

## Evaluation of ammonium and phosphate release from intertidal and subtidal sediments of a shallow coastal lagoon (Ria Formosa – Portugal): a modelling approach

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**Abstract** During an annual cycle, overlying water and sediment cores were collected simultaneously at three sites (Tavira, Culatra and Ramalhete) of Ria Formosa's intertidal muddy and subtidal sandy sediments to determine ammonium, nitrates plus nitrites and phosphate. Organic carbon, nitrogen and phosphorus were also determined in superficial sediments. Ammonium and phosphate dissolved in porewater were positively correlated with temperature ( $P < 0.01$ ) in muddy and sandy sediments, while the nitrogen-oxidized forms had a negative correlation ( $P < 0.02$ ) in muddy

sediments probably because mineralization and nitrification/denitrification processes vary seasonally. Porewater ammonium profiles evidenced a peak in the top-most muddy sediment (380  $\mu\text{M}$ ) suggesting higher mineralization rate when oxygen is more available, while maximum phosphate concentration (113  $\mu\text{M}$ ) occurred in the sub-oxic layer probably due to phosphorus desorption under reduced conditions. In organically poor subtidal sandy sediments, nutrient porewater concentrations were always lower than in intertidal muddy sediments, ranging annually from 20  $\mu\text{M}$  to 100  $\mu\text{M}$  for ammonium and from 0.05  $\mu\text{M}$  to 16  $\mu\text{M}$  for phosphate. Nutrient diffusive fluxes predicted by a mathematical model were higher during summer, in both muddy (104  $\text{nmol cm}^{-2} \text{d}^{-1}$ — $\text{NH}_4^+$ ; 8  $\text{nmol cm}^{-2} \text{d}^{-1}$ — $\text{HPO}_4^{2-}$ ) and sandy sediments (26  $\text{nmol cm}^{-2} \text{d}^{-1}$ — $\text{NH}_4^+$ ; 1  $\text{nmol cm}^{-2} \text{d}^{-1}$ — $\text{HPO}_4^{2-}$ ), while during lower temperature periods these fluxes were 3–4 times lower. Based on simulated nutrient effluxes, the estimated annual amount of ammonium and phosphate exported from intertidal areas was three times higher than that released from subtidal areas (22  $\text{ton year}^{-1}$ — $\text{NH}_4^+$ ; 2  $\text{ton year}^{-1}$ — $\text{HPO}_4^{2-}$ ), emphasizing the importance of tidal flats to maintain the high productivity of the lagoon. Global warming scenarios simulated with the model, revealed that an increase in lagoon water temperature only produces significant variations ( $P < 0.05$ ) for  $\text{NH}_4^+$  in porewater and consequent diffusive fluxes, what

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will probably affect the system productivity due to a N/P ratio unbalance.

**Keywords** Ammonium · Coastal lagoon · Geochemical processes · Modelling · Phosphate · Ria Formosa

## Introduction

In shallow coastal ecosystems, most part of particulate organic matter reaching bottom sediments is mineralised in the top sediment layer. As diagenetic processes depend on organic matter, temperature, oxygen availability and sediment grain size (Lerat et al. 1990; Kristensen 1993; Forja et al. 1994; Chapelle 1995; Asmus et al. 2000), benthic fluxes are influenced by these environmental factors (Nowicki and Nixon 1985; Van Raaphorst et al. 1992; Kristensen 1993; Wilson and Brennan 2004) leading to a spatial and temporal variability in sediment-water nutrient exchanges in most coastal environments (Lerat et al. 1990; Forja et al. 1994; Vidal and Morgu  1995).

Ammonium, the predominant form of inorganic nitrogen found in marine sediments, often differ from steady-state conditions reflecting the balance between production through organic matter mineralization (Bally et al. 2004), nitrification/denitrification (Vidal and Morgu  1995) and consumption by primary producers living near the sediment-water interface (Nian-Zhi and Wang 1994). Insufficient oxygen diffusion through the sediment, mainly in muddy areas, reduces rates of nitrification and may explain low concentrations of nitrates found in these sediments. Nitrification/denitrification processes are also temperature-dependent. Thus, during the period of higher temperature, denitrification of nitrate to gaseous forms of nitrogen ( $N_2$  and  $N_2O$ ) and ammonium may contribute to drop nitrate levels in porewater (Cartaxana et al. 1999).

Phosphorus reacts with a wide variety of surfaces, being taken up and released from biogenic and abiogenic particles (Van Raaphorst and Kloosterhuis 1994). The retention/release of phosphate in marine systems is controlled by temperature and dissolved oxygen as referred in several studies (Slomp et al. 1998; Asmus et al.

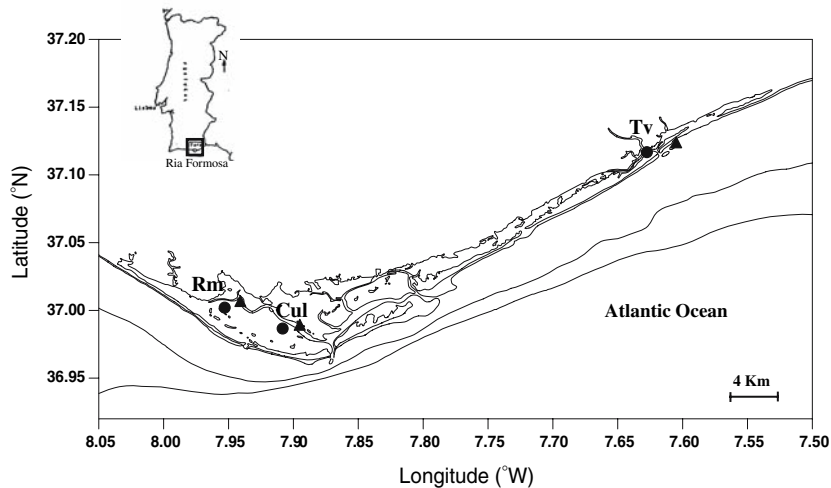
2000). Phosphorus accumulated in solid phase during winter, partially due to P-sorption onto iron oxides, is released to porewater and transferred to the overlying water in periods of higher temperature due to reducing sediment conditions (Ohtake et al. 1984; Van Raaphorst and Kloosterhuis 1994). Sorption of phosphate in aerobic sediment layers can temporarily trap phosphate, thus affecting the productivity of marine systems (Kristensen 1993; Asmus et al. 2000; Benitez-Nelson 2000; Aigars 2001).

