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The effect of benthic sediments on dissolved nutrient concentrations and fluxes

L. G. Murray · S. M. Mudge · A. Newton · J. D. Icely

Abstract The Ria Formosa is a meso-tidal coastal lagoon experiencing enhanced nutrient concentrations. Assessment of sediment–seawater interaction is essential if nutrient dynamics and the risk of eutrophication are to be fully understood. Pore water concentrations of dissolved inorganic and organic phosphorus, ammonium, nitrate and nitrite were determined in cores from six sites. Changes in nutrients concentrations were measured in intertidal pools on sand and mud between tides. Dissolved inorganic phosphorus (DIP) concentrations (~200 μmol l^{-1}) and effluxes (123 ± 14 μmol m^{-2} h^{-1}) were greater from sand than mud (37 ± 10 μmol m^{-2} h^{-1}), possibly due to the binding of P with the <63 μm fraction. NH$_4^+$ effluxes were high outside the Ancão Basin (821 ± 106 μmol m^{-2} h^{-1}) and were associated with *Enteromorpha* sp. mats. The greatest NO$_3^-$ efflux was from sediments near a salt marsh (170 ± 67 μmol m^{-2} h^{-1}). These sediment fluxes of P were not sufficient to account for elevated P concentrations seen by other workers on the ebb tide from the Ancão Basin. Intertidal pools were sinks for Dissolved Inorganic Nitrogen (DIN) and DIP over the 6 h exposure period. Thus, tidepools may be an important route of nutrients into sediments that enhances the effects of sediments on seawater nutrient concentrations.

Abbreviations

DIN	Dissolved inorganic nitrogen
DM	Deep mud
DS	Deep sand
DOP	Dissolved organic phosphorus
MP	Mud pool
NH$_3$	Ammonia
MR	Mud replicate
NH$_4^+$	Ammonium
OA	Outside Ancão
NO$_2^-$	Nitrite
SM	Salt marsh
NO$_3^-$	Nitrate
SP	Sand pool
P	Phosphorus
SR	Sand replicate

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Introduction

Water quality in coastal regions is increasingly affected by anthropogenic inputs, particularly in regions of restricted exchange (Cloern 2001; Tett et al. 2003). However, in shallow systems, water quality may be determined as much by sediment quality as by aqueous terrestrial pollutant inputs; sediments may act as sinks or sources of nutrients (Rowe et al. 1977; Falcão and Vale 1990; Mortimer et al. 1998; Hopkinson et al. 1999), metals (Colbert et al. 2001), organochlorines (Choi and Chen 1976; Fava et al. 2003) and oils (Hoffman and Quinn 1979; Mudge et al. 1995). Furthermore, the effects of natural nutrient inputs to the marine environment such as soil leachate, eroded material, runoff and vegetation may be buffered by the sediments. Organic matter may be buried or inorganic nutrients may diffuse deep into the sediment under one set of environmental conditions to be released under another (Campbell and McKenzie 2004). Thus, measuring nutrient concentrations in the water column may only provide information about short-term environmental quality.

Measurement of surface sediment and seawater nutrient concentrations allows instantaneous dissolved nutrient fluxes to be calculated using Fick's First Law of Diffusion. Such calculated fluxes are only valid at the time of sampling and often differ from fluxes measured with benthic chambers or core incubations (Mortimer et al. 1998; Clavero et al. 1999). However, where seawater nutrient composition remains fairly constant, an assessment of the impact of diagenetic processes on nutrient dynamics can be made, especially where sediment characteristics such as particle size and organic matter content are also quantified.

There are many factors influencing nutrient–sediment interactions. As salinity increases, the adsorption capacity of sediments decreases (Carrit and Goodgal 1954). Thus phosphorus (P) bound to suspended or benthic sediments may result in seawater dissolved inorganic phosphorus (DIP) concentrations in excess of concentrations measured in fresh water. Furthermore, in estuaries or coastal lagoons, where salinity is altered by fresh water inputs or high evaporation, the proportion of sediment-bound P will change accordingly.

