phytoplankton, they represent a net loss of total  
18 nitrogen for this environment. In comparison, in Mid-Atlantic Bight sediments, 57% of total  
19 mineralized nitrogen was lost as  $\text{N}_2$ , while 37% entered the water column as  $\text{NH}_4^+$  and 6% as  
20  $\text{NO}_3^- + \text{NO}_2^-$  (Laursen & Seitzinger 2002). In Massachusetts Bay sediments, 60% of total  
21 mineralized nitrogen was lost as  $\text{N}_2$ , while 34% was released to the water column as  $\text{NH}_4^+$  and  
22 6% as  $\text{NO}_3^- + \text{NO}_2^-$ ; whereas in Stellwagen Basin, 72% of total mineralized nitrogen was lost  
23 as  $\text{N}_2$ , whereas 16% was released as  $\text{NH}_4^+$  and 11% as  $\text{NO}_3^- + \text{NO}_2^-$  (Hopkinson et al. 2001).

24

## 1 CONCLUSIONS

2 Benthic fluxes of nutrients resulting from organic matter remineralization in sediments of the  
3 near-shore northeastern shelf of the Gulf of Cádiz provide, respectively, about 15% and 12%  
4 of inorganic nitrogen and phosphorus required for phytoplankton primary production.  
5 Furthermore, these sediments mineralize approximately 47% of the primary production  
6 carbon. These results highlight the significance of benthic remineralization processes in the  
7 biogeochemistry of coastal environments. In relation to sediment N cycling, estimated  
8 denitrification rates accounted for between 9-13% of total organic matter remineralization and  
9 were found to be correlated with the organic carbon content of surface sediments. Between  
10 61% and 67% of mineralized N was estimated to be lost as N<sub>2</sub> via denitrification, with the  
11 remaining portion recycled mostly as NH<sub>4</sub><sup>+</sup>. The regeneration of NH<sub>4</sub><sup>+</sup> was closely linked to  
12 carbon oxidation rates, which were strongly influenced by bulk organic carbon in surface  
13 sediments. Sediments behaved as a net source of dissolved N<sub>2</sub>O and, although benthic N<sub>2</sub>O  
14 fluxes were not significant in terms of the sedimentary N cycle, they were a considerable  
15 potential source of this gas to the water column. Phosphorus regeneration seemed to be  
16 mainly controlled by bottom water oxygen concentrations. The low P/C flux ratios reported  
17 indicated that up to 75% of mineralized P could be retained in the sediments by adsorption or  
18 mineral precipitation. No clear trends were observed between the macrofaunal community  
19 and benthic carbon mineralization rates or nutrient recycling.

20

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3

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1 FIGURE CAPTIONS

2 Figure 1. Map of the near-shore northeastern shelf of the Gulf of Cádiz showing the sampling  
3 sites and the location of the rivers and the Bay of Cádiz. Isolines represent the bathymetry in  
4 meters.

5 Figure 2. Surface and bottom water characteristics at the beginning of each chamber  
6 incubation versus distance to the coast for BC and GL sites.

7 Figure 3. (a) Total biomass (g AFDW m<sup>-2</sup>) and total abundance (ind m<sup>-2</sup>) of the macrofaunal  
8 groups at each station (b) Total biomass (ind m<sup>-2</sup>) and total abundance (g AFDW m<sup>-2</sup>) of the  
9 trophic groups at each station (C, carnivores; SD, surface deposit feeders; SSD, sub-surface  
10 deposit feeders; S, suspension feeders; O, others).

11 Figure 4. Measured fluxes of inorganic nitrogen vs. expected fluxes derived from carbon  
12 oxidation rates (a) assuming Redfield stoichiometry (b) assuming sediment C/N ratio for  
13 organic matter. White and black symbols represent, respectively, BC and GL sites. The lines  
14 represent the 1:1 relationship. Fluxes are in mmol N m<sup>-2</sup> d<sup>-1</sup>

15 Figure 5. Measured fluxes of phosphate vs. organic carbon oxidation rates. The dotted lines  
16 represent the indicated P:C molar ratios or remineralized organic matter. Units are in mmol m<sup>-2</sup>  
17 d<sup>-1</sup>

18 Figure 6. N cycle for the northeastern shelf of the Gulf of Cádiz. Units are in mmol N m<sup>-2</sup> d<sup>-1</sup>,  
19 except for net primary production (NPP) and C mineralization, which are in mmol C m<sup>-2</sup> d<sup>-1</sup>.  
20 Also shown are the percentages of N remineralized under the different pathways, the  
21 percentage of primary produced C remineralized in the sediments, and the percentage of  
22 phytoplankton required N supplied by benthic recycling (a) assuming Redfield stoichiometry  
23 (b) assuming sediment C/N ratio for organic matter.