In Ria Formosa, a shallow coastal lagoon with reduced freshwater inputs and intense water mass exchanges with the sea (40–75% during each semi-diurnal tidal cycle), bottom sediments may contribute largely for the lagoon water nutrient enrichment and consequently for the high productivity of this system (Falc o and Vale 2003). The aim of the present study was to quantify the annual amount of ammonium and phosphate exported from intertidal muddy and subtidal sandy areas in order to evaluate their contribution to the lagoon nutrient budget. This study is particularly important since little information is available for N and P cycling of organic-poor subtidal sandy sediments (Van Raaphorst et al. 1990). In order to achieve our goal, field data was used to calibrate and validate a mathematical model based on geochemical processes (sedimentation, mineralization, nitrification/denitrification, P-sorption/desorption and molecular diffusion), which predicts the daily sediment-water transport of ammonium and phosphate from these areas, allowing a more realistic evaluation of their contribute to the lagoon N and P cycles.

## Material and methods

### Study area

Ria Formosa is a shallow mesotidal coastal lagoon located at the south coast of Portugal, with a wet area of 105 km<sup>2</sup> (Fig. 1). The lagoon, constituted by several channels of coarse sand sediments and an extensive intertidal area (around 50% of the total area) of mud and muddy-sand flats (Falc o and Vale 1990), is separated from the Atlantic Ocean by several barrier islands. Tidal amplitude



**Fig. 1** Ria Formosa lagoon. Location of sampling sites: Ramalhete (Rm), Culatra (Cul) and Tavira (Tv): muddy stations (●); sandy stations (▲)

varies from 0.6 m to 3.5 m, implying that a rather intense exchange of water mass (40–75%) occurs at each tide (Sprung 1994) and large intertidal areas are exposed for several hours at each semi-diurnal tidal period. Fresh water input to the lagoon is negligible and salinity remains close to 36 except during sporadic and short periods of winter run-off (Falcão and Vale 1990).

### Field sampling

Sediment cores and overlying water (three replicates) were collected monthly throughout the year, at three sampling sites (Tavira-Tv, Culatra-Cul and Ramalhete-Rm). Samples were collected in intertidal muddy stations ( $Tv_m$ ,  $Cul_m$ ,  $Rm_m$ ) and in subtidal sandy stations ( $Tv_s$ ,  $Cul_s$ ,  $Rm_s$ ). At each station, six sediment cores (5 cm of diameter and 5 cm in length) were sampled. Cores were divided in two groups of three replicates: one for nitrogen (N) analysis and the other for phosphorus (P) analysis. Sediment cores of muddy stations were sliced in 0.5 cm sediment layers while sandy cores were sliced in 2 cm layers. Samples were immediately stored in polyethylene vials avoiding air presence by filling up completely. In order to eliminate any sediment oxidation, each sediment layer for P analysis was preserved under  $N_2$  atmosphere *in loco*. Sediment samples were transported to the laboratory under refrigerated

conditions. Overlying water was collected 2 cm above the sediment surface directly with pre-cleaned syringes. In each sampling site, suspended particles were also collected using a sediment-trap with six PVC tubes (5 cm of diameter, 50 cm in length).

### Laboratory analysis

Samples of overlying water were filtered through 0.45  $\mu\text{m}$  Millipore filters and stored at 4°C until analysis. Sediment samples for porewater analysis were centrifuged for 30 min at 3000 rpm to separate the solid fraction. Ammonium ( $\text{NH}_4^+$ ), nitrate plus nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) and phosphate ( $\text{HPO}_4^{2-}$ ) in porewater and overlying water were determined by colorimetry (Grasshoff 1983) using a “Skalar” autoanalyser with a detection limit of 0.2  $\mu\text{M}$  for  $\text{NH}_4^+$  and 0.05  $\mu\text{M}$  for  $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{HPO}_4^{2-}$ . Total and inorganic carbon, and nitrogen were determined in solid samples previously dried at 80°C until a constant weight was reached and grounded to a fine powder, using a CNH analyser “NC 2500 CE instruments” with acetanilide as reference material (Byers et al. 1978). Total phosphorus was determined by digestion “Büchi 430 digester” with HCl (1 N) during 20 min at 200°C according to Andersen (1976). Inorganic phosphorus was sequentially extracted according to Hosomi and Sudo (1982). Sediment granulometry was

determined by wet separation of muddy from sandy fractions with a sieve of 63  $\mu\text{m}$ . Afterwards, each fraction was dried and weighted. Grain size of the sandy fraction was measured through several sieves from 2 mm to 63  $\mu\text{m}$  set in a stirring. Porosity was calculated from sediment weight loss at 105°C.

### Model development

The transport of  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  across the sediment–water interface was modelled taking into account three major processes: sedimentation, mineralization and molecular diffusion. The  $\text{NH}_4^+$  model also considers nitrification and denitrification processes, whereas to simulate  $\text{HPO}_4^{2-}$  porewater concentrations and diffusive fluxes, sorption and desorption processes were taken into account, allowing sediments to act not only as a source but also as a sink for this nutrient.

Although model formulations were similar to those described in Chapelle (1995), some adaptations were made to account for the semi-diurnal tidal inundation of intertidal areas. Tide level (m)

was considered as one of the model forcing functions being simulated according to the following equation:  $\text{Tide\_level} = 1.5 + 1.5 \cdot \text{SIN}(\text{hour} - 6/2) / (6/2) \cdot \pi/2$ .

### Formulation of geochemical processes

To simulate the different geochemical processes in intertidal muddy areas and subtidal sandy areas, a suitable set of values for each type of sediment was set up as model parameters (Table 1).