Tidal exchange is of prime importance in determining the biogeochemical characteristics of semi-isolated bodies of water (Dahlgren and Kautsky 2004). Terrestrial inputs of nutrients to a coastal lagoon are likely to have greater impacts where tidal exchange is poor and residence times are great. By increasing residence time, lagoons become more vulnerable to eutrophication, as phytoplankton and macro-algae are exposed to nutrient-rich water for longer periods (Lin and Hung 2004) and organic matter is not immediately transported out of the lagoon. Remineralization of organic material returns inorganic nutrients to the sediments and seawater, depleting oxygen concentrations and altering the reduction–oxidation (redox) conditions and nitrogen (N) speciation.

The Ria Formosa (Fig. 1) is a meso-tidal lagoon extending ~55 km along the Atlantic south coast of Portugal, with a series of barrier islands forming the southern edge of the lagoon. The present study was conducted in, and immediately outside, the Ancão Basin, which forms the westernmost end of the lagoon and is partially isolated from the rest of the lagoon by a causeway and bridge. Tidal exchange between the Ancão Basin and the lagoon to the east occurs through a single main channel (~60 m wide) at low water, but beneath the whole length of a bridge (180 m) at high water.

The volume of water in the Ria Formosa is estimated at 88×10^6 m^3 at mean sea level, covering an area of 58 km^2, with an estimated fresh water inflow of 0.22×10^6 m^3 d^{-1} (Tett et al. 2003). The tidal range in the lagoon is between 2 and 4 m. The Ancão Basin is approximately 5 km long and a maximum of 1 km wide.

Newton et al. (2003) measured DIN:DIP ratios during summer months of up to 100 in the Ancão Basin at high water, with ratios falling to around 20 at low water. In the channel between the Ancão Basin and the outer lagoon, Fletcher (2002) found increasing DIP concentrations on the ebb tide. In contrast, NO_3^- concentrations did not show any clear correlation with tidal state. It appears that DIN concentrations are higher in the incoming flood tide and DIP concentrations are higher in the ebbing tide.

Santos et al. (2003) estimated that the net annual export of N and P from the Ancão Basin in

Fig. 1 Location of study sites in the Ria Formosa (Militar de Portugal, 1980). DS = Deep Sand; DM = Deep Mud; MR = Mud Replicates; SR = Sand Replicates; SM = Salt marsh; OA = Outside Ancão; SP = Sand Pool; MP = Mud Pool
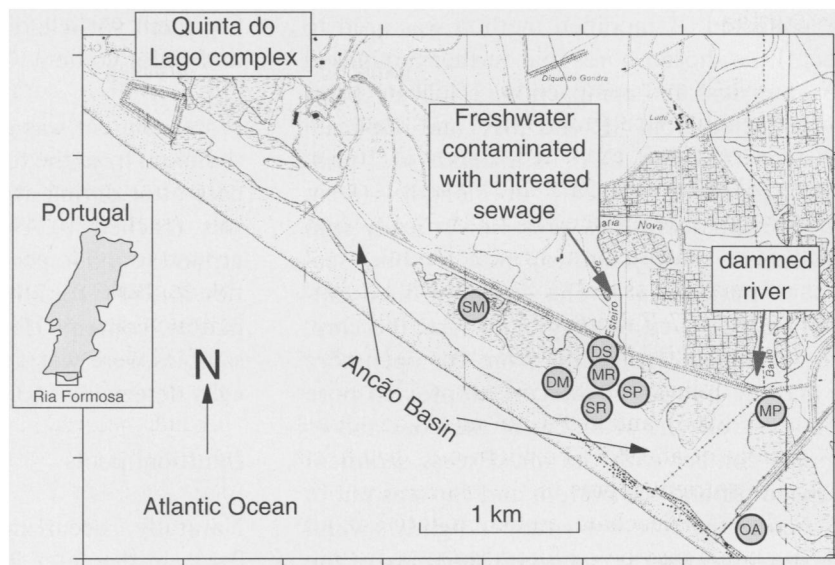
Zostera noltii leaves was 817 and 84 kg, respectively. Fletcher (2002) calculated a net DIN import to the Ancão Basin from the main area of the lagoon of 39.73 kg and a DIP export of 15.41 kg per 12 h. Therefore, *Z. noltii* detritus would only account for 0.2 kg of P exported over a 12-h tidal cycle and is not sufficient to account for the net export of P from the Ancão Basin.

