

# Benthic oxygen and nutrient fluxes in a coastal upwelling system (Ria de Vigo, NW Iberian Peninsula): seasonal trends and regulating factors

F. Alonso-Pérez\*, C. G. Castro

Instituto de Investigaciones Mariñas (IIM), CSIC, Vigo 36208, Spain

**ABSTRACT:** Benthic oxygen and nutrient fluxes play a key role in the biogeochemical cycles of carbon and nutrients in coastal regions. However, there are no previous studies focused on benthic fluxes in the NW Iberian coastal upwelling system on an annual basis. The present work analyses the seasonal trends of benthic oxygen and nutrient fluxes as well as the main factors controlling them in the Ría de Vigo. Between April 2004 and January 2005, 16 oceanographic cruises were carried out to measure water column properties, vertical fluxes of particulate organic matter by means of sediment traps, and oxygen and nutrient fluxes using a benthic chamber. Rates of sediment oxygen consumption ( $18$  to  $50$   $\text{mmol m}^{-2} \text{d}^{-1}$ ), phosphate ( $0.08$  to  $0.34$   $\text{mmol m}^{-2} \text{d}^{-1}$ ), silicate ( $1.7$  to  $10$   $\text{mmol m}^{-2} \text{d}^{-1}$ ), ammonium ( $1.1$  to  $4.9$   $\text{mmol m}^{-2} \text{d}^{-1}$ ) and nitrate ( $-0.95$  to  $0.78$   $\text{mmol m}^{-2} \text{d}^{-1}$ ) ranged near the upper limit of benthic fluxes found in similar coastal areas. Nitrogen fluxes were dominated by ammonium fluxes (83%). Benthic fluxes of oxygen, ammonium, phosphate and dissolved silicate were significantly lower during winter but did not show differences during spring, summer or autumn. The strong mutual correlations among fluxes points to the importance of aerobic respiration in the remineralization of organic matter. The amount and quality of organic matter appears to be a factor influencing benthic fluxes, but it seems that changes in temperature, modulated by upwelling/downwelling pulses, trigger and control the benthic fluxes on the short time scale. The study assesses the importance of benthic fluxes to the potential primary production of the system, as remineralized benthic nitrogen and phosphorus may account for up to 41 and 60%, respectively, of the nutrient inputs from the sum of upwelled and continental runoff waters.

**KEY WORDS:** Benthic fluxes · Galician Rías · Upwelling · Vertical fluxes · Remineralization · Nutrients · Oxygen

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## INTRODUCTION

Covering only 10% of the total ocean surface (Wolast 1998), ocean margins support an important fraction of global primary production (10 to 50%) and up to 83% of carbon mineralization occurs in coastal sediments (Middelburg et al. 1993). Benthic and pelagic processes are generally tightly coupled in shallow marine environments, where sediment nutrient regeneration is fueled by organic matter deposited in the sediments and previously produced in the water column (Nixon 1981). Conversely, benthic

remineralization of nutrients within shallow coastal systems may sustain high proportions of the water column primary production (Boynton et al. 1980, Grenz et al. 2010), which may supply up to 75% of phytoplankton nutrient requirements (Billen 1978). These processes are enhanced within coastal upwelling systems where higher rates of primary production promote higher vertical organic matter fluxes (Varela et al. 2004, Thunell et al. 2007), resulting in higher amounts of organic carbon being available for remineralization in the sediments (Jahnke 1996).

Benthic remineralization processes have shown to be influenced by several factors. Temperature has been identified as the main factor controlling the seasonal variation of benthic fluxes in temperate estuaries (Cowan et al. 1996) as it affects porewater solute transport (Jahnke 2005) as well as metabolic activities of most organisms (Lomas et al. 2002). Another important factor is the supply and quality of organic matter to the sediment (Nixon 1981, Farías et al. 2004, Ståhl et al. 2004). Inputs of organic matter to the benthic environment depend on primary production, primary production plus allochthonous organic matter and/or organic matter deposition rates (Hopkinson & Smith 2005). The redox status of the sediment and the overlying water column affects remineralization processes such as nitrification and denitrification (Sundby et al. 1992). Bottom water dissolved oxygen has also been reported as a factor controlling benthic flux rates (Caffrey et al. 2010), while nutrient concentrations of the overlying water influence diffusion gradients and, hence, flux direction (Boynton & Kemp 1985). Finally, feeding, bioturbation and burrowing of benthic macrofauna influence the rates of organic matter inputs to the sediment, the rates and pathways of organic matter mineralization and, thus, the amount of regenerated dissolved nutrients (Aller 1988, Kristensen 1988, Christensen et al. 2000).

The Rías Baixas (NW Iberian Peninsula, see Fig. 1) are 4 flooded tectonic valleys that act as an extension of the adjacent continental shelf. Their hydrographic regime is highly influenced by upwelling/downwelling dynamics, mainly controlled by the along-shore wind over the continental shelf (Rosón et al. 1995, Figueiras et al. 2002). The upwelling of nutrient-rich subsurface Eastern North Atlantic Central Waters (ENACW) favours the high primary production of the region (Fraga 1981). Several studies have shown that the nutrient content of ENACW is increased over the continental shelf (Álvarez-Salgado et al. 1997), with maximum values inside the Rías (Prego et al. 1999), probably due to intense benthic remineralization processes. In fact, measurements of the magnetical properties of the Rías Baixas sediments point to a strong early diagenesis, which gains intensity towards the Ría interior (Emiroglu et al. 2004, Mohamed et al. 2011). On the other hand, Álvarez-Salgado et al. (1996) and Rosón et al. (1999), using a 2-D non-stationary box model for the Ría de Arousa, concluded that 83% of the carbon fixed in this Ría during the upwelling period is exported to the adjacent continental shelf, and the other 17% settles on the sediment. In a more recent study, Gago et al. (2003), applying a simi-

lar box model for the Ría de Vigo, estimated a much higher fraction of organic material settling onto the sediments (~62%). Although these previous studies presented an estimate of the percentage of organic material deposited onto the sediments in the Rías, they were not able to distinguish between the remineralized and buried fractions of the organic matter. The only studies of directly measured diffusive benthic nutrient fluxes refer to the continental shelf off the NW Iberian coast (Epping et al. 2002) and inside the Ría de Pontevedra (Dale & Prego 2002). Recently, Alonso-Pérez et al. (2010) have measured the total nutrient benthic fluxes under a mussel raft in the Ría de Vigo during an upwelling event. In this context, the present study aims to quantify, for the first time in this coastal upwelling system, the benthic oxygen and nutrient fluxes over the course of one year, to study their main controlling factors and to evaluate the importance of the fluxes in the potential productivity of the system.

## MATERIALS AND METHODS

### Study area

The study site is located in the Ría de Vigo, a temperate coastal embayment and one of the 4 V-shaped Rías Baixas of the NW Iberian Peninsula. The Ría is oriented NE-SW, widens seawards, and is partially enclosed by the Cíes Islands (Fig. 1). From May to October, prevailing northerly winds cause the upwelling of cold, nutrient-rich subsurface ENACW, which enters the Ría. During upwelling conditions, primary production is increased (Fraga 1981), as is the potential export of biogenic carbon to the sediment and the adjacent shelf (Álvarez-Salgado et al. 2001). During the other half of the year, downwelling conditions, associated with prevailing southerly winds, are predominant.

### Sampling strategy and water sampling

In the framework of the Spanish project FLUVBE (coupling of benthic and pelagic fluxes in the Ría de Vigo), 16 oceanographic cruises were carried out at Stn FL, located in the inner part of the Ría de Vigo (Fig. 1). The sampling strategy of the cruises, which covered the period between April 2004 and January 2005, was intended to capture the predominant oceanographic conditions in the study area; i.e. spring bloom (April), summer upwelling-stratification

(July), autumn bloom (October) and winter mixing (January). During each period, the station was visited twice a week during a 15 d period. One-day cruises were carried out on board R/V 'Mytilus'; vertical profiles of temperature and dissolved oxygen were obtained with a SBE911plus CTD. Bottle casts (rosette sampler with 10 l PVC Niskin bottles) were run to obtain water samples for dissolved oxygen, dissolved inorganic nutrients, suspended particulate organic carbon and nitrogen concentrations (POC and PON, respectively). Dissolved oxygen was determined by Winkler potentiometric titration. The estimated analytical standard error (SE) was  $\pm 1 \mu\text{mol kg}^{-1}$ . Nutrient samples were determined by segmented flow analysis with Alpkem autoanalyzers following Hansen & Grasshoff (1983) with some improvements (Mouriño & Fraga 1985). The analytical SEs were  $\pm 0.02 \mu\text{mol kg}^{-1}$  for nitrite,  $\pm 0.05 \mu\text{mol kg}^{-1}$  for nitrate, ammonium and silicate and  $\pm 0.01 \mu\text{mol kg}^{-1}$  for phosphate. Total dissolved inorganic nitrogen (DIN) is the sum of  $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N and  $\text{NH}_4^+$ -N. For analysis of POC and PON, 250 ml of seawater were filtered on pre-weighed, pre-combusted (4 h,  $450^\circ\text{C}$ ) Whatman GF/F filters. Filters were vacuum dried and frozen ( $-20^\circ\text{C}$ ) before analysis. A Perkin Elmer 2400 CHN analyser was used for measurements of POC and PON, using an acetanilide standard daily. The precision (SE) of the method is  $\pm 3.6 \text{ mg C m}^{-3}$  and  $\pm 1.4 \text{ mg N m}^{-3}$ .