### Organic matter sedimentation

Particulate organic matter (POM) settled in the upper sediment layer is mineralised, recycling nutrients in porewater (Bally et al. 2004). The deposition rate of POM was considered constant over time, assuming values of 0.5  $\mu\text{g g}^{-1} \text{d}^{-1}$  for particulate organic nitrogen (PON) and particulate organic phosphorus (POP) in muddy sediments, according to an estimation based on data from the present study (Table 3), of PON and POP concentrations in superficial sediments and

**Table 1** Model parameters

Parameter	Definition	Value	Reference
$\text{minN}_s$	Benthic mineralization of organic N at 0°C ( $\text{d}^{-1}$ )	0.005	Billen and Lancelot (1988)
$K_T$	Temperature increasing rate ( $^{\circ}\text{C}^{-1}$ )	0.07	Ruardji and Van Raaphorst (1994)
$\text{minP}_s$	Benthic mineralization of organic P at 0°C ( $\text{d}^{-1}$ )	0.005	Van der Molen (1991)
$K_{\text{minO}_2}$	Half-saturation coefficient for $\text{O}_2$ limitation of mineralization ( $\text{g m}^{-3}$ )	0.5	Henriksen and Kemp (1988)
$k_{\text{nit}}$	Nitrification rate at 0°C ( $\text{d}^{-1}$ )	0.2	Henriksen and Kemp (1988)
$k_{\text{nitO}_2}$	Half-saturation coefficient for $\text{O}_2$ limitation of nitrification ( $\text{g m}^{-3}$ )	5 (mud); 9 (sand)	Model calibration
$k_{\text{denit}}$	Denitrification rate at 0°C ( $\text{d}^{-1}$ )	0.3	Henriksen and Kemp (1988)
$k_{\text{denitO}_2}$	Half-saturation coefficient for $\text{O}_2$ limitation of denitrification ( $\text{g m}^{-3}$ )	3 (mud); 4 (sand)	Model calibration
$\phi_{\text{mud}}$	Porosity of muddy sediments	0.6	Field data
$\phi_{\text{sand}}$	Porosity of sandy sediments	0.35	Field data
$D_{\text{m}}[\text{NH}_4^+]$	Diffusion coefficient for ammonium in sediment ( $\text{cm}^{-2} \text{s}^{-1}$ )	$18 \times 10^{-6}$	Aller (1980)
$D_{\text{m}}[\text{HPO}_4^{2-}]$	Diffusion coefficient for phosphates in sediment ( $\text{cm}^{-2} \text{s}^{-1}$ )	$7 \times 10^{-6}$	Aller (1980)
$k_a$	Adsorption rate in oxic conditions ( $\text{d}^{-1}$ )	200 (mud); 60 (sand)	Furumai et al. (1989); model calibration
$P_{\text{max}}$	Maximum P adsorption capacity for sediment ( $\mu\text{g g}^{-1}$ )	500 (mud); 500 (sand)	Field data
$k_d$	Desorption rate ( $\mu\text{g g}^{-1} \text{d}^{-1}$ )	80 (mud); 110 (sand)	Furumai et al. (1989); model calibration
$k'_a$	Adsorption rate in anoxic conditions ( $\text{d}^{-1}$ )	40 (mud); 40 (sand)	Van Raaphorst et al. (1992); model calibration

in particles deposited in the sediment trap. In sandy-sediments, PON and POP deposition rates were considered to be respectively, 0.4 and 0.3  $\mu\text{g g}^{-1} \text{d}^{-1}$ .

### Mineralization

In the present work, this process was modelled as a function of temperature (using monthly time series) and of dissolved oxygen. Oxygenation of the upper sediment layer is determined by the depth penetration of oxygen into sediment and varies semi-diurnally with tide (Brotas et al. 1990). In this lagoon,  $\text{O}_2$  concentrations of 0.5 and 0.1  $\text{g m}^{-3}$  were measured in intertidal muddy sediments during the flood and ebb tide respectively, while at subtidal sandy sediments oxygen in porewater remained constant over time (0.5  $\text{g m}^{-3}$ ).

Mineralization rates ( $\mu\text{mol dm}^{-3} \text{d}^{-1}$ ) followed a first-order equation (Chapelle 1995) dependent on temperature and oxygen:

$$N_{\min} = \min N_s \times e^{(kT \times T)} \times N_{\text{os}} \times f(\text{O}_2)$$

$$P_{\min} = \min P_s \times e^{(kT \times T)} \times P_{\text{os}} \times f(\text{O}_2)$$

where  $\min N_s$  and  $\min P_s$  are respectively the benthic mineralization rates of organic nitrogen and phosphorus, at 0°C ( $\text{d}^{-1}$ );  $K_T$  is the temperature increasing rate ( $^{\circ}\text{C}^{-1}$ );  $T$  is temperature ( $^{\circ}\text{C}$ );  $N_{\text{os}}$  and  $P_{\text{os}}$  are the PON and POP sediment concentrations ( $\mu\text{g g}^{-1} \text{dw}$ ) and  $f(\text{O}_2)$  is the oxygen limitation expressed by a Michelis–Menten equation:

$$f(\text{O}_2) = \frac{\text{O}_2}{\text{O}_2 + k_{\min} \text{O}_2}$$

where  $k_{\min} \text{O}_2$  is the half-saturation coefficient for mineralization ( $\text{g m}^{-3}$ ).

### Nitrification/Denitrification

Nitrification was described by a first-order equation according to Ruardji and Van Raaphorst (1994):

$$N_{\text{nitrif}} = k_{\text{nit}} \times \text{NH}_{4\text{s}} \times e^{(kT \times T)} \times g(\text{O}_2)$$

$k_{\text{nit}}$  is the nitrification rate ( $\text{d}^{-1}$ ) at 0°C;  $\text{NH}_{4\text{s}}$  is the ammonium concentration in porewater ( $\mu\text{mol dm}^{-3}$ );  $K_T$  is the temperature increasing rate ( $^{\circ}\text{C}^{-1}$ ) and  $T$  is temperature ( $^{\circ}\text{C}$ ). The oxygen effect on this process is expressed in the equation by  $g(\text{O}_2)$  term:

$$g(\text{O}_2) = \frac{\text{O}_2}{\text{O}_2 + k_{\text{nit}} \text{O}_2}$$

where  $k_{\text{nit}} \text{O}_2$  is the half-saturation coefficient for  $\text{O}_2$  limitation of nitrification ( $\text{g m}^{-3}$ ).

Nitrate produced by nitrification is then reduced to  $\text{NH}_4^+$  through denitrification. This process follows a first order kinetics and is also temperature and oxygen dependent as shown by the Billen and Lancelot (1988) equation:

$$N_{\text{denit}} = k_{\text{denit}} \times \text{NO}_{3\text{s}} \times e^{(kT \times T)} \times h(\text{O}_2)$$

The influence of oxygen on denitrification can be expressed by the following formula:

$$h(\text{O}_2) = \frac{\text{O}_2}{\text{O}_2 + k_{\text{denit}} \text{O}_2}$$

where  $k_{\text{denit}} \text{O}_2$  is the half-saturation coefficient for  $\text{O}_2$  limitation of denitrification ( $\text{g m}^{-3}$ ).