The aim of the current study was to ascertain whether intertidal sediments, including tidepools, are a source or sink of nutrients in the intertidal zone of the Ancão Basin, contributing to the DIN and DIP values observed on the ebb tide.

Materials and methods

Sampling sites

Eight sites were studied, seven in the Ancão Basin, and one 50 m to the east of the Ancão Basin (Fig. 1). Replicate 10 cm long cores ($n = 3$) were collected from sandy (23% ≤ 63 μm, site SR) and muddy (70% ≤ 63 μm, site MR) locations. Two individual deep cores (~45 cm long) were also collected from sand (14% ≤ 63 μm, site DS) and mud (71% ≤ 63 μm, site DM) to determine nutrient concentrations in deeper sediments (see following section). Duplicate 10 cm long cores ($n = 2$) were collected from a salt marsh channel

(SM) and from outside the Ancão Basin (OA). Individual intertidal pools inside the Ancão Basin were studied on sand (SP) and mud (MP).

Core collection and seawater sampling

Deep cores were collected by digging holes in the sediments and pressing square section plastic guttering (8 cm wide $\times$ 10 cm deep) into a vertical face of the sediment in order to avoid compression of the cores. Redox potential was measured along cores using a WTW Multiline P4 Universal meter with a platinum electrode. Measured values were adjusted by adding 240 mV, to give E_h relative to a standard hydrogen (H) electrode. In these deep cores, redox potential at the centre of the cores was measured in the field at 1 cm intervals in the top 10 cm of the cores and at 2 cm intervals below this depth. Sediments were sufficiently fine to retain water and were enclosed on three sides and at the top and bottom, as well as being wrapped tightly in plastic film. Cores were sectioned in the field and each of the layers were placed in plastic bags and sealed after removing as much air as possible. The bags were chilled (<8°C) until returning to the laboratory (<30 min) where samples were refrigerated at 4°C.

To assess spatial variation in nutrient profiles and intra-site variability, short replicate cores

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were collected. A modified method was used to collect these shorter cores that further minimised pore water loss and compaction. Triplicate cores were collected from SR and MR, and duplicate cores from SM and OA, to a depth of 10 cm. Plastic guttering 10 cm in length (8 cm wide × 10 cm deep) was pressed vertically into the sediment, the top end cap with a rubber seal was then put in place. The sediment-filled guttering was removed by digging around the core, leaving sediment protruding from the open core face and the bottom of the core to prevent pore water loss from the sediment in the core and to minimize contact with the air. Excess sediment was sliced-off and the bottom end cap was put in place before the core was wrapped tightly several times in plastic film to ensure no slumping of the core face or water loss occurred. Cores were chilled in a cool box (<8°C) and transported vertically and were returned to the laboratory within 30 min before being refrigerated (4°C). Redox potentials were measured at the centre of the cores within 2 h of collection time, in accordance with Mortimer et al. (1998). Cores were sliced in the laboratory and pore water was extracted immediately; during all the stages the cores were kept vertical.