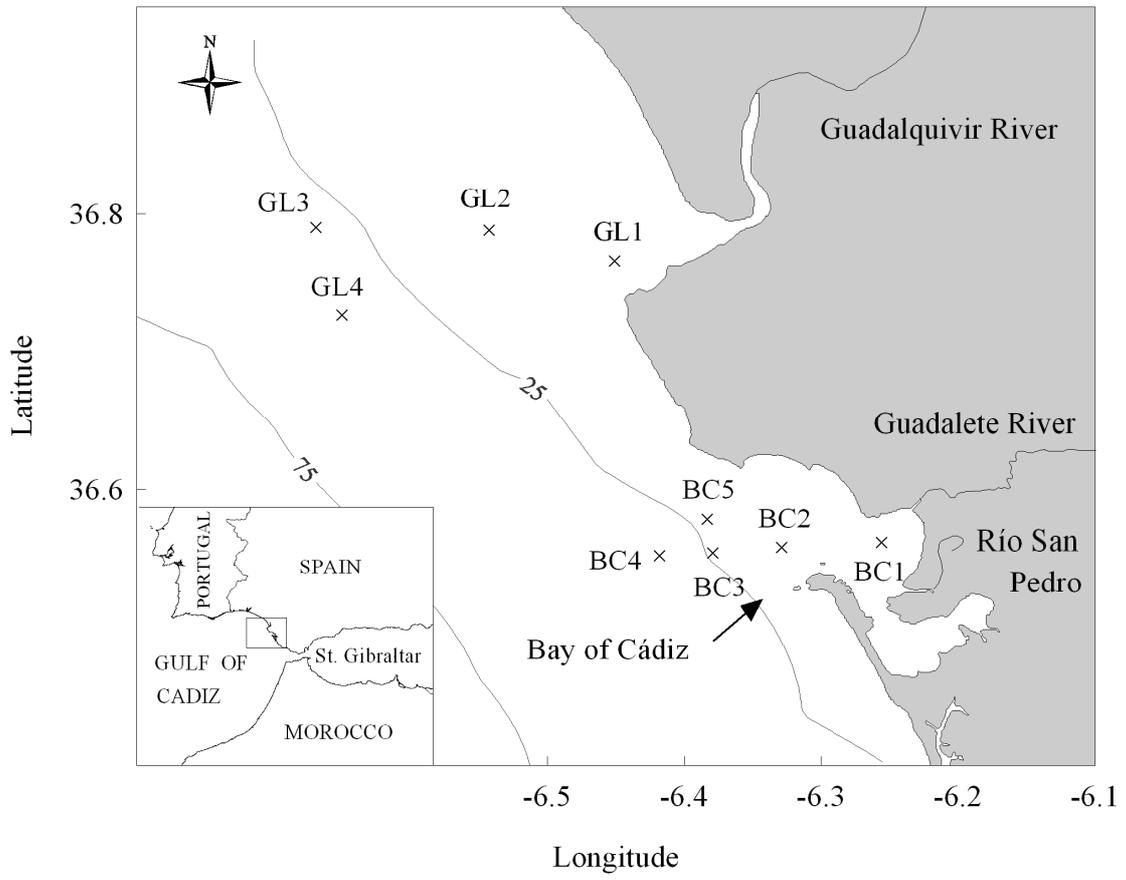


Fig. 1

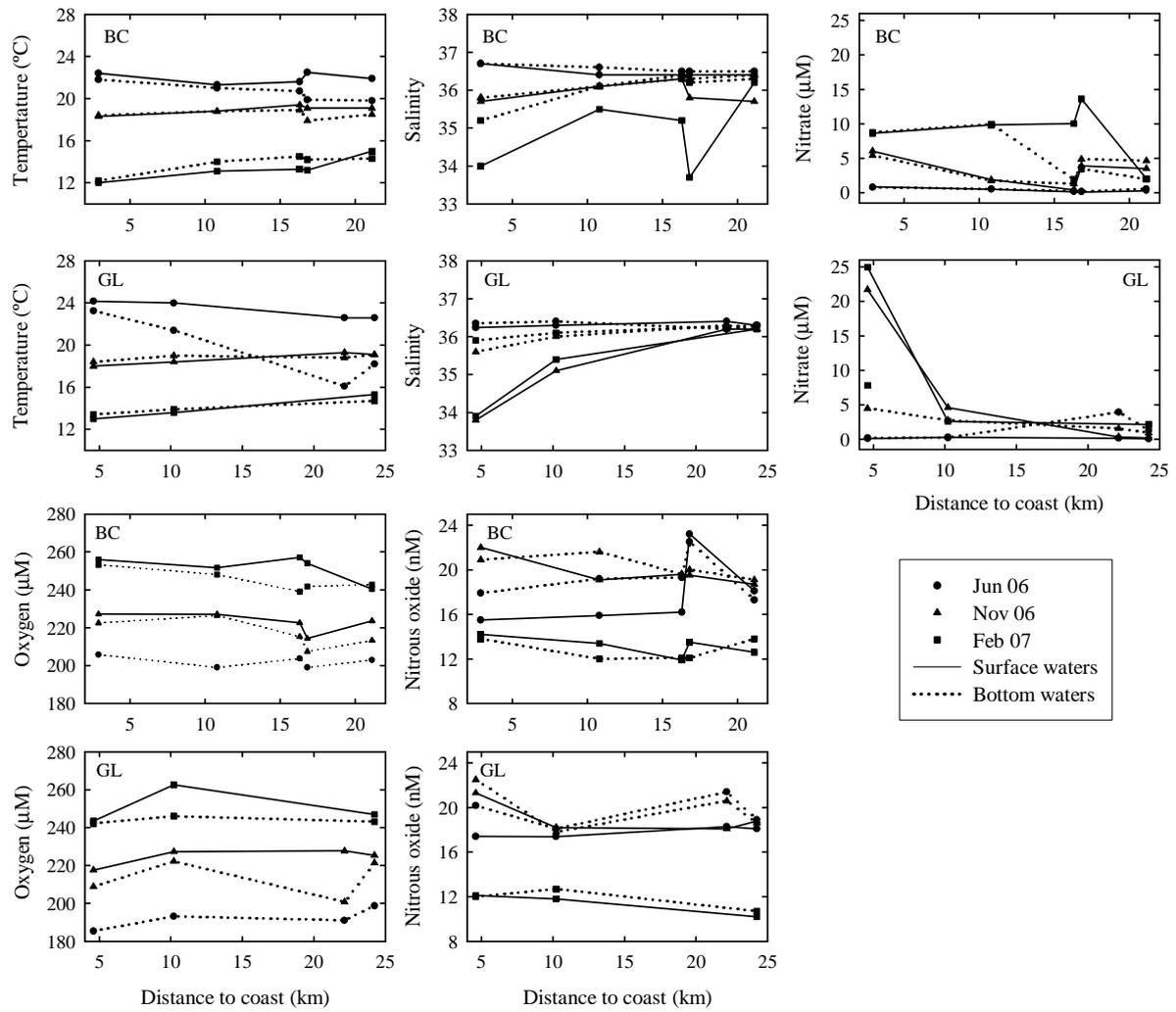


Fig. 2

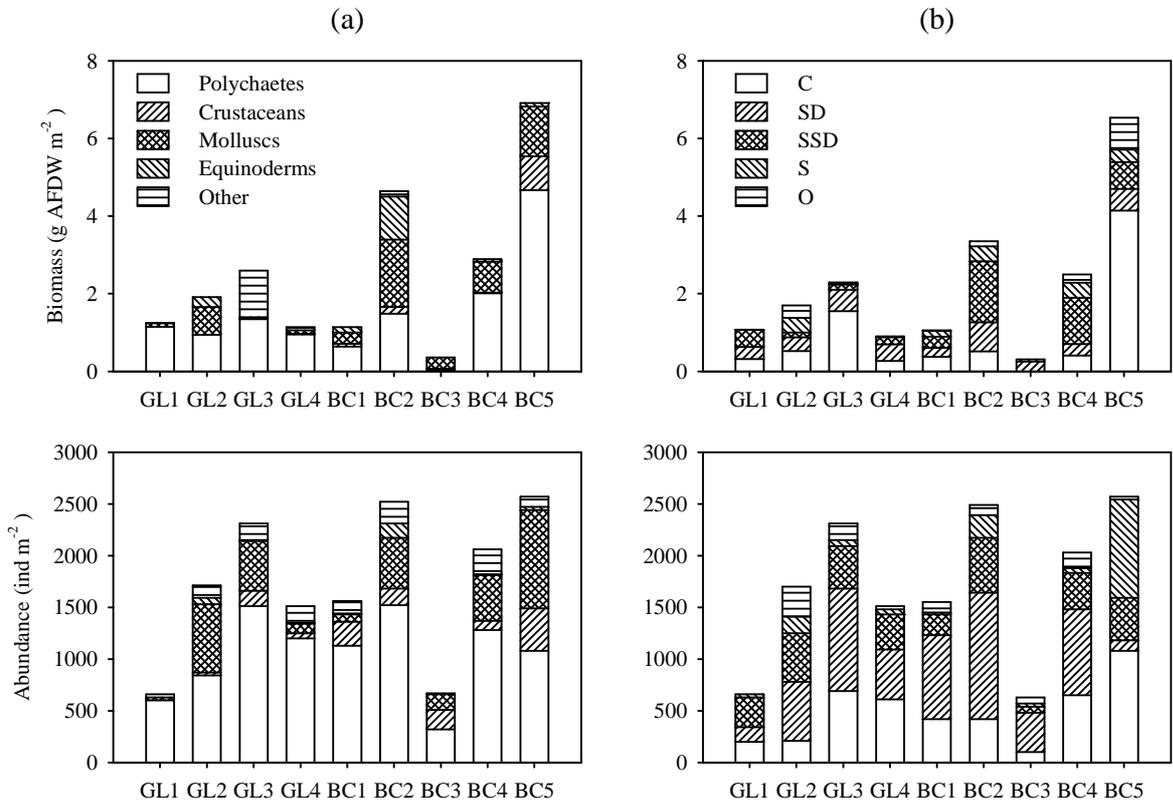


Fig. 3

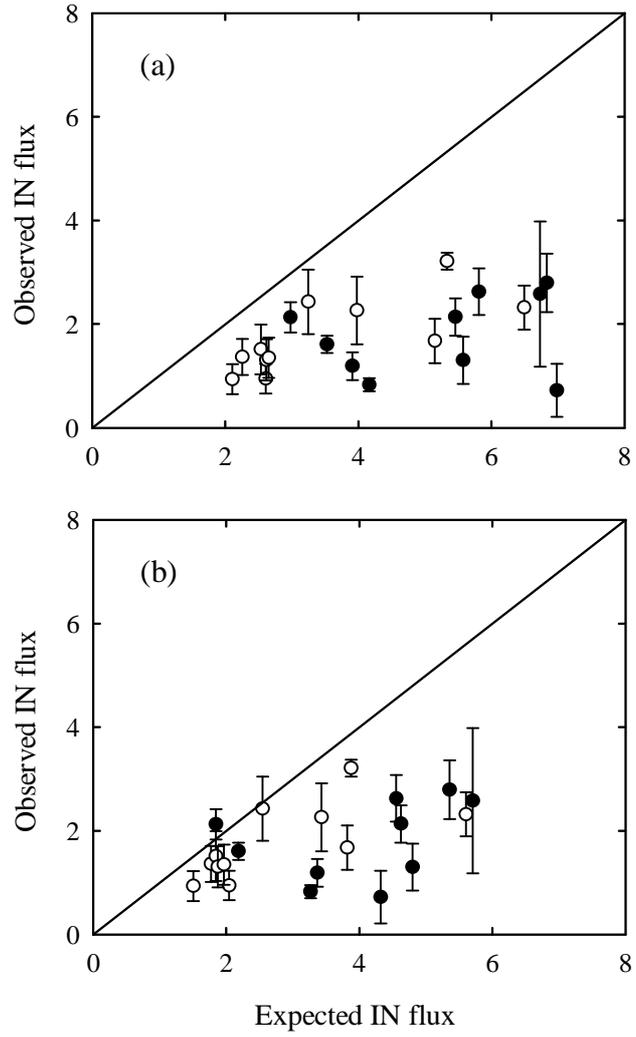


Fig. 4

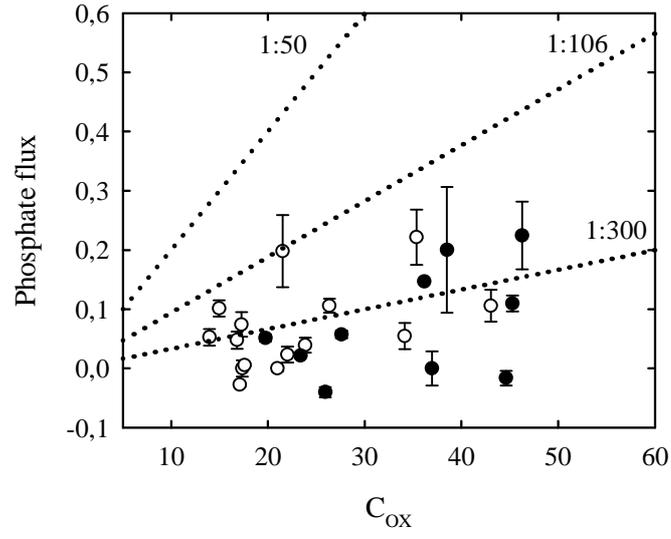


Fig. 5

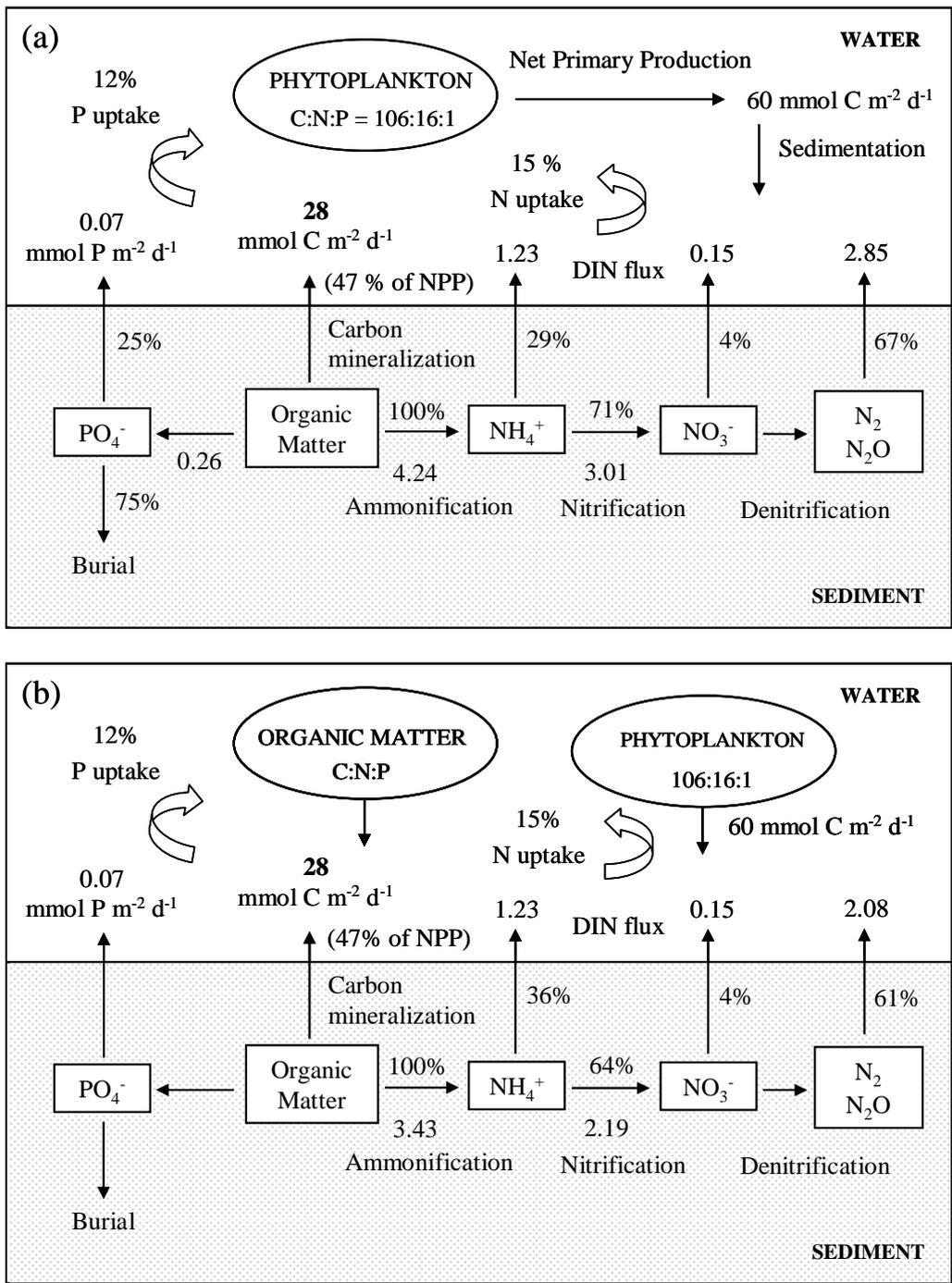


Fig. 6

Table 1. Depth, sediment organic carbon content (OC), nitrogen content (N), molar C:N ratio and median grain size ( $D_{50}$ ) for each station.

	<i>Depth</i>	<i>OC</i>	TN	<i>C:N</i>	<i>D<sub>50</sub></i>
BC1	8	$0.25 \pm 0.01$	$0.04 \pm 0.01$	8.2	372
BC2	18	$0.47 \pm 0.15$	$0.06 \pm 0.02$	8.8	61
BC3	22	$0.29 \pm 0.04$	$0.03 \pm 0.01$	8.4	421
BC4	32	$0.64 \pm 0.03$	$0.08 \pm 0.01$	8.8	78
BC5	22	$0.75 \pm 0.28$	$0.12 \pm 0.07$	7.0	76
GL1	13	$1.18 \pm 0.25$	$0.18 \pm 0.03$	7.9	12
GL2	18	$0.83 \pm 0.05$	$0.11 \pm 0.01$	8.4	13
GL3	29	$0.80 \pm 0.07$	$0.12 \pm 0.01$	9.4	27
GL4	34	$0.93 \pm 0.03$	$0.14 \pm 0.01$	7.7	6.8

Table 2. Date of sampling and benthic fluxes of ammonium ( $F_{\text{NH}_4}$ ), nitrate ( $F_{\text{NO}_3}$ ), nitrite ( $F_{\text{NO}_2}$ ), phosphate ( $F_{\text{PO}_4}$ ), silicate ( $F_{\text{Si}}$ ), and nitrous oxide ( $F_{\text{N}_2\text{O}}$ ) for each station. Units in  $\text{mmol m}^{-2} \text{d}^{-1}$ , except for nitrous oxide ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ ). Negative values denote fluxes into the sediment. Uncertainties are estimated from the errors in the slope of the regression of concentration with time, multiplied by the height of the benthic chamber.