The upwelling index was estimated using the component  $-Q_x$  of the Ekman transport following Bakun's (1973) method:

$$-Q_x = \frac{\rho_{\text{air}} C |V|}{f \rho_{\text{sw}}} V_H$$

where  $\rho_{\text{air}}$  is the density of air ( $1.22 \text{ kg m}^{-3}$  at  $15^\circ\text{C}$ ),  $C$  is an empirical dimensionless drag coefficient ( $1.4 \times 10^{-3}$  according to Hidy 1972),  $f$  is the Coriolis parameter ( $9.946 \times 10^{-5}$  at  $43^\circ\text{N}$ ),  $\rho_{\text{sw}}$  is the density of seawater ( $1025 \text{ kg m}^{-3}$ ) and  $|V|$  and  $V_H$  are the average daily modulus and northerly component of the geostrophic winds centred at  $43^\circ\text{N}$ ,  $11^\circ\text{W}$ . Average daily geostrophic winds were estimated from atmospheric pressure charts. Positive values of  $-Q_x$  indicate upwelling and correspond to predominance of northerly winds.

### Vertical particle fluxes

Vertical particle fluxes were estimated using a homemade multitrapp collector system. It was composed by 4 PVC trap baffled cylinders of  $28 \text{ cm}^2$  collecting area and aspect ratio of 10.8. Sediment traps were deployed at Stn FL at approximately 16 m depth ( $\sim 5 \text{ m}$  above sea bottom) for a 24 h period, filled with brine solution (5 PSU in excess) without the addition of any preservatives. A subsample of 200 ml of the material collected in each cylinder was used for analysis of POC and PON. Filters were vacuum dried and frozen ( $-20^\circ\text{C}$ ) before analysis. Samples for POC and PON were determined as described for suspended organic matter in the previous section. Biogenic silica concentrations ( $\text{bSiO}_2$ ) were determined by filtering a 200 ml subsample onto a  $0.6 \mu\text{m}$  polycarbonate filter under gentle vacuum, followed by a 30 min digestion with 0.2 M NaOH at  $95^\circ\text{C}$  (Brzezinski & Nelson 1989). Silicic acid concentrations of the digested samples were determined using standard autoanalyser methods as described for nutrient analysis in the 'Sampling strategy and water sampling' subsection (above, this section).

In order to determine phytoplankton-derived carbon settled in the traps ( $C_{\text{phyto}}$ ), a fraction of 100 ml preserved in Lugol's iodine was employed for microplankton determination. Depending on the chl *a* concentration, a volume ranging from 10

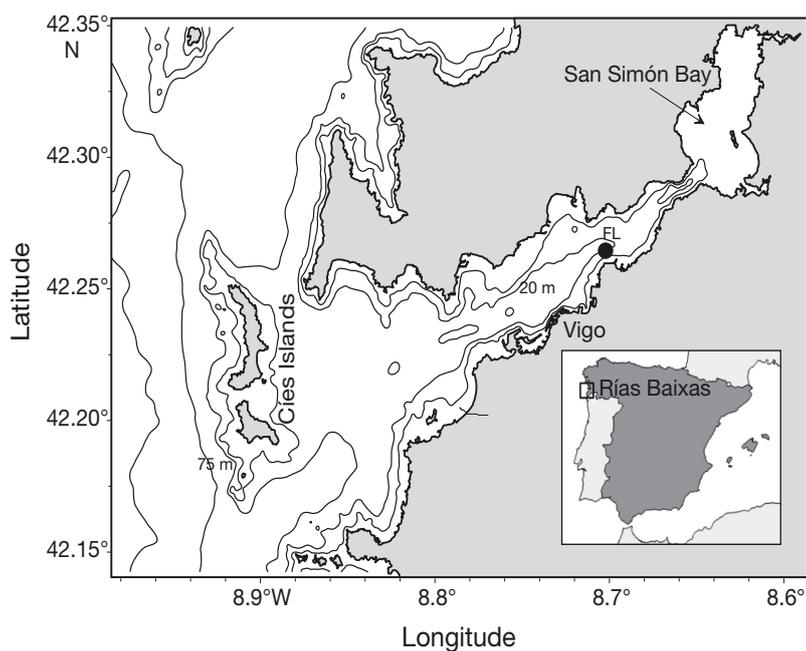


Fig. 1. Ría de Vigo, NW Iberian Peninsula (inset), showing bathymetry and the location of the sampling station, Stn FL (●)

to 50 ml was sedimented in composite sedimentation chambers and observed through an inverted microscope. The phytoplankton organisms were counted and identified to species level. Dimensions were taken to calculate cell biovolumes after approximation to the nearest geometrical shape (Hillebrand et al. 1999), and cell carbon was calculated following Strathmann (1967) for diatoms and dinoflagellates, Verity et al. (1992) for other flagellates ( $>20\ \mu\text{m}$ ) and Putt & Stoecker (1989) for ciliates. Unfortunately, subsamples for  $\text{bSiO}_2$  and  $C_{\text{Phyto}}$  were not available for the spring period.

### Benthic fluxes

Fluxes of oxygen and dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate and silicate) at the sediment–water interface were measured *in situ* by means of a benthic chamber (Ferrón et al. 2008), placed by a diver directly on the sediment surface at the FL station. The equipment consisted of a PVC opaque cylindrical chamber, which incubated 140 l of overlying seawater, and covered  $0.64\ \text{m}^2$  of sediment surface. Three centrifugal pumps stirred the incubated water by means of a stepper motor, at adjustable stirring rates. Inside the chamber, sensors for temperature (SBE 39), turbidity (Seapoint Turbidity Meter) and dissolved oxygen (SBE 43) gave a continuous recording of these variables during the incubation time (~8 h). Data was monitored in real time using a 2-way GSM communication system located at the mooring buoy. Discrete samples were withdrawn from the chamber at prefixed times with a multiple water KC Denmark sampler provided with 12 syringes of 50 ml capacity. Samples for dissolved inorganic nutrients were determined as described for water column measurements in ‘Sampling strategy and water sampling’.

### Statistical data processing

Benthic fluxes of oxygen and nutrients were estimated by empirical linear fittings based on changes in concentration over time. Uncertainties of the fluxes account for the fit of the data to a linear function and the propagation of random errors. In order to test seasonal statistical difference of the benthic fluxes, Student *t*-test of the means were performed (Statistica, StatSoft 6.0). Correlation coefficient *r* between benthic fluxes and selected vertical fluxes and bottom water variables was calculated and presented as a

correlation matrix. A forward stepwise regression model was applied to determine how much variability of the benthic fluxes may be described by different environmental parameters including seabed properties, upwelling index and vertical fluxes (Statistica, StatSoft 6.0). Only variables with statistical significance ( $p < 0.1$ ) were included in the results. Seasonal and annual averages are presented as  $\pm\text{SD}$ .

## RESULTS

### Hydrography

An exhaustive analysis of the hydrographic conditions during the study year is explained in detail by Villaceros-Robineau et al. (2013). Here, we briefly describe the hydrographic situation during the 4 seasonal studies. The spring period was characterized by a transition from downwelling to upwelling conditions, reflected by  $-Q_x$  values, which varied from negative to positive values (Fig. 2). Upwelling produced the entry of cold,  $\text{NO}_3^-$ -rich and relative  $\text{O}_2$ -depleted ENACW. During this upwelling episode increased primary production in surface waters was associated with high suspended POC concentrations ( $240\ \text{mg m}^{-3}$ ) and high values of dissolved oxygen (up to  $280\ \mu\text{mol kg}^{-1}$ ). The summer period was characterised by constant but not very intense upwelling conditions ( $-Q_x = 518 \pm 501\ \text{m}^3\ \text{s}^{-1}\ \text{km}^{-1}$ ). Nutrients were consumed in surface waters by primary producers, generating a high standing stock of suspended organic matter ( $\text{POC} > 400\ \text{mg m}^{-3}$ ) and a higher dissolved oxygen concentration, which decreased with depth as a result of higher proportions of ENACW and remineralization processes. During autumn, a strong negative peak of the  $-Q_x$  ( $-4000\ \text{m}^3\ \text{s}^{-1}\ \text{km}^{-1}$ ) just before the second sampling day interrupted previous upwelling conditions. After that, there was a homogenization of the water column, at a constant temperature of  $15^\circ\text{C}$ , low nitrate and suspended POC concentrations ( $<4\ \mu\text{mol kg}^{-1}$  and  $<150\ \text{mg m}^{-3}$ , respectively). The winter period showed a strong mixing in the water column, marked by low temperatures ( $<13^\circ\text{C}$ ), high nitrate concentrations (7 to  $8\ \mu\text{mol kg}^{-1}$ ) and low suspended POC concentrations ( $<150\ \text{mg m}^{-3}$ ).