Pore water extraction

Pore water was extracted from the deep cores by centrifugation at 4,000 rpm for 30 min. The supernatant was frozen in sealed plastic centrifuge tubes for nutrient analysis. Due to the greater depth resolution in the 10 cm cores, pore water was extracted by low pressure vacuum filtration through Whatman GF/F glass fibre filters with a nominal pore size of 0.7 μm. Pore water could be more rapidly extracted from greater volumes of sediment even using a weak vacuum, particularly from sandy sediments. Glass fibre filters of varying grades have been used to remove particulate material in several other studies (e.g. Hopkinson 1987; Lillebø et al. 2004). A new filter was used for each core layer. Sediment was pressed firmly into the Buchner funnel and covered with plastic film to ensure air was not sucked through the sample and only a small proportion of the sediment was ever exposed to air.

Sediment particle diameter, organic matter and water content

Water content was determined gravimetrically in sediment from the top, middle and bottom of each core after drying at 60°C until a constant weight was reached (~24 h). The sediment was then ground to a fine powder and loss of mass on ignition at 450°C for 2 h was used to estimate organic matter content (Parker 1983). Sediment subsamples were wet sieved and dried to gravimetrically determine >63 μm and ≤ 63 μm fractions.

Intertidal pools

Naturally occurring tidepools approximately 0.4 m in diameter and 5 cm deep, on sand (SP) and mud (MP), were found in the mid-shore region within 30 min of being exposed on the ebb tide. Seawater (80 ml) was collected from each pool using a plastic syringe at mid-ebb tide and thereafter at 30 min intervals until recovered at mid-flood tide. For each 80 ml sample, four 20 ml extractions were made from different areas of the pools to ensure a representative sample was obtained. Temperature and redox potential were also measured at 30 min intervals. Water samples were kept cool (<8°C) and in the dark until they could be returned to the laboratory at the end of the sampling period and frozen.

To estimate the change in nutrient concentrations and redox potential in seawater isolated from the sediment, seawater was collected from the Ancão Basin adjacent to the pools as the tide ebbed. Three plastic trays, approximately the same size as the intertidal pools (40 × 30 cm), were each filled with 3 l of the seawater within 1 h of its collection and left in full sunlight. Seawater was extracted from the trays in the same manner as from the intertidal pools, at 30 min intervals. Redox potential and temperature were also measured. Salinity was measured in all seawater samples on returning to the laboratory using a WTW salinometer.

Nutrient analysis

Pore water and seawater samples were analysed manually in triplicate for dissolved organic

phosphorus (DOP), dissolved inorganic phosphorus (DIP), nitrate (NO_3^-), nitrite (NO_2^-) and ammonium + ammonia ($NH_4^+ + NH_3$) using the methods of Hansen and Koroleff (1999). $NH_4^+ + NH_3$ is henceforth referred to as NH_4^+. DOP was oxidised to DIP using an alkaline persulphate oxidising solution. Absorbance was measured using a Milton Roy Spectronic 1201 spectrophotometer. Detection limits were as follows (coefficients of variation in brackets): DIP, 0.01 μmol l^{-1} ($\pm 2.8\%$); NO_2^-, 3 nmol l^{-1} ($\pm 2.6\%$); NO_3^-, 3 nmol l^{-1} ($\pm 3\%$); NH_4^+, 0.05 μmol l^{-1} ($\pm 4.2\%$)

Calculations

Sediment porosity (ϕ) was calculated using the method of Berner (1971) from the proportion water content by mass (W) and average densities of sediment (d_s, 2,650 kg m^{-3}, Balouin et al. 2005) and overlying seawater (d_w, 1,025 kg m^{-3}, Newton and Mudge 2005; Balouin et al. 2005), where

$$\phi = \frac{Wd_s}{((1-W)d_w) + Wd_s}$$

Fluxes (J) were calculated from concentration gradients (C) and distance (Z) across the sediment–seawater interface using Fick's First Law of Diffusion:

$$J = -\phi D_s \left(\frac{\partial C}{\partial Z}\right)$$

C was calculated from the bottom water nutrient concentration minus the nutrient concentration in the upper sediment layer. Z was the distance from the surface to the middle of the first sediment layer (0.25 cm) (Hopkinson et al. 1999). Diffusion coefficient values (D_s, in cm^2 s^{-1}) for NH_4^+ (1.957×10^{-5}), NO_2^- (1.912×10^{-5}), NO_3^- (1.902×10^{-5}) and PO_4^{3-} (0.824×10^{-5}) were taken from Lide (2002) and assume a temperature of 25°C, appropriate given the temperatures measured in the intertidal pools (24.5 $\pm$ 1.0°C).