Site	Date	$F_{\text{NH}_4}$	$F_{\text{NO}_3}$	$F_{\text{NO}_2}$	$F_{\text{PO}_4}$	$F_{\text{Si}}$	$F_{\text{N}_2\text{O}}$
BC1	17.06.06	$0.65 \pm 0.20$	$0.15 \pm 0.06$	$0.15 \pm 0.03$	$0.07 \pm 0.02$	$1.02 \pm 0.09$	$10.4 \pm 5.6$
BC2	18.06.06	$3.10 \pm 0.13$	$0.02 \pm 0.02$	$0.09 \pm 0.02$	$0.22 \pm 0.05$	$2.87 \pm 0.20$	$7.24 \pm 3.5$
BC3	19.06.06	$-0.33 \pm 0.10$	$-0.23 \pm 0.07$	$-0.09 \pm 0.04$	$0.04 \pm 0.01$	$1.06 \pm 0.13$	$-1.2 \pm 0.6$
BC4	20.06.06	$1.57 \pm 0.37$	$0.10 \pm 0.05$	nm	$0.05 \pm 0.02$	$2.55 \pm 0.23$	$9.1 \pm 2.4$
BC5	21.06.06	$2.00 \pm 0.38$	$0.22 \pm 0.02$	$0.10 \pm 0.02$	$0.11 \pm 0.03$	$2.13 \pm 0.16$	$3.8 \pm 0.6$
GL2	24.06.06	$2.37 \pm 0.33$	$0.23 \pm 0.11$	$0.03 \pm 0.01$	$0.20 \pm 0.02$	$0.84 \pm 0.16$	$3.5 \pm 1.3$
GL3	26.06.06	$0.96 \pm 0.43$	$-0.16 \pm 0.05$	$-0.08 \pm 0.03$	$0.22 \pm 0.11$	$0.95 \pm 0.17$	$3.2 \pm 1.1$
GL4	27.06.06	$1.63 \pm 0.30$	$-0.21 \pm 0.07$	$-0.12 \pm 0.09$	nm	$0.12 \pm 0.47$	$3.6 \pm 3.0$
BC1	19.11.06	$0.58 \pm 0.15$	$0.86 \pm 0.18$	$-0.07 \pm 0.02$	$0.10 \pm 0.01$	$0.96 \pm 0.11$	$6.9 \pm 3.3$
BC2	20.11.06	$0.49 \pm 0.32$	$0.97 \pm 0.14$	$0.05 \pm 0.03$	$0.05 \pm 0.02$	$1.24 \pm 0.16$	$7.3 \pm 1.4$
BC3	21.11.06	$0.77 \pm 0.27$	$0.38 \pm 0.06$	$0.15 \pm 0.06$	nm	$1.08 \pm 0.11$	$9.4 \pm 3.7$
BC4	22.11.06	$0.20 \pm 0.11$	$-0.57 \pm 0.17$	$-0.13 \pm 0.03$	nm	$0.21 \pm 0.07$	$9.7 \pm 0.8$
BC5	23.11.06	$1.95 \pm 0.48$	$0.36 \pm 0.17$	$-0.04 \pm 0.01$	$0.11 \pm 0.01$	$1.46 \pm 0.44$	$10.1 \pm 0.2$
GL1	29.11.06	$1.89 \pm 0.29$	$0.18 \pm 0.06$	$0.07 \pm 0.01$	$0.15 \pm 0.03$	$1.67 \pm 0.26$	$7.9 \pm 11.6$
GL2	28.11.06	$2.31 \pm 0.47$	$0.33 \pm 0.04$	$0.15 \pm 0.05$	$0.11 \pm 0.01$	$1.68 \pm 0.21$	$2.5 \pm 0.4$
GL3	27.11.06	$1.57 \pm 0.12$	$0.50 \pm 0.12$	$0.07 \pm 0.05$	$0.05 \pm 0.01$	$0.47 \pm 0.07$	$3.7 \pm 1.8$
GL4	26.11.06	$0.80 \pm 0.17$	$0.29 \pm 0.07$	$0.10 \pm 0.02$	$-0.04 \pm 0.01$	$2.14 \pm 0.45$	$3.0 \pm 2.5$
BC1	31.01.07	$1.52 \pm 0.38$	$0.64 \pm 0.18$	$0.26 \pm 0.06$	$0.20 \pm 0.061$	$0.82 \pm 0.13$	$2.2 \pm 1.1$
BC2	01.02.07	$-0.87 \pm 0.21$	$0.15 \pm 0.05$	$-0.25 \pm 0.03$	$-0.03 \pm 0.003$	$0.48 \pm 0.11$	$3.3 \pm 0.3$
BC3	02.02.07	$0.85 \pm 0.25$	$0.13 \pm 0.02$	$-0.04 \pm 0.01$	$0.05 \pm 0.014$	$1.09 \pm 0.13$	$2.1 \pm 0.7$
BC4	03.02.07	$1.22 \pm 0.33$	$0.08 \pm 0.04$	$0.05 \pm 0.01$	$0.01 \pm 0.001$	$0.78 \pm 0.10$	$3.3 \pm 0.6$
BC5	04.02.07	$-1.21 \pm 0.13$	nm	$-0.06 \pm 0.02$	$0.02 \pm 0.014$	$0.52 \pm 0.07$	$1.7 \pm 0.9$
GL1	06.02.07	$3.50 \pm 0.97$	$-0.86 \pm 0.41$	$-0.07 \pm 0.02$	$-0.02 \pm 0.008$	$2.22 \pm 0.58$	$3.1 \pm 0.6$
GL2	07.02.07	$0.42 \pm 0.09$	$0.38 \pm 0.03$	$0.03 \pm 0.01$	$0.06 \pm 0.013$	$1.38 \pm 0.10$	$0.7 \pm 0.1$
GL3	08.02.07	$1.48 \pm 0.14$	$0.17 \pm 0.02$	$-0.05 \pm 0.01$	$0.02 \pm 0.006$	$1.60 \pm 0.29$	$1.3 \pm 0.6$

nm: not measurable

Table 3. Principal components analysis of sediment and bottom water properties and benthic fluxes for the northeastern shelf of the Gulf of Cádiz. Associations of parameters with a component are considered significant if the score is  $> 0.5$ .