### Vertical fluxes

For the spring period, POC vertical fluxes varied almost 2-fold, ranging from 586 to  $1295\ \text{mg C m}^{-2}\ \text{d}^{-1}$

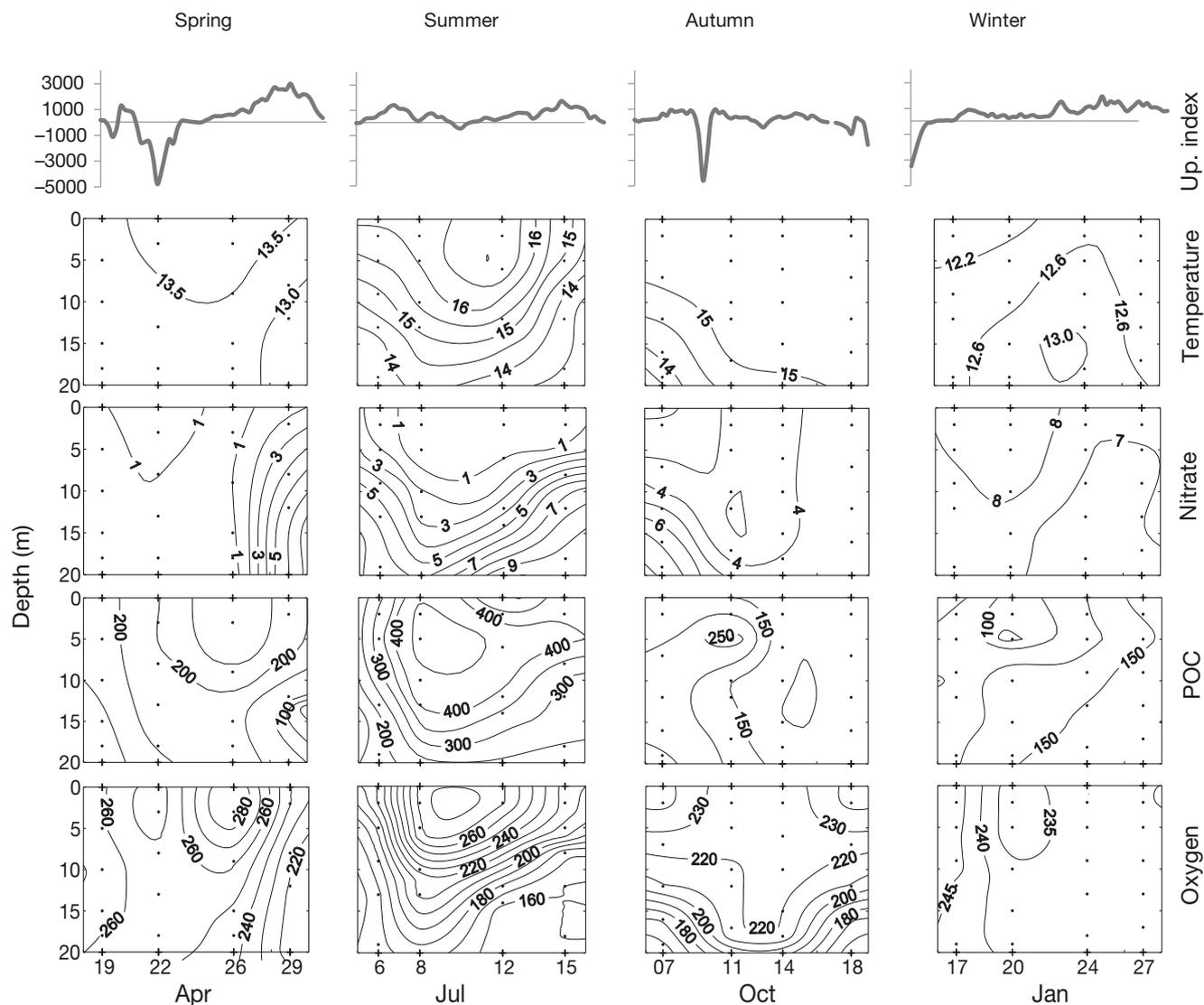


Fig. 2. Time series of depth profiles for upwelling index ( $\text{m}^3 \text{s}^{-1} \text{km}^{-1}$ ), temperature ( $^{\circ}\text{C}$ ), nitrate concentration ( $\mu\text{mol kg}^{-1}$ ), particulate organic carbon (POC,  $\text{mg m}^{-3}$ ) and dissolved oxygen ( $\mu\text{mol kg}^{-1}$ ). Dots represent sampling depths

(Fig. 3). However, the C:N ratio of the settling material did not vary among the sampling days ( $7.3 \pm 1.6$ ) except on the last sampling day, when it reached 9.3. In general, the low C:N ratio of the material collected in the sediment traps pointed to the arrival of relatively fresh organic matter to the sea bottom. During summer, higher POC vertical fluxes were recorded at both ends of the sampling period, when upwelled waters occurred. In contrast,  $C_{\text{phyto}}$  (Fig. 3) increased to a maximum value of  $546 \text{ mg C m}^{-2} \text{ d}^{-1}$  on July 12, followed by a decrease to a still elevated value of  $300 \text{ mg C m}^{-2} \text{ d}^{-1}$  on the last sampling day. These elevated vertical fluxes of fresh  $C_{\text{phyto}}$  led to a decrease in the C:N ratio during this period. In addition, measured  $\text{bSiO}_2$  fluxes were also the highest for

the study year as a result of the dominance of diatoms in the phytoplankton registered in the trap material (Zúñiga et al. 2011). Downwelling and relaxation provoked an increase of the settling material during autumn, with C:N ratios increasing and  $C_{\text{phyto}}$  decreasing as the period progressed. The  $\text{bSiO}_2$  fluxes were lower than during summer ( $534 \pm 112 \text{ mg Si m}^{-2} \text{ d}^{-1}$ ), showing a decreasing trend during the 4 autumn samplings. During winter, the strong water column mixing resulted in relatively high amounts of POC captured in the sediment traps, probably resulting from resuspension and river inputs. The trap material was characterized by high C:N ratios and very low values of  $C_{\text{phyto}}$  ( $28 \pm 5 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) and  $\text{bSiO}_2$  ( $323 \pm 70 \text{ mg Si m}^{-2} \text{ d}^{-1}$ ).

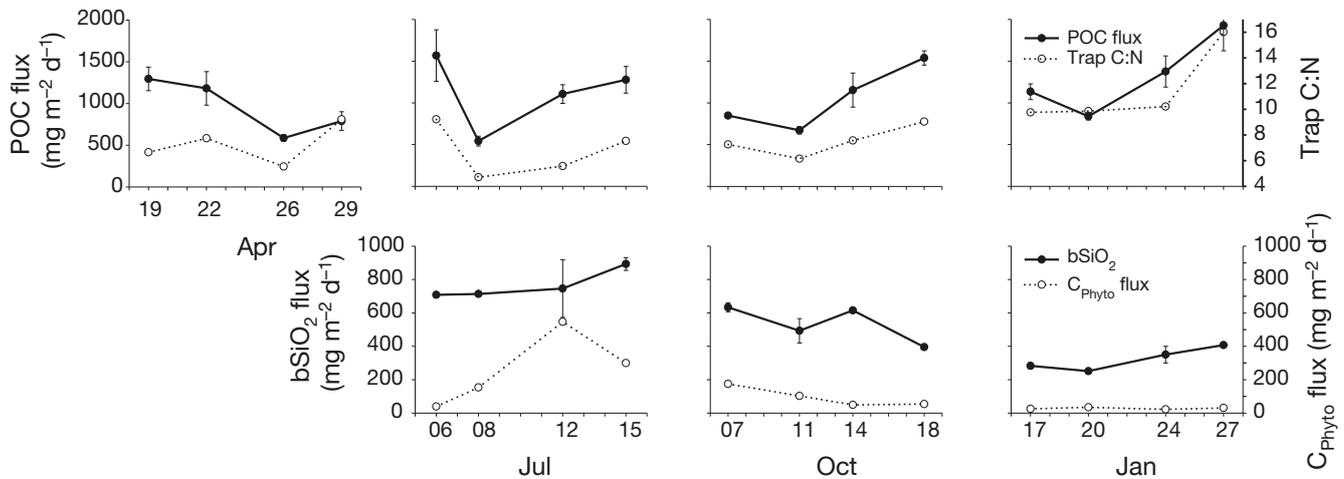


Fig. 3. Seasonal vertical fluxes of particulate organic carbon (POC), C:N ratio (M:M) of the material collected in sediment traps, carbon derived from phytoplankton ( $C_{\text{Phyto}}$ ) and biogenic silica ( $b\text{SiO}_2$ ) (no data for spring  $C_{\text{Phyto}}$  and  $b\text{SiO}_2$ ). Error bars represent SD