As salinity would not be altered by loss of water to the sediments, nutrient concentrations that would result due to changes in pool volume (C_e), resulting from evaporation, were calculated from salinity (S) changes between measurements:

$$C_e = C_i \left(\frac{S_{i+1}}{S_i}\right)$$

Observed nutrient concentrations in the pools were adjusted based on the mean differences between observed and predicted nutrient concentrations in the trays, which was taken as representing the change in nutrient concentrations due to biological activity (ΔC_b). Constants, calculated as the average change in nutrient concentrations in the trays of seawater (after the change due to evaporation had been accounted for) were used to adjust concentration changes in intertidal pools. The constants (k) were DIP, -1.347 μmol l^{-1} h^{-1}; DOP, 2.414 μmol l^{-1} h^{-1}; DIN, -3.858 μmol l^{-1} h^{-1}. Fluxes were calculated based on the difference between the observed concentrations (C_i) and predicted concentrations of the nutrient under study due to evaporation (C_e) after time between measurements, t. C_i was adjusted for biological activity in seawater to give $C_b = C_i kt$. Initial pool volume (V_i) was estimated from depth, length and width measurements. The volume of water (V_{i+1}) after t was calculated from the change in salinity between measurements:

$$V_{i+1} = V_i \left(\frac{S_i}{S_{i+1}}\right)$$

Thus multiplying by V_i gives the quantity of the nutrient under study in the pool. Dividing by t gives the change in nutrient concentration per unit time. Multiplying by the reciprocal of A gives the change in nutrient concentration per unit time per unit area. Thus:

$$\Delta C_s = V_i \left(\frac{C_b - C_e}{t}\right)\frac{1}{A}$$

where ΔC_s = change in nutrient concentration due to sediment–seawater fluxes. ΔC_s includes the effect of diffusive fluxes, settlement and burial of phytoplankton (not uptake of nutrients and remineralization occurring while in suspension, ΔC_b). Changes in nutrient concentrations due to evaporation (ΔC_e) must also be considered, thus in summary:

$$C_{i+1} = C_i + \Delta C_e + \Delta C_b + \Delta C_s$$

All statistical analyses were conducted using Minitab.

Results

Seawater composition

In all cases, sediment pore water concentrations of nutrients exceeded seawater concentrations (Table 1), except NO_2^- at site OA, where the surface 0.5 cm of sediment contained only 0.06 μmol l^{-1} of NO_2^-. DIP concentrations ranged from 1.27 (OA) to 29.5 μmol l^{-1} (MR) whereas the range of DOP concentrations was much lower (0 at MR to 4.91 μmol l^{-1} at SR). DIN concentrations ranged from 5.25 μmol l^{-1} (OA) to 260.06 μmol l^{-1} (SM).

Sediment characteristics

Sediment water content ranged from ~21% at SR and DS to 44% at OA. Percent ≤ 63 μm particle size ranged from 12% at DS to 78% at MR. Porosity generally decreased with depth with a mean surface porosity across all sites of 0.53, compared to 0.49 at 9.5 cm. This reflects the decreasing water content of sediments with depth (Table 2). Porosity ranged from 0.41 ± 0.01 at site SR to 0.66 ± 0.01 at site OA.