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>C<sub>OX</sub></b>	<b>0.90</b>	0.10	0.11	0.04
<b>F<sub>NH4</sub></b>	<b>0.81</b>	0.32	-0.03	-0.03
<b>F<sub>NO3</sub></b>	-0.47	<b>0.62</b>	-0.12	0.31
<b>F<sub>NO2</sub></b>	0.06	<b>0.80</b>	0.05	-0.11
<b>F<sub>PO4</sub></b>	0.22	<b>0.76</b>	0.07	0.16
<b>F<sub>Si</sub></b>	<b>0.74</b>	0.23	0.30	-0.01
<b>OC</b>	<b>0.84</b>	-0.28	-0.15	0.08
<b>C:N</b>	-0.40	-0.15	0.19	0.41
<b>D<sub>50</sub></b>	<b>-0.71</b>	0.27	0.07	-0.54
<b>Biomass</b>	0.16	0.01	0.09	<b>0.86</b>
<b>Abundance</b>	-0.01	0.04	0.10	<b>0.95</b>
<b>Oxygen</b>	-0.04	<b>-0.65</b>	-0.18	0.36
<b>NO<sub>3</sub><sup>-</sup></b>	-0.05	-0.20	<b>-0.90</b>	-0.07
<b>Salinity</b>	0.06	0.26	<b>0.81</b>	0.06
<b>Temperature</b>	-0.04	-0.32	<b>0.89</b>	0.12
<b>% of variance</b>	25.6	18.8	17.5	12.6

Table 4. Average carbon mineralization rates ( $C_{ox}$ ;  $\text{mmol C m}^{-2} \text{ d}^{-1}$ ), nitrification rates ( $F_{nit}$ ;  $\text{mmol N m}^{-2} \text{ d}^{-1}$ ), denitrification rates ( $F_{dent}$ ;  $\text{mmol N m}^{-2} \text{ d}^{-1}$ ), percent of mineralized N denitrified (% DNF), and percent of mineralized P recycled (%  $P_{recyc}$ ) for each sampling site.

Site	$C_{ox}$ <sup>a</sup>	$F_{nit}$ <sup>b</sup>	$F_{nit}$ <sup>c</sup>	$F_{dent}$ <sup>b</sup>	$F_{dent}$ <sup>c</sup>	% DNF <sup>b</sup>	% DNF <sup>c</sup>	% $P_{recyc}$ <sup>b</sup>
BC1	17.9	1.79	1.27	1.12	0.61	42.7	29.2	71.7
BC2	23.1	2.57	1.71	2.23	1.37	72.6	63.6	26.5
BC3	18.4	2.34	1.76	2.24	1.66	74.5	67.8	28.7
BC4	24.2	2.66	1.75	2.81	1.90	77.4	69.9	10.1
BC5	28.9	3.69	3.42	3.50	3.23	81.9	80.8	26.6
<i>Mean ± SD</i>	<i>22.8 ± 5.1</i>	<i>2.6 ± 0.7</i>	<i>2.0 ± 0.8</i>	<i>2.4 ± 0.9</i>	<i>1.8 ± 1.0</i>	<i>70 ± 16</i>	<i>62 ± 20</i>	<i>33 ± 23</i>
GL1	40.4	3.40	2.45	3.74	2.78	61.3	54.1	19.6
GL2	37.1	3.90	2.69	3.52	2.31	64.6	54.9	34.3
GL3	29.8	3.16	1.82	3.01	1.67	57.5	39.4	29.6
GL4	31.4	3.53	2.88	3.50	2.84	73.1	68.8	-16.4
<i>Mean ± SD</i>	<i>34.7 ± 4.9</i>	<i>3.5 ± 0.3</i>	<i>2.5 ± 0.5</i>	<i>3.4 ± 0.3</i>	<i>2.4 ± 0.5</i>	<i>64 ± 7</i>	<i>54 ± 12</i>	<i>17 ± 23</i>

<sup>a</sup> Taken from Ferrón et al. (submitted).

<sup>b</sup> Calculations made assuming a Redfield stoichiometry for organic matter.

<sup>c</sup> Calculations made assuming the surface sediment C/N ratio for organic matter.

APPENDIX I: Abundance (ind m<sup>-2</sup>) and species richness of benthic macrofaunal species collected at the nine sites in November 2006. The trophic group (TG) is also included (C, carnivores; S, suspension feeders; SD, surface deposit feeders; SSD, sub-surface deposit feeders; O, others).