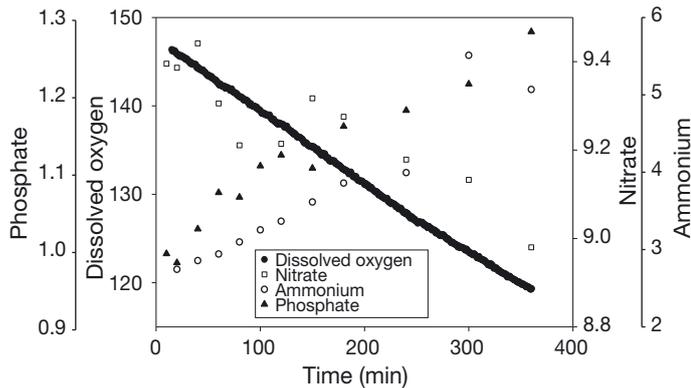


Fig. 4. Example of the evolution in the concentration (in  $\mu\text{mol kg}^{-1}$ ) of dissolved oxygen, nitrate, ammonium and phosphate during chamber incubation (15 July 2004)

### Benthic fluxes

Following the oxidative decomposition and remineralization of organic matter in the sediments, benthic oxygen fluxes were negative, averaging  $-34 \pm 10 \text{ mmol m}^{-2} \text{ d}^{-1}$  for the whole study year. As an example, the decrease in oxygen concentration during benthic chamber incubation on 15 July 2004 is presented in Fig. 4. Benthic fluxes of ammonium, phosphate and silicate were always towards the water column (Fig. 5, see Table 1), increasing their concentrations during incubation (Fig. 4). Benthic fluxes of nitrate were taken up by the sediment during summer and autumn. In the other 2 seasons, daily fluxes were in the same range as for autumn, despite a transition from release to uptake during spring and conversely during winter. In fact, average nitrate

fluxes for these 2 periods were not significantly different from zero.

During spring, relatively high and constant benthic oxygen fluxes during the first 3 sampling days ( $-43.7 \pm 2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ , Fig. 5) were followed by an abrupt decrease in the oxygen uptake by the sediment ( $-28 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) on 29 April 2004 as upwelled ENACW entered the Ría. The earlier water was replaced by colder ( $12.7^\circ\text{C}$ ) and less oxygenated waters ( $215 \mu\text{mol kg}^{-1}$ ), which appears to slow down the benthic oxygen fluxes. The same pattern is also observed for the benthic fluxes of phosphate, silicate and ammonium, which decreased in magnitude at the end of the period when the upwelling occurred. Benthic nitrate fluxes reversed from being released ( $0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) to being taken up ( $-0.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) by the sediments.

Benthic fluxes responded to the gravitational stability of the water column during summer. Oxygen uptake by the sediments was almost constant for the whole period ( $-34.6 \pm 3.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ ), concomitant with constant sea-bottom temperature ( $13.22 \pm 0.08^\circ\text{C}$ ). Ammonium and silicate also show relatively small variations in the benthic fluxes during the summer period ( $2.4 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $5.8 \pm 1.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively). However, they appear to covary with the concentration of dissolved oxygen in sea-bottom waters (Fig. 5). Nitrate fluxes were consistently negative throughout the period ( $-0.7 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) coinciding with the lowest concentrations of dissolved oxygen of sea-bottom waters of the whole year ( $162 \pm 7 \mu\text{mol kg}^{-1}$ ).

During autumn, an abrupt change in the hydrographic conditions appears to have had a strong

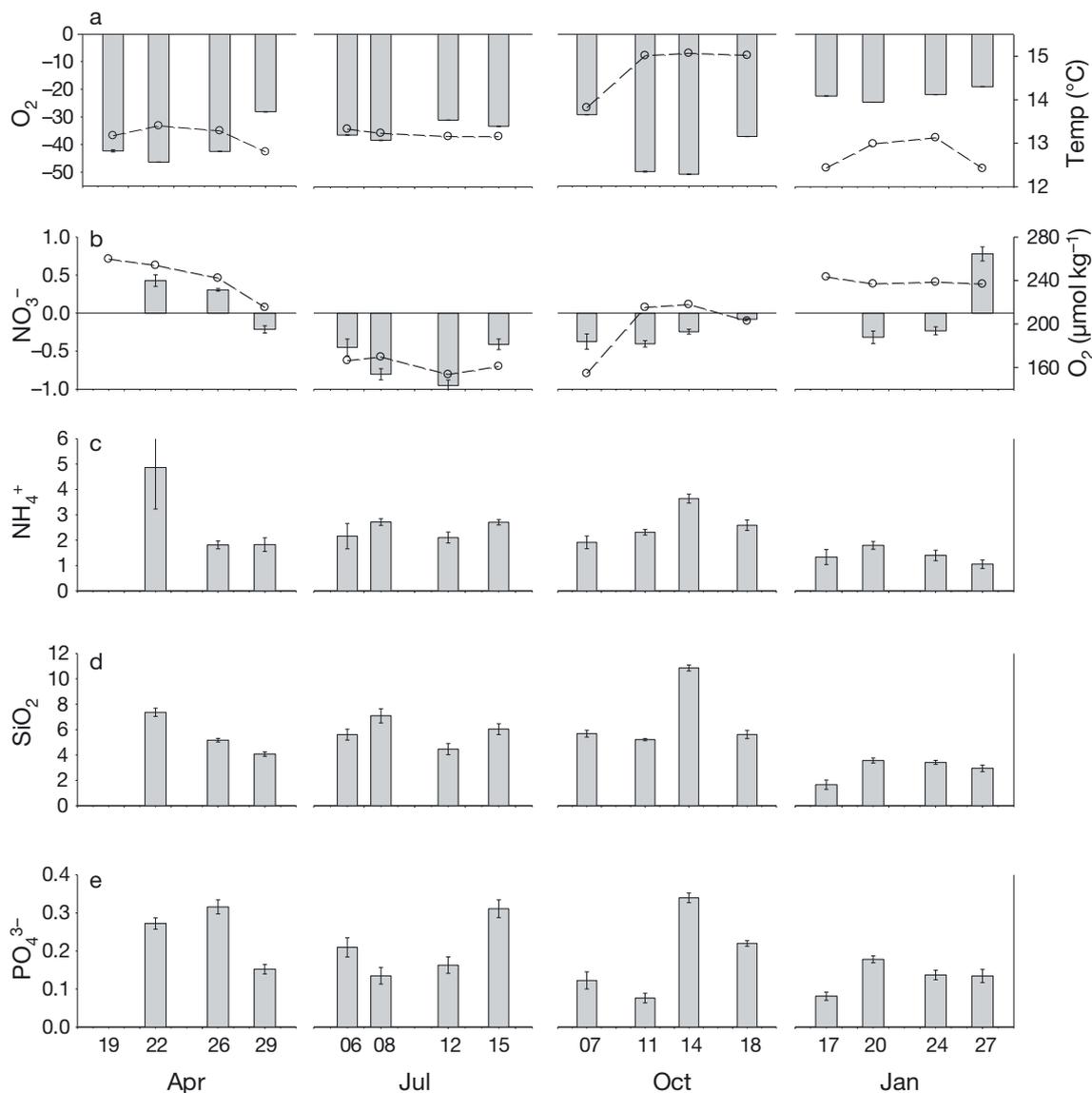


Fig. 5. Seasonal (a) benthic flux of oxygen along with sea-bottom temperature (dashed line, right axis), (b) benthic flux of nitrate along with sea-bottom dissolved oxygen (dashed line, right axis), as well as benthic fluxes of (c) ammonium, (d) silicate and (e) phosphate. Fluxes are in  $\text{mmol m}^{-2} \text{d}^{-1}$ . Error bars are based on the propagation of random errors from measured benthic fluxes

influence in the benthic fluxes. On 10 October 2004, downwelling provoked the replacement of previous cold waters ( $13.6^{\circ}\text{C}$ ) by warmer ( $15.1^{\circ}\text{C}$ ) and more oxygenated sea-surface waters ( $154$  to  $215 \mu\text{mol kg}^{-1}$ ). Benthic oxygen uptake by the sediment responded to this change with an increase from  $-29$  to  $-50 \text{ mmol m}^{-2} \text{d}^{-1}$  (Fig. 5). The same pattern is observed for ammonium, silicate and phosphate fluxes, which attained maximum benthic fluxes on 14 October ( $3.6$ ,  $10.9$  and  $0.34 \text{ mmol m}^{-2} \text{d}^{-1}$ , respectively). Nitrate fluxes are negative for all the period, though its magnitude tends to decrease. The lowest values of benthic oxygen fluxes were recorded dur-

ing winter ( $-21.8 \pm 2.3 \text{ mmol m}^{-2} \text{d}^{-1}$ ) as was the case for the benthic fluxes of ammonium ( $1.4 \pm 0.3 \text{ mmol m}^{-2} \text{d}^{-1}$ ), phosphate ( $0.13 \pm 0.04 \text{ mmol m}^{-2} \text{d}^{-1}$ ) and silicate ( $2.9 \pm 0.9 \text{ mmol m}^{-2} \text{d}^{-1}$ ).