Redox potential was similar at DS and DM except for a mid-core increase between 10 and 28 cm at DM, reaching –51 mV (Fig. 2). At MR and OA (Fig. 3) and SR and SM (Fig. 4), the redox potential decreased with increasing depth. Across all sites, redox potential ranged from a minimum value of –265 mV in core DS (Fig. 2), to a maximum of +60 ± 35 mV at site SR (Fig. 4). SR was the only site to exhibit oxic ($E_h > 0$ mV) sediments, from 0–1, 3–4 and 5–6 cm. Site OA (Fig. 3) had a mean along-core redox potential of –202 ± 11 mV, with redox potential decreasing with increasing depth.

Nutrient profiles

There was no clear pattern in the DIP or DOP concentrations with depth at DS or DM (Fig. 2). NH_4^+ constituted from 45% (2.5 cm depth) to 94% (7 cm) of DIN at DS; NO_3^- constituted from 5% (7 cm) to 52% (27 cm) of DIN. The percentage of DIN present as NO_2^- ranged from 1% (1.5 cm) to 9% (11 cm) at DS. DIN concentrations at DS ranged from 29 (11 cm) to 402.1 μmol l^{-1} (15.5 cm). At DM the minimum percentage of DIN present as NH_4^+ was 42% (1 cm depth); NO_3^- formed the maximum percentage, at 1 cm (55%) (Fig. 2). The maximum percentage of NH_4^+ (94%), corresponding with the minimum percentage of NO_3^- (5%), at DM was at 23 cm depth, where there was a spike in the NH_4^+ concentration (777.6 μmol l^{-1}).

DIP and DOP concentrations at MR were inversely related and DOP concentrations generally

Table 1 Salinity, dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP) concentrations with appropriate ratios in seawater from the five coring sites within the Ancão Basin and one outside of the basin, in intertidal pools on sand and mud in the Ancão Basin and in trays of seawater

	Site	DIP	DOP	NO_2^-	NO_3^-	NH_4^+	DIN:DIP	Salinity
Coring sites	DS	9.38	2.55	1.10	1.20	11.60	1.47	29.4
	DM	19.54	1.11	0.09	2.97	3.64	0.34	34.5
	MR	29.52	0.00	0.79	0.75	30.22	1.08	29.0
	SR	3.29	4.91	0.00	0.86	25.68	7.55	36.0
	SM	4.23	4.24	0.64	7.12	252.3	61.42	38.5
	OA	1.27	3.11	0.20	1.18	3.87	4.13	38.5
	Mean ± 1 SD	11.21±11.12	2.65±1.86	0.47±0.44	2.35±2.47	54.55±97.50	12.67±24.03	34.3±4.2
Inter-tidal pools	MP	13.21	3.16	0.32	4.61	5.28	0.38	37.2
	SP	8.80	7.39	5.29	0.00	3.88	0.95	37.0
	Trays	12.82	2.20	0.32	6.05	3.47	0.77	37.5
	Mean ± 1SD	11.61±2.44	4.25±2.76	1.98±2.87	3.55±3.16	4.21±0.95	0.70±0.29	37.2±0.3

Samples were collected from June to August 2004. All nutrient concentrations are shown in units of μmol l^{-1}

Table 2 Sediment characteristics of replicate 10-cm cores collected from four sites in the Ria Formosa during August 2004

Site	Depth in core (cm)	Water content (%)	≤ 63 μm (%)	Organic matter (%)
DM	0–1	34.0	73.3	7.7
	5–6	32.4	70.7	5.5
	9–10	33.1	70.3	2.6
DS	0–1	29.2	14.3	2.0
	5–6	21.2	14.3	1.2
	9–10	23.7	12.1	1.1
SM	0–1	29.3	27.0	2.0
	5–6	24.0	34.3	1.2
	9–10	24.0	21.9	2.1
OA	0–1	44.0	51.7	3.7
	5–6	42.4	52.5	3.7
	9–10	40.9	42.7	3.2
MR	0–1	42.6 ± 2.4	77.6 ± 6.7	7.3 ± 1.2
	5–6	33.1 ± 1.0	67.9 ± 2.5	2.1 ± 0.5
	9–10	33.9 ± 0.5	65.1 ± 3.0	8.1 ± 1.2
SR	0–1	21.0 ± 4.0	26.2 ± 5.4	3.5 ± 5.8
	5–6	21.7 ± 0.7	20.9 ± 1.7	1.7 ± 0.9
	9–10	24.2 ± 14.74	22.0 ± 10.5	1.5 ± 19.3