	TG	GL1	GL2	GL3	GL4	BC1	BC2	BC3	BC4	BC5
<b>Polychaetes</b>										
Ampharetidae	SD		10						30	
<i>Capitella capitata</i>	SSD				10	20				
<i>Chaetozone</i> sp.	SD						10		20	
<i>Diopatra neapolitana</i>	C	10				40				
<i>Diplocirrus</i> sp.	SD				10					
<i>Euclymene</i> sp.	SSD	20				130	310	10		10
<i>Galathowenia</i> sp.	S		10	10			20		10	
<i>Glycera</i> sp.	C		20		20		40		10	50
<i>Glycera unicornis</i>	C		10	10						40
<i>Glycinde</i> sp.	C						50			10
Hesionidae	C		40	40	10	50	60		10	20
<i>Heteromastus filiformis</i>	SSD	50	10	60	50				70	30
<i>Hyalinoecia</i> sp.	C								20	
<i>Laonice cirrata</i>	SD		20	240	200		30		50	30
<i>Lumbrineris</i> sp.	C	130	300	430	390		40		260	420
<i>Magelona alleni</i>	SD				10		10		10	
<i>Magelona minuta</i>	SD	10	140	230	100		350		280	150
<i>Maldane glebifex</i>	SSD		40	10					30	100
<i>Mediomastus fragilis</i>	SSD					20	40	40	10	
<i>Melinna palmata</i>	SD	40								
<i>Monticellina</i> sp.	SD		10		40	160	40		90	10
<i>Nephtys</i> sp.	C	50	30	60	10	260	30	80	70	10
<i>Notomastus</i> sp.1	SSD		10	20	20				80	80
<i>Notomastus</i> sp.2	SSD					20	10			
Orbiniidae	SSD							10		10
<i>Owenia fusiformis</i>	S						10			
Paraonidae	SSD		90	280	150	10	30		150	70
<i>Pectinaria</i> sp.	SSD		10							
<i>Phyllodoce</i> sp.	C					10	10			
Phyllodocidae	C				20				40	10
<i>Polycirrus</i> sp.	SD	50	10							
<i>Polydora</i> sp.	SD	10				10				20
<i>Prionospio</i> sp.1	SD	10	50	50	40	260	70		10	10
<i>Prionospio</i> sp.2	SD					90		160		
Sabellidae	S			10			10	10	10	
<i>Scolecopsis</i> sp.	SD						20			
<i>Sigalion mathildae</i>	C							10		
<i>Sphaerosyllis</i> sp.	C					30				
<i>Spiochaetopterus</i> sp.	SD		50	30	10		40			
<i>Spiophanes</i> sp.	SD					10	280			
<i>Sternaspis scutata</i>	SSD	220	10	30	110				10	

Terebellidae	SD					10			
<i>Terebellides stroemi</i>	SD		10			10		10	10
<b>Molluscs</b>									
<i>Abra</i> sp.	SD		10		10			10	10
<i>Acteon tornatilis</i>	C	10							
<i>Antalis novemcostata</i>	SD		40			40	10	50	60
Bivalvia	-		20	10		10	90	20	50
<i>Chamelea striatula</i>	S		10		10				10
<i>Corbula gibba</i>	SD	20	30	30	40	50	50		20
<i>Cylichna cylindracea</i>	C		10				10		
<i>Epitonium</i> sp.	O		10				30		
Gastropoda	O								50
<i>Hyalia vitrea</i>	O		160	80	20		90		70
<i>Kurtiella bidentata</i>	S		10	10					30
<i>Mangelia</i> sp.	C		10				40		
<i>Nassarius</i> sp.	O					10			
<i>Nucula</i> sp.	SD		50	110			70	10	130
<i>Nuculana</i> sp.	SD							30	
<i>Spisulla</i> sp.	S							10	
<i>Tellina serrata</i>	SD								10
Tellinidae	SD		10	10			30	20	10
<i>Thyasira flexuosa</i>	SD		160	150			40		140
<i>Turritella communis</i>	O		130	80	10			50	70
									560
<b>Crustaceans</b>									
<i>Ampelisca brevicornis</i>	SD					10			
<i>Ampelisca</i> sp.	SD			30			50		20
Amphipoda	SD		10			40		30	
<i>Apseudes</i> sp.	SD				10	20		50	
<i>Bodotria</i> sp.	SD			10		10	10		
Cumacea	DS			10		10		10	
<i>Diastylis</i> sp.	DS		10	30	10		40	10	10
<i>Diogenes pugilator</i>	DS					10		40	
<i>Eurydice</i> sp.	O							10	
Gnathiidae	C								10
<i>Harpinia pectinata</i>	SSD			60	10				10
<i>Iphinoe</i> sp.	DS		10	10				10	10
<i>Leptocheirus</i> sp.	DS								10
<i>Leucothoe incisa</i>	DS						10		10
<i>Liocarcinus</i> sp.	C								30
<i>Nebalia</i> sp.	DS						10		
Paguroidea	DS							20	10
<i>Processa</i> sp.	C								10
Tanaidacea	DS							10	
<i>Upogebia</i> sp.	O						10		
<i>Urothoe</i> sp.	S					130			
<b>Echinoderms</b>									
<i>Amphiura filiformis</i>	S								10
<i>Amphiura</i> sp.	S		40						
<i>Echinocardium cordatum</i>	SSD					10	140		
Holothuroidea	-		20	10					
Ophiuroidea	S				10	10			

**Other invertebrates**

<i>Cerebratulus</i> sp.	C			10						
Chaetognatha	C						10			
<i>Edwardsia</i> sp.	C				10					
Nemertina	C		100	140	130	20	130	10	230	30
Oligochaeta	O					20			10	30
<i>Phascolion strombi</i>	DS						10			
Phoronida	S	30	20	10	20		50			10
PyCogonida	C						20			
<b>Abundance (ind m<sup>-2</sup>)</b>		660	1740	2320	1490	1490	2500	670	2190	2560
<b>Species richness</b>		14	40	34	29	30	45	24	44	49