Seasonally averaged benthic fluxes of oxygen showed no significant differences for spring, summer and autumn periods, with values ranging between  $-35$  and  $-42 \text{ mmol m}^{-2} \text{d}^{-1}$  (Table 1). However, oxygen uptake during winter ( $-21.8 \text{ mmol m}^{-2} \text{d}^{-1}$ ) was significantly lower than the 3 other periods (spring:  $p < 0.05$ , summer:  $p < 0.01$ , autumn:  $p < 0.01$ ; Table 2). Benthic fluxes of nutrients, silicate, ammonium and phosphate followed the same trend as oxygen, with the lowest

Table 1. Seasonal benthic fluxes (mean  $\pm$  SD, in  $\text{mmol m}^{-2} \text{d}^{-1}$ ) of oxygen, nitrate, ammonium, silicate and phosphate

Flux	Apr	Jul	Oct	Jan
O <sub>2</sub>	-39.8 $\pm$ 8.0	-34.6 $\pm$ 3.2	-41.7 $\pm$ 10.4	-21.8 $\pm$ 2.3
NO <sub>3</sub> <sup>-</sup>	0.2 $\pm$ 0.3	-0.7 $\pm$ 0.3	-0.3 $\pm$ 0.1	0.1 $\pm$ 0.5
NH <sub>4</sub> <sup>+</sup>	2.8 $\pm$ 1.8	2.4 $\pm$ 0.3	2.6 $\pm$ 0.7	1.4 $\pm$ 0.7
SiO <sub>2</sub>	5.5 $\pm$ 1.7	5.8 $\pm$ 1.1	6.8 $\pm$ 2.7	2.9 $\pm$ 0.9
PO <sub>4</sub> <sup>3-</sup>	0.25 $\pm$ 0.08	0.20 $\pm$ 0.08	0.19 $\pm$ 0.12	0.13 $\pm$ 0.04

Table 2. Statistical significances in the seasonal variability of benthic fluxes (see Table 1), according to Student's *t*-test. *p*-values (above the diagonal) are given if significant ( $p < 0.1$ ); ns: not significant

Flux		Apr	Jul	Oct	Jan
O <sub>2</sub>	Apr	-	ns	ns	<0.05
	Jul		-	ns	<0.01
	Oct			-	<0.01
	Jan				-
NO <sub>3</sub> <sup>-</sup>	Apr	-	<0.05	<0.1	ns
	Jul		-	<0.05	<0.05
	Oct			-	ns
	Jan				-
NH <sub>4</sub> <sup>+</sup>	Apr	-	ns	ns	ns
	Jul		-	ns	<0.01
	Oct			-	<0.05
	Jan				-
SiO <sub>2</sub>	Apr	-	ns	ns	<0.05
	Jul		-	ns	<0.01
	Oct			-	<0.05
	Jan				-
PO <sub>4</sub> <sup>3-</sup>	Apr	-	ns	ns	<0.1
	Jul		-	ns	ns
	Oct			-	ns
	Jan				-

values during winter and insignificant differences among spring, summer and autumn. Benthic silicate fluxes ranged between 5.5 and 6.8  $\text{mmol m}^{-2} \text{d}^{-1}$  from April to October and decreased significantly (Table 2) to 2.9  $\text{mmol m}^{-2} \text{d}^{-1}$  during winter. Ammonium benthic fluxes were reduced from between 2.4 and 2.8  $\text{mmol m}^{-2} \text{d}^{-1}$  in spring, summer and autumn to 1.4  $\text{mmol m}^{-2} \text{d}^{-1}$  during winter. In the case of phosphate, we also obtained lower values of benthic fluxes during winter (0.13  $\text{mmol m}^{-2} \text{d}^{-1}$ ) than for the other seasons (0.19–0.25  $\text{mmol m}^{-2} \text{d}^{-1}$ ), although the difference was only significant between winter and spring ( $p < 0.1$ ). Negative nitrate fluxes during summer and autumn were significantly different from nitrate fluxes in April (summer:  $p < 0.05$ , autumn:  $p < 0.1$ ) and nitrate uptake by the sediment was higher during summer than autumn ( $p < 0.05$ ).

Table 3. Correlation matrix between benthic fluxes and selected vertical fluxes and bottom water variables. Benthic fluxes (oxygen, nitrate, ammonium, silicate and phosphate) are in  $\text{mmol m}^{-2} \text{d}^{-1}$ . C<sub>Phyto</sub>: phytoplankton-derived carbon; POC: particulate organic carbon; bSiO<sub>2</sub>: biogenic silica; Temp.: temperature. \* $p < 0.05$ , \*\* $p < 0.01$ , all others,  $p < 0.10$ . ns: not significant

	F_O <sub>2</sub>	F_NO <sub>3</sub> <sup>-</sup>	F_NH <sub>4</sub> <sup>+</sup>	F_SiO <sub>2</sub>	F_PO <sub>4</sub> <sup>3-</sup>
<b>Benthic fluxes</b>					
F_O <sub>2</sub>	1				
F_NO <sub>3</sub> <sup>-</sup>	ns	1			
F_NH <sub>4</sub> <sup>+</sup>	-0.793**	ns	1		
F_SiO <sub>2</sub>	-0.801**	ns	0.926**	1	
F_PO <sub>4</sub> <sup>3-</sup>	-0.723**	ns	0.610*	0.723**	1
<b>Vertical fluxes</b>					
Trap C:N	0.570*	ns	-0.640*	ns	ns
Trap C <sub>Phyto</sub>	-0.555	ns	0.716**	0.622*	ns
Trap bSiO <sub>2</sub>	-0.546	-0.571	0.608*	0.619*	0.561
Trap POC	ns	ns	ns	ns	ns
<b>Bottom water</b>					
Temp.	-0.707**	ns	0.717**	0.644**	0.553*
O <sub>2</sub>	ns	0.738**	ns	ns	ns
NO <sub>3</sub> <sup>-</sup>	0.700**	-0.507	ns	ns	ns
NO <sub>2</sub> <sup>-</sup>	ns	-0.681**	ns	ns	ns
SiO <sub>2</sub>	ns	-0.589**	ns	ns	ns
PO <sub>4</sub> <sup>3-</sup>	ns	-0.650**	ns	ns	ns

Table 3 shows that sediment oxygen uptake was strongly negatively correlated with benthic fluxes of ammonium, phosphate and silicate ( $p < 0.01$ ) to the water column, as a result of the organic matter decomposition and remineralization; the more nutrient fluxes the more oxygen uptake by the sediment. Benthic oxygen fluxes also correlated negatively with sea-bottom temperature ( $r = -0.707$ ,  $p < 0.01$ ) and positively with sea-bottom nitrate concentration ( $r = 0.700$ ,  $p < 0.01$ ). No significant correlation was found between upwelling index and the oxygen and nutrient benthic fluxes (not shown). Vertical fluxes of C<sub>Phyto</sub> and vertical bSiO<sub>2</sub> fluxes correlated negatively with the benthic oxygen fluxes. In terms of nutrient fluxes, except for nitrate, they correlated with each other positively and were strongly affected by temperature and vertical fluxes of bSiO<sub>2</sub> as well. Parameters related with the quality of settling material (C:N and C<sub>Phyto</sub>) seem to affect the benthic fluxes of ammonium and silicate. The only nutrient not significantly affected by sea-bottom water temperature was nitrate. However, this nutrient was highly correlated with sea-bottom water dissolved oxygen ( $r = 0.738$ ,  $p < 0.01$ ) and with sea-bottom concentration of nitrite ( $r = -0.681$ ,  $p < 0.01$ ), phosphate ( $r = -0.650$ ,  $p < 0.01$ ) and silicate ( $r = -0.589$ ,  $p < 0.01$ ).