### Adsorption/Desorption

The kinetics of phosphorus adsorption ( $P_{\text{adsorp}}$ ) and desorption ( $P_{\text{desorp}}$ ) processes was formulated according to Furumai et al. (1989):

$$P_{\text{adsorp}} = k_a \times (1 - P_{\text{ads}}/P_{\text{max}}) \times P_{\text{pw}}$$

$$P_{\text{desorp}} = k_d \times (P_{\text{ads}}/P_{\text{max}})$$

where  $k_a$  is the adsorption rate ( $\text{d}^{-1}$ ),  $k_d$  is the desorption rate ( $\mu\text{mol dm}^{-3} \text{d}^{-1}$ ),  $P_{\text{ads}}$  is the inorganic phosphorus adsorbed to the sediment ( $\mu\text{g g}^{-1} \text{dw}$ ),  $P_{\text{pw}}$  is the inorganic phosphorus in porewater ( $\mu\text{M}$ ) and  $P_{\text{max}}$  is the maximum P adsorption capacity by the sediment ( $\mu\text{g g}^{-1} \text{dw}$ ). When oxygen in porewater drops below a threshold value of 0.1  $\text{g m}^{-3}$ , the sediment is assumed to be anoxic. The same formulations were applied for

oxic and anoxic situations however different adsorption rates were assumed.

### Molecular diffusion

Nutrients dissolved in the upper sediment layer are released to the water column according to concentration gradients between sediment and overlying water. Ammonium and phosphate diffusive fluxes across the sediment–water interface ( $F$ ) were modelled according to the Fick's first law of diffusion (Berner 1980):

$$F = -\phi D_s (C_o - C_p) / (\Delta x)$$

where  $\phi$  is the porosity,  $D_m$  is the molecular diffusion coefficient ( $D_m = 18 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{NH}_4^+$ ;  $D_m = 7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{HPO}_4^{2-}$  in Aller 1980),  $C_o$  is the  $[\text{NH}_4^+]$  or  $[\text{HPO}_4^{2-}]$  in overlying water,  $C_p$  is the  $[\text{NH}_4^+]$  or  $[\text{HPO}_4^{2-}]$  in porewater and  $\Delta x$  is the distance across the interface where concentrations were measured (2 cm).

### Model implementation

The model was implemented in *Stella*<sup>TM</sup> 5.1.1. Nutrient concentrations and diffusive fluxes were simulated over a period of 1 year at the scale of  $1 \text{ cm}^2$ . After determination of initial and boundary conditions and input of model parameters, fluxes and porewater concentrations were computed over time using Runge-Kutta fourth-order integration with a time step of 1 h.

### Statistical analysis

The existence of significant seasonal differences on nutrient concentrations were tested using the

non-parametric Wilcoxon test of the *Statistica 3.2. software*.

The overall correspondence between observed and predicted porewater nutrient concentrations was analysed with a Model II linear regression analysis, following Laws and Archie (1981), with the major axis regression method as recommended by Mesplé et al (1996) and described in Sokal and Rohlf (1995). The significance of the slopes and  $y$ -intercepts obtained were tested as well as the significance of the variance explained by the model, using ANOVA. When the slope is not significantly different (s.d.) from one and the  $y$ -intercept not s.d. from zero, there is a good agreement between model and observations. When the  $y$ -intercept is s.d. from zero, there is a constant difference between model and observations. When the slope is not s.d. from one but s.d. from zero, the differences between model and observations are proportional to the value of the variable, but the model may explain a significant proportion of total variance.

## Results

### Sediment characterization

Intertidal muddy sediments were mostly constituted by silt and clay (<0.063 mm) while subtidal sandy sediments have a minor fraction of these particles (0.01%), being mainly fine sands. Sediment granulometry agrees with its porosity, which was two times higher in muddy sediments (Table 2). Organic carbon, nitrogen and phosphorus in the upper layer of muddy sediments were clearly higher than in sandy sediments, mainly during summer (Table 3).

**Table 2** Grain size (in percentage) and porosity of superficial sediments (0–2 cm) from muddy and sandy stations

	Grain size (%)			Porosity
	Gross sands >2 (mm)	Fine sands 0.5–0.063 (mm)	Silt + clay <0.063 (mm)	
Muddy-sediments (0–2 cm)	8	36	56	0.64 ± 0.021
Sandy-sediments (0–2 cm)	4	96	0.01	0.32 ± 0.033

## Intertidal muddy sediments

*Ammonium, nitrate+nitrite and phosphate in overlying water and porewater*

Ammonium dissolved in overlying water varied annually from 0.2  $\mu\text{M}$  to 4  $\mu\text{M}$  while in porewater, concentrations were 2 to 3 orders of magnitude higher, reaching a maximum of 380  $\mu\text{M}$  in the upper sediment layer (Fig. 2). In porewater, this nutrient exhibited a clear seasonal pattern, with values significantly higher during the warmer period (Wilcoxon test;  $P < 0.01$ ). A significant exponential fit was obtained between  $\text{NH}_4^+$  in porewater and water temperature ( $T$ ):  $[\text{NH}_4^+] = 10.904 * e^{(0.129 * T)}$ ;  $r^2 = 0.89$ ; ( $P < 0.01$ ).