## DISCUSSION

### Comparison with other coastal systems

Results analysed here represent the first study of oxygen and nutrient benthic fluxes on a seasonal scale for the NW Iberian coast, which is the only upwelling system in Europe. Rates of oxygen and nutrient fluxes between the sediment and the overlying water column are at the upper limits of benthic rates reported for similar coastal areas (Devol & Christensen 1993, Hammond et al. 1999, Hopkinson et al. 2001, Ferrón et al. 2009a) and much higher than deeper sediments, such as the Mid-Atlantic continental slope (Jahnke & Jahnke 2000). The average sediment oxygen demand in the present study ( $-34 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) is double the average value of benthic community respiration ( $-17 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) for the European coastal zone (Gazeau et al. 2004) and coincides with the mean global respiration for estuarine benthic systems ( $-34 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) obtained by Hopkinson & Smith (2005).

Although nitrate fluxes were consistently negative during summer and autumn, sediments were a net source of inorganic N as DIN was dominated by ammonium fluxes, averaging 83% of the total DIN fluxes. This pattern is very common in coastal benthic N fluxes (Hopkinson et al. 2001); however, there have been cases where  $\text{NO}_3^-$  fluxes exceeded  $\text{NH}_4^+$  fluxes (Billen 1978, Devol & Christensen 1993), where there was no net fluxes of DIN (Berelson et al. 2003) or even where there was net DIN uptake (Berelson et al. 1996). In contrast to the ammonium fluxes, which were positive and directed towards the water column for the Ría de Vigo, Farías et al. (2004) found a larger range of fluxes in the upwelling system off Central Chile, ranging from  $-14$  to  $10 \text{ mmol m}^{-2} \text{ d}^{-1}$ . These authors suggest that maximum ammonium uptake was probably caused either by ammonium assimilation from bacteria or by anammox processes. Off Washington State, USA, Devol & Christensen (1993) measured positive ammonium fluxes of up to  $1.54 \text{ mmol m}^{-2} \text{ d}^{-1}$ , although combined inorganic nitrogen flux was always negative because benthic nitrogen cycling was dominated by denitrification. For our study site, we did not expect to find a prevalence of anaerobic processes as described for the Chilean and US coastal upwelling systems, mainly due to presence of well-ventilated upwelled ENACW ( $\text{O}_2 > 200 \text{ } \mu\text{mol kg}^{-1}$ ; Castro et al. 2000). We therefore suggest that ammonium effluxes are mainly driven by aerobic respiration, as explained in the next section.

In terms of benthic phosphate fluxes, the literature reveals high variability, ranging from sites where P is taken up by the sediment (Fisher et al. 1982) to sites where P is mainly released to the overlying water column (Hammond et al. 1999, Ferrón et al. 2009b), at rates as high as  $2 \text{ mmol m}^{-2} \text{ d}^{-1}$  in Port Philip Bay, Australia (Berelson et al. 1998). Benthic phosphate flux in the Ría de Vigo averaged  $0.2 \pm 0.09 \text{ mmol m}^{-2} \text{ d}^{-1}$  and was always released from the sediment. This value is similar to the highest fluxes obtained by Berelson et al. (2013) and Hopkinson et al. (2001) on the Oregon/California shelf and in Massachusetts Bay, USA, respectively. Benthic silicate fluxes ranged from  $1.8$  to  $10.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ , being lowest during winter and highest during autumn. These fluxes are in the range obtained by Berelson et al. (2013) and higher than those found on the coast of SW Spain (Ferrón et al. 2009b), where silicate fluxes did not exceed  $3 \text{ mmol m}^{-2} \text{ d}^{-1}$  during an annual study. Rates were similar to those found by Hammond et al. (1999) in the Adriatic Sea and in the lower range of fluxes obtained in Port Phillip Bay, Australia (Berelson et al. 1998).

### Factors controlling benthic fluxes in the Ría de Vigo

#### Benthic oxygen fluxes

Seabed temperature and dissolved oxygen have been reported as the most relevant factors influencing benthic oxygen and nutrient fluxes (Cowan et al. 1996). Moreover, sediments located in coastal upwelling areas, as for our study region, receive larger amounts of organic matter (Jahnke 1996), and thus, factors such as primary production and concentration of labile organic matter in the sediments may have major influence on these fluxes (Farías et al. 2004). While it seems that sea-bottom dissolved oxygen has no clear influence on the benthic oxygen fluxes (Fig. 6a), it is evident that temperature significantly affected the magnitude of benthic fluxes despite the restricted range of seabed temperature ( $12.4$  to  $15.1^\circ\text{C}$ ). Benthic oxygen uptake becomes higher as temperature increases ( $r = -0.707$ ,  $p < 0.01$ ; Table 3). Hopkinson & Smith (2005) reported that a large percentage of the variance in benthic fluxes is explained by seasonal temperature change. However, in the Ría de Vigo, sea-bottom temperature is not controlled by atmospheric temperature but by the upwelling/downwelling processes driven by along-shore wind over the adjacent shelf (Nogueira et al.

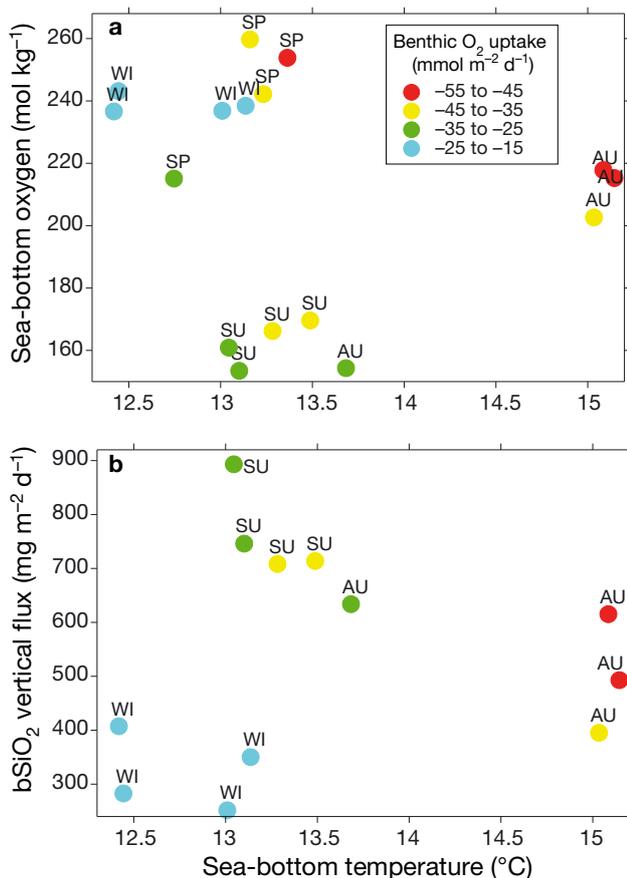


Fig. 6. Seasonal benthic oxygen fluxes depending on (a) sea-bottom dissolved oxygen and temperature, and (b) vertical fluxes of biogenic silica (bSiO<sub>2</sub>) and sea-bottom temperature. SP: spring, SU: summer, AU: autumn, WI: winter

1997). The entrance of cold, upwelled ENACW in the Ría reduces seabed temperature while downwelling processes introduce oceanic warm surface waters towards the bottom (Nogueira et al. 1997). This is probably the reason why there were no significant seasonal differences in benthic oxygen fluxes among the spring, summer and autumn periods, i.e. the benthic oxygen fluxes are mainly modulated by the presence/absence of cold, upwelled water.

Benthic oxygen fluxes were separated into 3 groups based on bottom temperature and dissolved oxygen (Fig. 6a). The major group, characterized by low temperatures (12.4 to 13.5°C) and high concentration of dissolved oxygen (215 to 260  $\mu\text{mol kg}^{-1}$ ), includes data from winter and spring periods. However, the magnitude of benthic oxygen fluxes was significantly higher in spring than in winter ( $p < 0.05$ ). Though bottom waters had high levels of dissolved oxygen during winter, as a result of vertical

mixing, net community production was lowest during this period ( $0.22 \text{ g C m}^{-2} \text{ d}^{-1}$ , Arbones et al. 2008), and consequently, settling of fresh organic material was low ( $28 \pm 8 \text{ mg C}_{\text{Phyto}} \text{ m}^{-2} \text{ d}^{-1}$ ). Besides, the winter C:N ratio of the settling material was the highest of the whole study ( $11.3 \pm 3.0$ ) and vertical fluxes of bSiO<sub>2</sub> the lowest ( $< 400 \text{ mg m}^{-2} \text{ d}^{-1}$ ). Therefore, low values of sediment oxygen uptake obtained during winter appear to be caused by the combination of low sea-bottom temperatures and low levels of fresh organic compounds arriving at the sediment. In contrast, the spring period, while having similar values of sea-bottom temperature and dissolved oxygen as during winter, was characterized by higher levels of net community production ( $1 \text{ g C m}^{-2} \text{ d}^{-1}$ , Arbones et al. 2008) and lower C:N ratio of the material settled in the traps ( $7.3 \pm 1.3$ ), reflecting fresher organic material available for remineralization. The resulting higher benthic oxygen fluxes in spring than winter explain the correlation between the benthic oxygen fluxes and the quality of the settling material (C:N and  $\text{C}_{\text{Phyto}}$ ; Table 3). Summer data and the first sampling day of autumn present similar benthic oxygen fluxes under similar hydrographic conditions, and consequently, they are grouped together by low temperatures (13 to 13.6°C) and low dissolved oxygen ( $< 170 \mu\text{mol kg}^{-1}$ , Fig. 6a) at the bottom, due to the entrance of more remineralized ENACW upwelled waters as the upwelling season progresses (Álvarez-Salgado et al. 1997). The most favourable scenario for the highest sediment oxygen uptake appeared in autumn, after a strong downwelling and subsequent relaxation in the water column. The arrival of surface warmer ( $> 15^\circ\text{C}$ ) and well-oxygenated waters at the bottom ( $205$  to  $220 \mu\text{mol kg}^{-1}$ ) favours decomposition of the organic matter, and consequently, the sediment oxygen uptake.