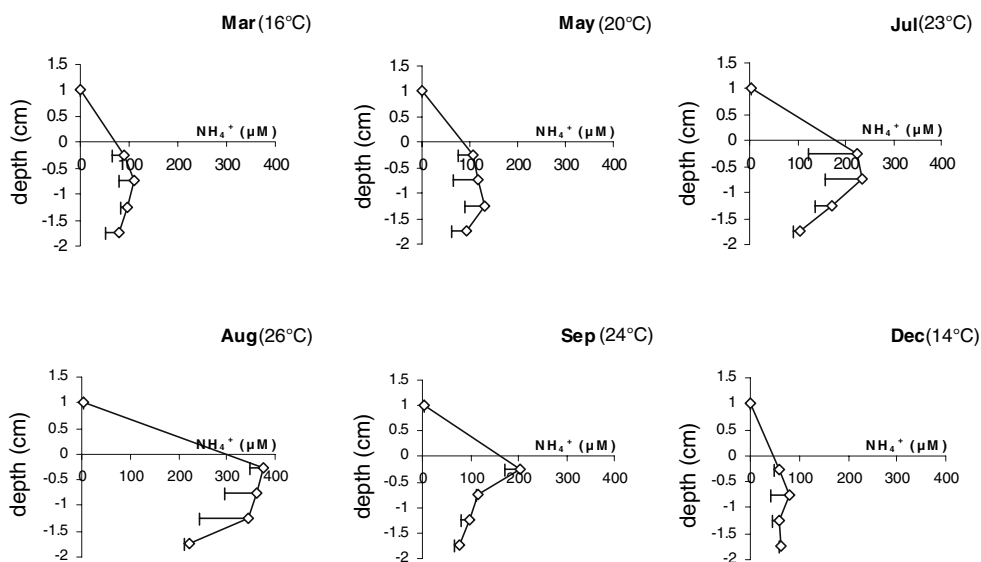
Conversely, nitrogen oxidized forms ( $\text{NO}_3^- + \text{NO}_2^-$ ) dissolved in porewater along sediment profiles reached the maximum values in December (46–125  $\mu\text{M}$ ), contrasting with those obtained in July–August (Fig. 3). Thus, seasonal variability of  $\text{NO}_3^- + \text{NO}_2^-$  may be traduced by the significant inverse linear relationship between porewater concentrations and water temperature:  $[\text{NO}_3^- + \text{NO}_2^-] = -0.1387T + 23.7$ ;  $r^2 = 0.6$ ; ( $P < 0.02$ ).

Low  $\text{HPO}_4^{2-}$  concentrations in overlying water (0.2–2.3  $\mu\text{M}$ ) contrasted with those obtained in porewater, which were 1 to 2 orders of magnitude higher, reaching the maximum (113  $\mu\text{M}$ ) in deeper layers (Fig. 4). When temperature reached the peak (August),  $\text{HPO}_4^{2-}$  exhibited large variability

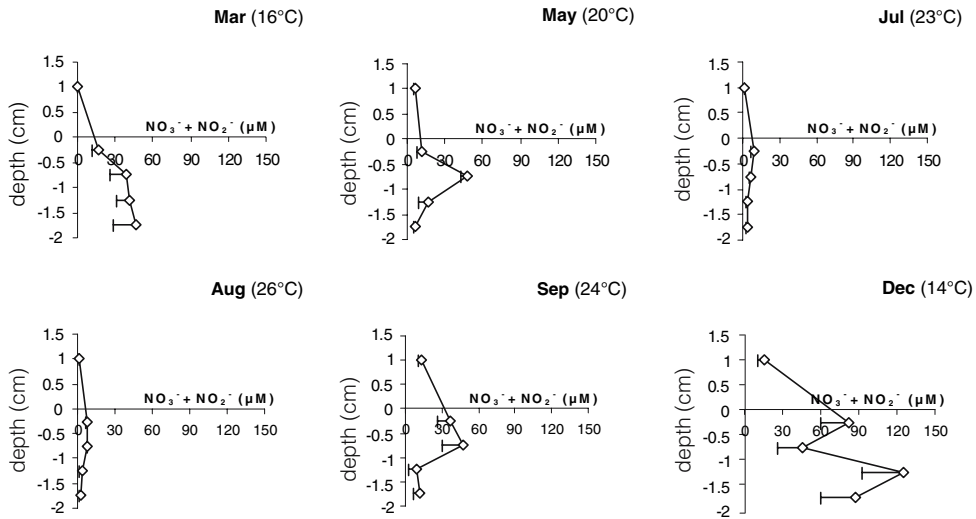
**Table 3** Mean percentage ( $\pm$ s.d.) of total organic carbon (TOC), total organic nitrogen (TON) and total organic phosphorus (TOP) in superficial sediments (0–2 cm) of

muddy and sandy stations and, in particles deposited in sediment-trap: summer and winter values

		TOC ( $\mu\text{mol g}^{-1}$ )		TON ( $\mu\text{mol g}^{-1}$ )		TOP ( $\mu\text{mol g}^{-1}$ )	
		Summer	Winter	Summer	Winter	Summer	Winter
Superficial sediments	Mud	1477 $\pm$ 450	1038 $\pm$ 86	54 $\pm$ 35	46 $\pm$ 7.5	4.9 $\pm$ 2.29	1.3 $\pm$ 0.62
	Sand	708 $\pm$ 247	417 $\pm$ 12	6.5 $\pm$ 2.5	1.1 $\pm$ 0.30	3.6 $\pm$ 0.99	1.8 $\pm$ 0.50
Particles in sediment-trap		1790 $\pm$ 110	1660 $\pm$ 300	176 $\pm$ 91	91 $\pm$ 26	10 $\pm$ 4.7	3.1 $\pm$ 1.23



**Fig. 2** Average ( $\pm$ s.d.)  $\text{NH}_4^+$  concentrations in overlying water and along porewater profile (0–2 cm) of muddy stations ( $\text{Rm}_m$ ,  $\text{Cul}_m$ ,  $\text{Tv}_m$ ) in March, May, July, August, September and December



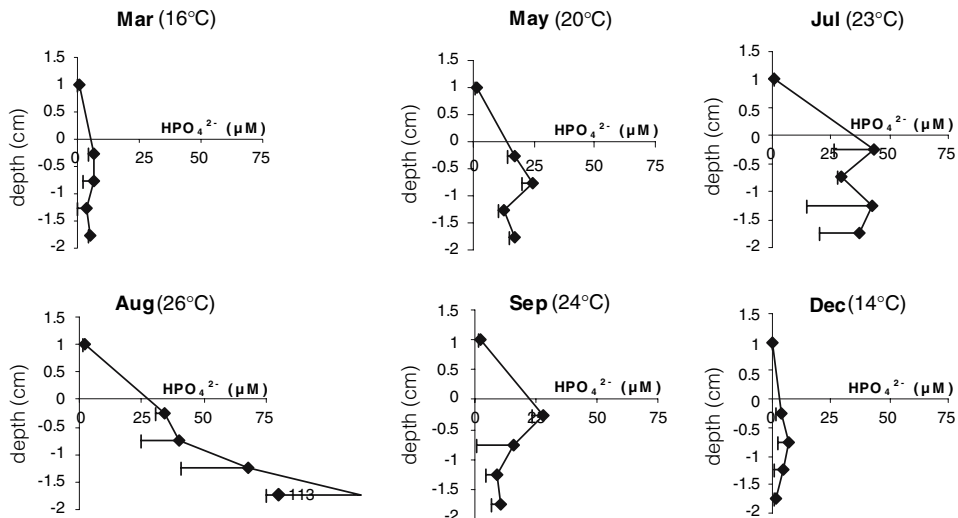
**Fig. 3** Average (-s.d.)  $\text{NO}_3^- + \text{NO}_2^-$  concentrations in overlying water and along porewater profile (0–2 cm) of muddy stations ( $\text{Rm}_m$ ,  $\text{Cul}_m$ ,  $\text{Tv}_m$ ) in March, May, July, August, September and December

along porewater profiles, while during the period of lower temperature  $\text{HPO}_4^{2-}$  varied within a narrow range (1.4–6.7  $\mu\text{M}$ ). During the warmer period,  $\text{HPO}_4^{2-}$  concentrations were significantly higher than in winter (Wilcoxon test;  $P < 0.01$ ) as it can be accurately described by the exponential equation:  $[\text{HPO}_4^{2-}] = 0.250 * e^{(0.208 * T)}$ ;  $r^2 = 0.95$  ( $P < 0.01$ ).