A stepwise regression analysis indicates that seabed temperature in our study region explains as much as 74% of the variability in benthic oxygen fluxes (Table 4). Considering bSiO<sub>2</sub> vertical fluxes as well, the variability of the benthic oxygen fluxes explained is raised to 87%. In contrast to similar studies in other regions (e.g. Cowan et al. 1996), sea-bottom oxygen concentration does not have a clear influence on the benthic oxygen fluxes and is not a limiting factor. Thus sediment oxygen uptake in the Ría de Vigo is highly influenced by sea-bottom temperatures, mainly modulated by upwelling/downwelling processes, and to some extent by the amount and quality of the settled organic material. The presence of labile organic matter in the sediments is essential for regenerating processes, but physical

Table 4. Stepwise regression between benthic fluxes (oxygen, nitrate, ammonium, silicate and phosphate) and main variables affecting benthic fluxes. There is no multicollinearity among predictor variables. T: temperature; bSiO<sub>2</sub>: biogenic silica

Flux	Variable	Cumulative R <sup>2</sup>	R <sup>2</sup> change	p
O <sub>2</sub>	Bottom T	0.742	0.742	<0.001
	Trap bSiO <sub>2</sub>	0.866	0.122	0.019
NO <sub>3</sub> <sup>-</sup>	Bottom O <sub>2</sub>	0.544	0.544	0.002
NH <sub>4</sub> <sup>+</sup>	Bottom T	0.505	0.505	0.009
	Trap bSiO <sub>2</sub>	0.756	0.251	0.014
SiO <sub>2</sub>	Bottom T	0.456	0.456	0.016
	Trap bSiO <sub>2</sub>	0.723	0.267	0.016
PO <sub>4</sub> <sup>3-</sup>	Bottom T	0.390	0.390	0.039
	Trap bSiO <sub>2</sub>	0.584	0.194	0.089

factors appear to trigger these processes in the short term. In this sense, Boynton et al. (1991) shows a delay in degradation of deposited material until temperature increases in late spring. We have also observed a similar pattern in our study region in a plot of sea-bottom temperature versus bSiO<sub>2</sub> flux (Fig. 6b). Major vertical bSiO<sub>2</sub> fluxes occur during summer stratification and the first sampling day of autumn, but it is just after the autumn downwelling, when sea-bottom temperature increased, that sediment oxygen uptake increased as well. Another key factor is macrofauna activity mediating bioturbation and bioirrigation (Hammond et al. 1985, Aller 1994, Welsh 2003). Median grain size (MGS) for the FL station was  $12.3 \pm 1.8 \mu\text{m}$ , indicating this sample site comprised muddy sediments. Previous studies in the Ría de Vigo (Cacabelos et al. 2009, Rodil et al. 2009) showed that sediments with similar MGS (10 to 13  $\mu\text{m}$ ) were dominated by surface and subsurface deposit feeders. Deposit feeders obtain their nutritional intake mainly from sedimented organic matter (Heip et al. 1995) and would mainly favour aerobic processes and oxidized sediment conditions as they enhance oxygen transfer to the sediment burrow irrigation (Welsh 2003). Unfortunately, we lack information to determine seasonal influence of macrofaunal activities on the benthic fluxes. Further studies are necessary to address this important issue.

#### Benthic nutrient fluxes

The benthic fluxes of ammonium, silicate and phosphate showed a strong correlation with the benthic oxygen fluxes (Table 3), pointing to similar bio-

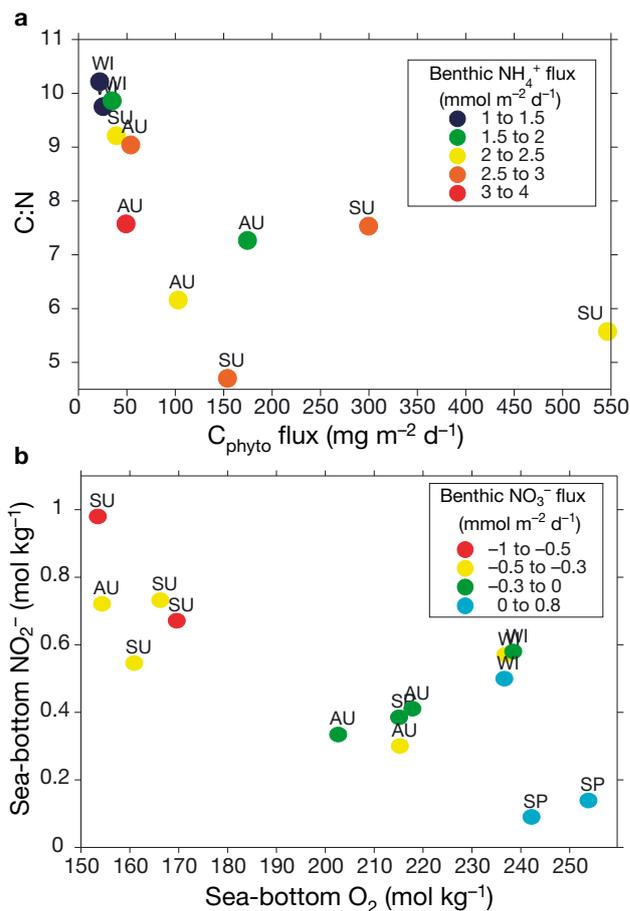


Fig. 7. Seasonal benthic fluxes of (a) ammonium depending on C:N ratio from trap material and vertical flux of phytoplankton carbon ( $C_{\text{phyto}}$ ), and (b) benthic nitrate fluxes depending on sea-bottom nitrite concentration and sea-bottom dissolved oxygen. SP: spring, SU: summer, AU: autumn, WI: winter

geochemical processes. Benthic fluxes of ammonium dominated DIN fluxes during the entire study ( $83 \pm 10\%$ ) and were in all cases from the sediment to the water column, leading to a net positive efflux of DIN. Blackburn & Henriksen (1983) estimated that about 10 to 70% of DIN effluxes to the water column were due to ammonium excretion by macrofauna. In the Ría de Vigo, benthic fluxes of ammonium were influenced by seabed temperature and the quality of the settling material. Fluxes were lowest during winter, when vertical fluxes of bSiO<sub>2</sub> and organic carbon derived from phytoplankton were minimum and C:N ratio of this material highest, indicating less labile organic matter (Fig. 7a, Table 4).

Dale & Prego (2002) suggested that the mixing of bottom waters during upwelling was an important factor for the large diffusive ammonium fluxes they obtained in the Ría de Pontevedra. However, during

the present study ammonium benthic fluxes had their maximum values after 2 downwelling events: 4.9 and 3.6 mmol m<sup>-2</sup> d<sup>-1</sup> for spring and autumn, respectively. In fact, Villaceros-Robineau et al. (2013) found that the most energetic periods of bottom shear stress, and thus, of most probable surface sediment resuspension, occurred during downwelling conditions and strong southerly swells. Moncoiffé et al. (2000) have previously described for the Ría de Vigo that N-assimilative processes dominate during the upwelling and N-regeneration processes in the water column predominate during downwelling conditions. However, both processes may be coupled during moderate upwelling events when an efficient consumption of upwelled N nutrients occurs (Álvarez-Salgado & Gilcoto 2004). Therefore, the benthic ammonium fluxes seem to account for an important amount of the observed N that was regenerated inside the Ría de Vigo during downwelling periods. Since the concentration of ammonium in the oceanic ENACW that upwells in the Ría from the continental shelf is <0.5 μmol kg<sup>-1</sup> (Álvarez-Salgado et al. 1997, Castro et al. 2000), the high ammonium levels inside the Ría are mostly regenerated *in situ*. Álvarez-Salgado et al. (2010), by means of a 2-D non-stationary box model for the Ría de Arousa during the upwelling season, indirectly estimated an extra flux of DIN of 2.5 mmol m<sup>-2</sup> d<sup>-1</sup> due to *in situ* pelagic and benthic nitrogen regeneration processes. This additional input enriched the nitrogen content of upwelled waters by 18%. Results from the present study obtained benthic DIN fluxes of 2 mmol m<sup>-2</sup> d<sup>-1</sup>, which represent ~80% of this extra DIN, pointing to the importance of benthic remineralization processes in the Ría.