Subtidal sandy sediments

*Ammonium, nitrate+nitrite and phosphate in overlying water and porewater*

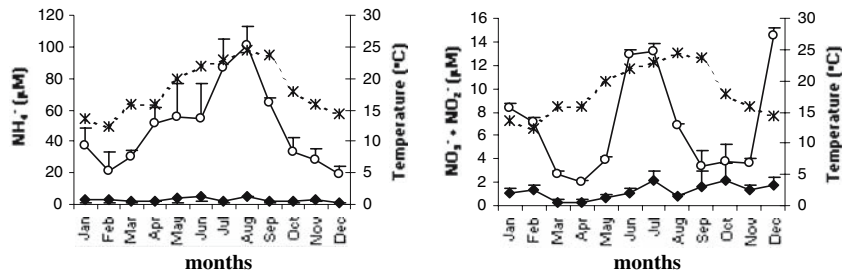
Ammonium in overlying water varied within a narrow range in all stations (0.2–3.2  $\mu\text{M}$ ), while in



**Fig. 4** Average (-s.d.)  $\text{HPO}_4^{2-}$  concentrations in overlying water and along porewater profile (0–2 cm) of muddy stations ( $\text{Rm}_m$ ,  $\text{Cul}_m$ ,  $\text{Tv}_m$ ) in March, May, July, August, September and December

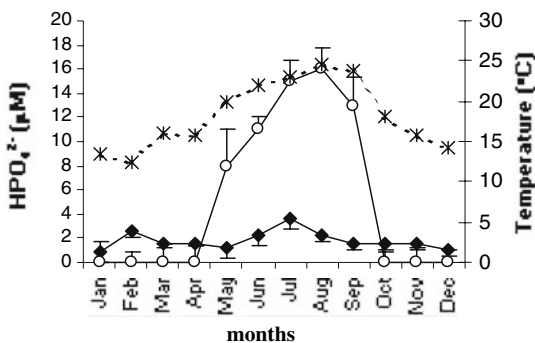


**Fig. 5** Annual variation of average (+s.d.)  $\text{NH}_4^+$  and  $\text{NO}_3^- + \text{NO}_2^-$  concentrations in overlying water (●) and porewater (○) of superficial sediments (0–2 cm) of sandy stations (Rm<sub>s</sub>, Cul<sub>s</sub>, Tv<sub>s</sub>); Water temperature (\*)



porewater, concentrations were up to 2–3 orders of magnitude higher (19.4–110 μM), as shown in Fig. 5. As for intertidal muddy sediments, the clear seasonal pattern described by porewater  $\text{NH}_4^+$  concentrations may be explained by a significant exponential relationship between

$\text{NH}_4^+$  in porewater and water temperature:  $[\text{NH}_4^+] = 9.344 * e^{(0.09 * T)}$ ;  $r^2 = 0.64$  ( $P < 0.02$ ). For sandy sediment, no relationship was found between  $\text{NO}_3^- + \text{NO}_2^-$  and temperature since higher concentrations ( $\approx 12 \mu\text{M}$ ), were reached in both winter and summer (Fig. 5).



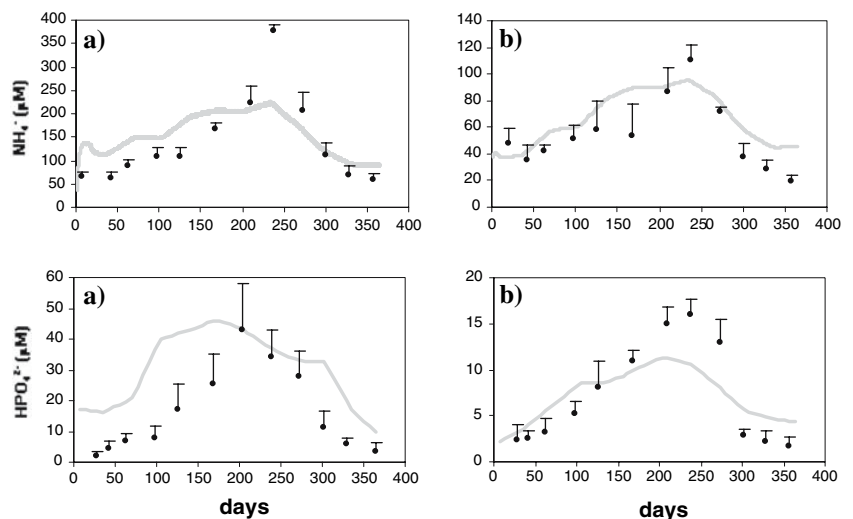
**Fig. 6** Annual variation of average (+s.d.)  $\text{HPO}_4^{2-}$  concentrations in overlying water (●) and porewater (○) of superficial sediments (0–2 cm) of sandy stations (Rm<sub>s</sub>, Cul<sub>s</sub>, Tv<sub>s</sub>); Water temperature (\*)

Phosphate in overlying water remained low throughout the year (0.3–1.7 μM), contrasting with porewater concentrations that varied from 1.7 μM to 16 μM (Fig. 6). A sharp increase of  $\text{HPO}_4^{2-}$  in porewater occurred when water temperature rose above 22°C, while the lowest levels were recorded in December (14°C). Seasonal variation of  $\text{HPO}_4^{2-}$  in porewater is accurately described by the equation:  $[\text{HPO}_4^{2-}] = 0.177 * e^{(0.184 * T)}$ ;  $r^2 = 0.86$  ( $P < 0.01$ ).

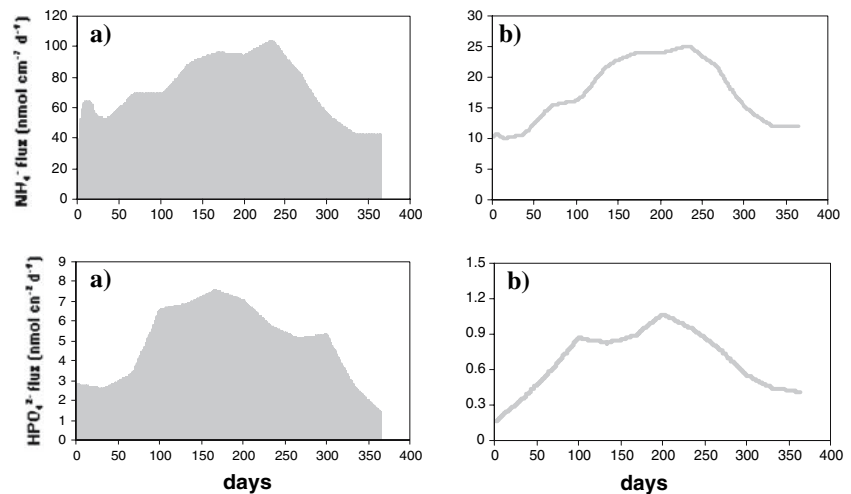
Model simulations

The slope of Model II regressions between predicted and measured porewater nutrient values was not significantly different from one and

**Fig. 7** Simulated (—) and average (+s.d.) field (●)  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  porewater concentrations in muddy (a) and sandy (b) sediments, over the year



**Fig. 8** Simulated  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  diffusive fluxes in muddy (a) and sandy (b) sediments over the year



the y-intercept was not s.d. from zero ( $P < 0.05$ ) in the cases of  $\text{NH}_4^+$  porewater concentrations (Fig. 7) in sandy sediments, demonstrating the good model fit to observed data. In all remaining cases both the slopes and the y-intercepts differed significantly from zero. However, the variance explained by the model was significant ( $P < 0.01$ ) for all simulations, suggesting that, even though the model could under or over estimate observed data, it explained a significant part of data variance. Furthermore, the difference between predicted and observed average values was generally less than 10%.

As expected from porewater nutrient concentrations simulated by the model,  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  diffusive fluxes of muddy and sandy sediments exhibited a clear seasonal variation (Fig. 8). In muddy sediments,  $\text{NH}_4^+$  fluxes varied from 18 nmol cm<sup>-2</sup> d<sup>-1</sup> to 104 nmol cm<sup>-2</sup> d<sup>-1</sup>, while in sandy sediments this variation was smoother (10–26 nmol cm<sup>-2</sup> d<sup>-1</sup>). Regarding  $\text{HPO}_4^{2-}$  fluxes, values varied from 0.8 nmol cm<sup>-2</sup> d<sup>-1</sup> to 8 nmol cm<sup>-2</sup> d<sup>-1</sup> in muddy sediments, while in sandy sediments the range was narrower (0.2–1.1 nmol cm<sup>-2</sup> d<sup>-1</sup>).

Several scenarios of global warming were simulated with the model in order to predict the effects on  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  cycling. Changes of a 2°C increase in mean annual lagoon water temperature resulted in a significant 5% variation of  $\text{NH}_4^+$  in porewater of muddy and sandy sediments ( $P < 0.01$ ), whereas  $\text{HPO}_4^{2-}$  concentra-

tions remained practically unchanged. As expected, a significant variation ( $P < 0.01$ ) was also observed for  $\text{NH}_4^+$  diffusive fluxes although at a lower level (2% variation). According to some authors (Miranda et al. 2002) there is a general tendency in the Portuguese climate for the increase of both minimum and maximum temperatures. For that reason we looked at two scenarios, respectively of 1°C and 2°C increase in water temperature during winter and summer seasons. For both situations, only  $\text{NH}_4^+$  in porewater varied significantly ( $P < 0.01$ ), increasing respectively 2 and 3%. In what concerns  $\text{NH}_4^+$  sediment-water fluxes, a significant variation ( $P < 0.05$ ) was only observed for the 2°C increase scenario for the winter and summer periods.

## Discussion

In muddy areas of high organic matter content,  $\text{NH}_4^+$  dissolved in porewater reached the peak at top layer sediment during the warmer period (380 μM), since its accumulation is linked to the breakdown of fresh organic matter, temperature and oxygen availability (Lerat et al. 1990; Kristensen 1993; Chapelle 1995; Vidal and Morguñ 1995). Organic material, settled in the upper sediment layers associated to high temperatures, accelerates mineralization processes due to an increase in the microbial metabolism, leading to intense  $\text{NH}_4^+$  production during that period

**Table 4** Variation coefficient (%) of  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  in porewater obtained from the model sensitivity analysis

	Variation coefficient (%)	
	$\text{NH}_4^+$	$\text{HPO}_4^{2-}$
Model parameters		
Organic matter deposition rate	6	0.3
Initial N and P organic concentrations	4	0.1
Initial porewater concentrations	0.02	0
$\text{minN}_s$	4	
$K_T$	4	0.05
$\text{minP}_s$		0.2
$k_{\text{minO}_2}$	2	0.2
$k_{\text{nit}}$	0.03	
$k_{\text{nitO}_2}$	0.02	
$k_{\text{denit}}$	0.03	
$k_{\text{denitO}_2}$	0.03	
$\phi$	10	0.1
$k_a$		3
$P_{\text{max}}$		10
$k_d$		8
$k'_a$		5

(Nowicki and Nixon 1985; Van Raaphorst et al. 1992; Kristensen 1993; Chapelle 1995; Asmus et al. 2000; Wilson and Brennan 2004). On the other hand, nitrification/denitrification processes are also temperature-dependent (Cartaxana et al. 1999). The low  $\text{NO}_3^- + \text{NO}_2^-$  levels found in porewater profiles during the warmer period may be explained by denitrification of  $\text{NO}_3^-$  to gaseous forms of N and  $\text{NH}_4^+$  as described by other authors (Cartaxana et al. 1999).