Benthic fluxes of nitrate showed a different behaviour from the rest of the benthic nutrient and oxygen fluxes, with no correlation with any of them. Nitrate fluxes were constantly towards the sediment during summer and autumn periods (Fig. 5). They appeared to be strongly and positively influenced by sea-bottom concentration of dissolved oxygen and negatively correlated to initial concentrations of dissolved nutrients: nitrite, phosphate, silicate and to a minor extent nitrate (Table 3). Dissolved oxygen concentration explained 54% of the variability of the nitrate benthic fluxes (Table 4). The influence of dissolved oxygen and nitrite concentrations is clearly shown in Fig. 7b. Nitrate tends to be taken up by sediments when dissolved oxygen in the overlying water is low and nitrite concentration is high. This process is particularly evident when hydrodynamic changes occur (i.e. during spring and autumn cruises). Fennel et al.

(2009) found an increase in total denitrification with increasing bottom-water nitrate concentrations as well as an increase in the rate of direct denitrification. In this sense, the entrance of upwelled waters into the Ría, conveying high levels of both N-nutrients (nitrate and nitrite) probably enhances denitrification processes and thus may be responsible for the consistent benthic nitrate fluxes towards the sediment during the upwelling periods. Following the findings of Fennel et al. (2009), nitrate-enriched upwelled waters seems to favour direct denitrification with respect to coupled nitrification–denitrification, though both processes may occur.

In terms of total DIN, dominance of ammonium fluxes may indicate that probably not all the ammonium generated by ammonification is rapidly oxidised to nitrate by nitrification processes. Although part of the ammonium effluxes might also be provided by other metabolic processes, such as dissimilatory nitrate reduction to ammonium (Giblin et al. 2013), sulphate reduction or Mn/Fe reduction, the good correlation of ammonium fluxes with sediment oxygen consumption ( $r = 0.79$ ) and the well-oxygenated bottom waters in the Ría de Vigo suggest that ammonification is probably the main process behind the observed ammonium effluxes.

The main factors controlling sediment phosphate dynamics in the Ría de Vigo were water temperature at the seabed and vertical bSiO<sub>2</sub> fluxes. Temperature alone explained 39% of the benthic flux variability (Table 4) and, together with vertical bSiO<sub>2</sub> fluxes, raises the explained variability to 58%. Vertical fluxes of bSiO<sub>2</sub> are directly related to the arrival of fresh phytoplankton material to the surface sediment, as diatoms dominated the phytoplankton community in the sediment traps (Zúñiga et al. 2011). All these data suggest that phosphate fluxes are enhanced by the increasing rates of organic matter decomposition as sea-bottom temperature increases and by the presence of recent organic matter settling on the sediment.

Although previous studies showed positive correlations between benthic phosphate fluxes and bottom oxygen concentration (e.g. Fernandez 1995) as well as negative correlations with salinity (Cowan et al. 1996), the present study did not show such relationships. The magnitude of the benthic fluxes are also influenced by the sediment redox state; several studies have shown that the release of phosphate to the overlying water is reduced in oxygenated sediments or even that phosphate is taken up by sediments (Sundby et al. 1986, Skoog et al. 1996, Viktorsson et al. 2012) due to phosphate adsorption to iron and

manganese oxyhydroxides within the sediment. On the other hand, phosphate may be released to the water column if the metal is reduced under anoxic conditions (Sundby et al. 1992). Thus, in spite of expecting phosphorus adsorption in surface sediments due to the oxic conditions of bottom waters in the Ría de Vigo, we have always observed a positive flux of phosphate towards the overlying waters, suggesting that phosphorus adsorption does not seem to be a dominant process in these sediments. Additionally, a value of 114 for the  $-\Delta\text{O}_2 : \Delta\text{P}$  benthic flux ratio indicates that adsorption/desorption processes might be slightly balanced towards desorption and there might be an additional  $\text{O}_2$  consumption for reoxidation of reduced inorganic forms produced by anaerobic respiration in the sediments. Mohamed et al. (2011), analysing the magnetic properties of sediments from the Ría de Vigo, found that the suboxic part of the sediment, characterized by a progressive reduction of magnetic iron oxides increasing sulphate reduction, lies closer to the surface towards the inner parts of the Ría de Vigo, being about 1 cm below the surface sediment close to our study site (Santos-Echeandia et al. 2009). Based on this vertical zonation, we could expect little phosphate retention in the upper part of the sediment due to iron oxide reduction. Thus, we conclude that oxygenated overlying water would favour the aerobic mineralization of recent organic matter arriving to the sediment, releasing phosphate to the water column. Moreover, the proximity of reducing conditions to the upper millimeters of the sediment would prevent phosphate retention and also may enhance phosphate efflux through the reduction of Mn and Fe oxides which, on the other hand, would favour reoxidation of reduced inorganic compounds with an additional oxygen consumption.

Benthic silicate fluxes were mainly controlled by sea-bottom water temperature and the amount of  $\text{bSiO}_2$  settled into the sediment traps. Dissolution rates of silica exponentially increases with temperature as it is a physically rather than biologically driven process (Conley & Malone, 1992). Hurd & Birdwhistell (1983) found a 50-fold increase in the opal dissolution velocity between 0 and 25°C. Only temperature explained 46% of the variability in the silicate fluxes (Table 4), which is very close to the value of 48% obtained by Cowan et al. (1996), and taking into account the  $\text{bSiO}_2$  vertical flux, the explained variability increases to 72%. Moreover, any process removing organic matter from the opal surfaces, like microbial degradation or grazing, exposes silica directly to seawater, enhancing its dissolution

rate (Bidle & Azam 1999) and therefore the benthic silicate fluxes. The high correlation of silicate benthic fluxes with benthic fluxes of oxygen and ammonium support this idea.

Evaluating the importance of benthic fluxes on the biogeochemical cycles of the nutrients in the Ría de Vigo, we estimated that on annual basis, benthic remineralization provides 1300 t N  $\text{yr}^{-1}$  and 255 t P  $\text{yr}^{-1}$  of inorganic nitrogen and inorganic phosphorus, respectively. In these calculations, we have assumed the same benthic rates for all the surface sediment of the Ría de Vigo (117 km<sup>2</sup>, not taking into account the innermost part of the Ría, San Simón Bay, Fig. 1). On the other hand, Prego (1993, 1994) obtained an average influx of inorganic nitrogen and phosphate into the Ría from upwelled waters of 3000 t N  $\text{yr}^{-1}$ , and 350 t P  $\text{yr}^{-1}$  by means of a box model. Reported inputs of inorganic nitrogen from continental runoff are 160 t N  $\text{yr}^{-1}$  (Gago et al. 2005) and in the range of 8 t P  $\text{yr}^{-1}$  (Gago et al. 2005) to 80 t P  $\text{yr}^{-1}$  (Prego 1993) for phosphate. Based on all these data, we estimate that benthic fluxes account for ~43% of the nitrogen provided from upwelled waters and ~41% of the total inorganic nitrogen entering the Ría from outside waters. Regarding phosphate, sediment remineralization would contribute to ~60% of the total phosphate that the Ría receives and ~72% of the upwelled phosphate.

## CONCLUSIONS

Muddy sediments of the Ría de Vigo play an important role in the degradation of organic material supplied from the water column, and subsequently, in the supply of inorganic nutrients from the sediment back to the water column. Apart from winter, benthic fluxes did not show seasonal differences; instead, benthic fluxes in the Ría de Vigo appeared to be highly influenced by sea-bottom temperature, which is modulated to some extent by upwelling/downwelling oceanographic pulses. Benthic fluxes tend to respond on a short time scale to these processes. The amount and quality of the organic matter deposited on the sediments have also been shown to control the dynamics of benthic fluxes in the Ría de Vigo. The high correlation between benthic fluxes of phosphate, silicate and ammonium and the sediment oxygen uptake pointed to the importance of the aerobic respiration processes in the remineralization. In contrast, nitrate benthic fluxes acted in a different way; they were highly influenced by seabed concentration of dissolved oxygen and the N-nutrients nitrite and

nitrate. Denitrification seems to be a key process in the uptake of nitrate by the sediments. There is a clear need for further studies of properties of the sediment such as labile organic matter content and benthic macrofauna, which may also be important factors controlling the magnitude of benthic fluxes, as has been found in other coastal studies.

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