The large variability of  $\text{HPO}_4^{2-}$  in muddy sediment porewater profiles during the warmer period, that reaches higher concentrations in deeper layers ( $>50 \mu\text{M}$ ), may be explained by the increase of organic matter mineralization rates under high temperatures and P-desorption due to iron oxides reduction (Chapelle 1995; Asmus et al. 2000). These findings are reinforced by other studies, in which  $\text{HPO}_4^{2-}$  in porewater were positively correlated with bottom water temperature (Jensen et al. 1995; Lillebø et al. 2004), and negatively correlated with dissolved oxygen (Jensen et al. 1995). During the period of lower temperatures, the oxygen availability increases in porewater due to an increase of its solubility (Ohtake et al. 1984; Moutin 1992), which turns the iron and sulphur cycles very

reactive (Sundby et al. 1992; Bally et al. 2004; Caetano et al. 2003). The low levels of  $\text{HPO}_4^{2-}$  found in porewater of muddy sediments ( $<10 \mu\text{M}$ ) may be partially explained by P-sorption onto iron oxides formed under oxic conditions (Sundby et al. 1992; De Jonge et al. 1993; Van Raaphorst and Kloosterhuis 1994; Slomp et al. 1998; Perkins and Underwood 2001), since there is a large iron availability in the intertidal muddy sediments of this lagoon (Caetano et al. 2002).

A sensitivity analysis performed to the model, consisting of a 10% variation in model parameters and initial conditions, revealed that  $\text{NH}_4^+$  in porewater was particularly sensitive to organic matter deposition, N mineralization rate ( $\text{minN}_s$ ), temperature ( $K_T$ ) and sediment porosity, which agrees with field data (Table 4). Conversely, an increase/decrease in nitrification/denitrification related parameters did not change  $\text{NH}_4^+$  concentrations. Phosphate in porewater was more sensitive to adsorption/desorption processes than to organic matter deposition and mineralization. Indeed, a 10% increase/decrease on the rate of organic matter deposition and  $\text{minP}_s$  did not affect  $\text{HPO}_4^{2-}$  in porewater, whilst the same variation of  $k_a$ ,  $P_{\text{max}}$  and  $k_d$  produced a significant variation ( $P < 0.01$ ) on  $\text{HPO}_4^{2-}$  concentrations (Table 4).

Studies developed in this lagoon have shown that N and P entering the system are quickly removed by primary producers (Falcão and Vale 2003) what might explain the low  $\text{NH}_4^+$  ( $<4 \mu\text{M}$ ) and  $\text{HPO}_4^{2-}$  levels ( $<2 \mu\text{M}$ ) in overlying water over the year. These values, 2–3 orders of magnitude lower than those found in porewater lead to concentration gradients between sediment and overlying water that drives nutrient sediment-water exchanges (Trimmer et al. 1998; Wilson and Brennan 2004). Solute diffusion is particularly important for nutrient cycling in muddy sediments where diagenesis takes an active part in the biogeochemical cycles of elements (Aller 1980; Nowicki and Nixon 1985; Lerat et al. 1990; Bally et al. 2004). The annual range of  $\text{NH}_4^+$  ( $10\text{--}104 \text{ nmol cm}^{-2} \text{ d}^{-1}$ ) and  $\text{HPO}_4^{2-}$  ( $0.2\text{--}8 \text{ nmol cm}^{-2} \text{ d}^{-1}$ ) effluxes, predicted by the model for both types of sediments, are similar to those described by other authors for this system (Falcão

and Vale 1998; Asmus et al. 2000). In those studies, muddy sediments  $\text{NH}_4^+$  fluxes ranged from  $72 \text{ nmol cm}^{-2} \text{ d}^{-1}$  to  $127 \text{ nmol cm}^{-2} \text{ d}^{-1}$  whereas for  $\text{HPO}_4^{2-}$ , negative fluxes were determined pointing to sediment P-uptake. The present fluxes were also comparable with those found in other marine systems (Pregall and Miller 1988; Lerat et al. 1990; Kristensen 1993; Asmus et al. 2000). Maximum  $\text{NH}_4^+$  exchange rates of 96 and  $144 \text{ nmol cm}^{-2} \text{ d}^{-1}$  have been reported for marine environments in the coast of Ireland (Wilson and Brennan 2004). In the organically-rich Tamar estuary (SW of England), a broader range of  $\text{NH}_4^+$  ( $-57$ – $408 \text{ nmol cm}^{-2} \text{ d}^{-1}$ ) and  $\text{HPO}_4^{2-}$  fluxes ( $-17$ – $48 \text{ nmol cm}^{-2} \text{ d}^{-1}$ ) were referred by Watson et al. (1993), while in the carbonate-rich sands of the Great Barrier Reef (Australia),  $\text{NH}_4^+$  effluxes varied from  $14 \text{ nmol cm}^{-2} \text{ d}^{-1}$  to  $48 \text{ nmol cm}^{-2} \text{ d}^{-1}$  and  $\text{HPO}_4^{2-}$  from  $0 \text{ nmol cm}^{-2} \text{ d}^{-1}$  to  $3 \text{ nmol cm}^{-2} \text{ d}^{-1}$  (Hansen et al. 1987).

Based on nutrient fluxes simulated by the model, and assuming that in Ria Formosa intertidal muddy areas correspond to 2000 ha of Ria Formosa and subtidal sandy areas to 2500 ha, the contribution of N and P effluxes to the lagoon nutrient budget was evaluated. The amount of  $\text{NH}_4^+$  and  $\text{HPO}_4^{2-}$  released from muddy areas was estimated respectively in  $61 \text{ ton y}^{-1}$  and  $6 \text{ ton y}^{-1}$  while subtidal sandy areas contribute annually with 22 ton of  $\text{NH}_4^+$  and 2 ton of  $\text{HPO}_4^{2-}$ . This evaluation shows the importance of mudflats for the maintenance of a high productivity in this system (Falcão and Vale 2003), since the contribution of these areas to the water column nutrient enrichment is clearly higher than the one from sandy areas.

Given the importance of bottom sediments to the water column nutrient enrichment of shallow coastal ecosystems (Falcao and Vale 1998), it is important to predict what will happen to sediment-water nutrient exchanges as a result of global warming. The general trend for increase in the mean annual surface air temperature in Portuguese land areas at an average warming rate of  $0.17$ – $0.6^\circ\text{C}$  per decade (Miranda et al. 2002), will be accompanied by an ocean warm up (IPCC 2001). For the scenarios simulated with the model, a significant variation ( $P < 0.05$ ) was only observed for  $\text{NH}_4^+$  in porewater and

consequent diffusive fluxes, what will probably affect the system productivity due to a N/P ratio unbalance.

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