Values are means ± 1 S.D. (where $n = 3$). Replicate sand (SR) and mud (MR) cores ($n = 3$), cores from a salt marsh channel (SM) ($n = 2$) and individual deep sand (DS) and mud (DM) cores were collected from the Ancão Basin. Cores ($n = 2$) were also collected from immediately outside the Ancão Basin from sand/mud (OA). All parameters were estimated by loss of mass

exceeded DIP concentrations (Fig. 3). NH_4^+ constituted between 78% (0.75 cm depth) and 93% (9.5 cm) of DIN at MR, while NO_2^- comprised only 0.2–0.9%. The percentage of DIN present as NO_3^- at MR ranged from 7% (9.5 cm) to 21% (0.75 cm). DIN concentrations ranged from 250.8 $\mu mol\ l^{-1}$ (0.75 cm) to 764.3 $\mu mol\ l^{-1}$ (5.5 cm).

DIP and DOP concentrations were lower at OA than MR (Fig. 3). NH_4^+ concentrations increased with depth at OA and were higher than at any other site. The percentage of DIN present as NH_4^+ at OA ranged from 87% (0.25 cm) to 98% (9.5 cm), compared to 2% (3.75 cm) to 13% (0.25 cm) for NO_3^-. There were peaks in all DIN species between 5 and 7 cm depth.

DIP concentrations showed little variation with depth at SR (Fig. 4) compared to DOP. The percentage of DIN present as NH_4^+ at SR ranged from 60% (5.5 cm depth) to 87% (1.75 cm); NO_3^- constituted from 9% (2.75 cm) to 62% (4.25 cm) of DIN. At SM (Fig. 4), DIP concentrations were lower than at any other site. DOP concentrations were more variable. The percentage of DIN present as NH_4^+ at SM ranged from 42% (3.75 cm) to 81% at 9.5 cm, where there was an NH_4^+ peak (368.6 $\mu mol\ l^{-1}$). NO_3^- constituted from

21% (0.25 cm) to 57% (3.75 cm) of DIN, and NO_2^- 1% (1.75 cm) to 7% (7.5 cm).

There were significant correlations between DIN concentration and depth at all sites ($R^2 > 0.7$, $P \leq 0.001$) except DS and SR. Figure 5a, b show trends in DIN concentration with depth (the two isolated peaks in NH_4^+ concentration have been removed from the DM profile). At DM (Fig. 5a) DIN concentrations increased below 20 cm depth, reaching over 300 $\mu mol\ l^{-1}$ at 37 cm. A slight increase in DIN concentrations towards the surface was also apparent. Site SM (Fig. 5b) showed a similar polynomial trend but with a more pronounced increase in DIN concentrations towards the surface. There were no clear trends in DIN concentrations with depth at the predominately sandy sites, DS (Fig. 5a) and SR (Fig. 5b). At MR there was a linear increase in DIN concentrations with depth. At OA there was a similar increase with depth but a greater drop in concentration towards the surface.

Nutrient fluxes

Based on calculated fluxes across the sediment–seawater interface, sediments at all sites were

Fig. 2 Pore water nutrient concentrations and redox profiles in sand (DS, solid) (14% ≤ 63 μm) and mud (DM, open/dashed) (71% ≤ 63 μm) sediment cores collected from the Ancão Basin. Cores were collected up to 30 min before low water within 2 m of the tidal level at time of collection
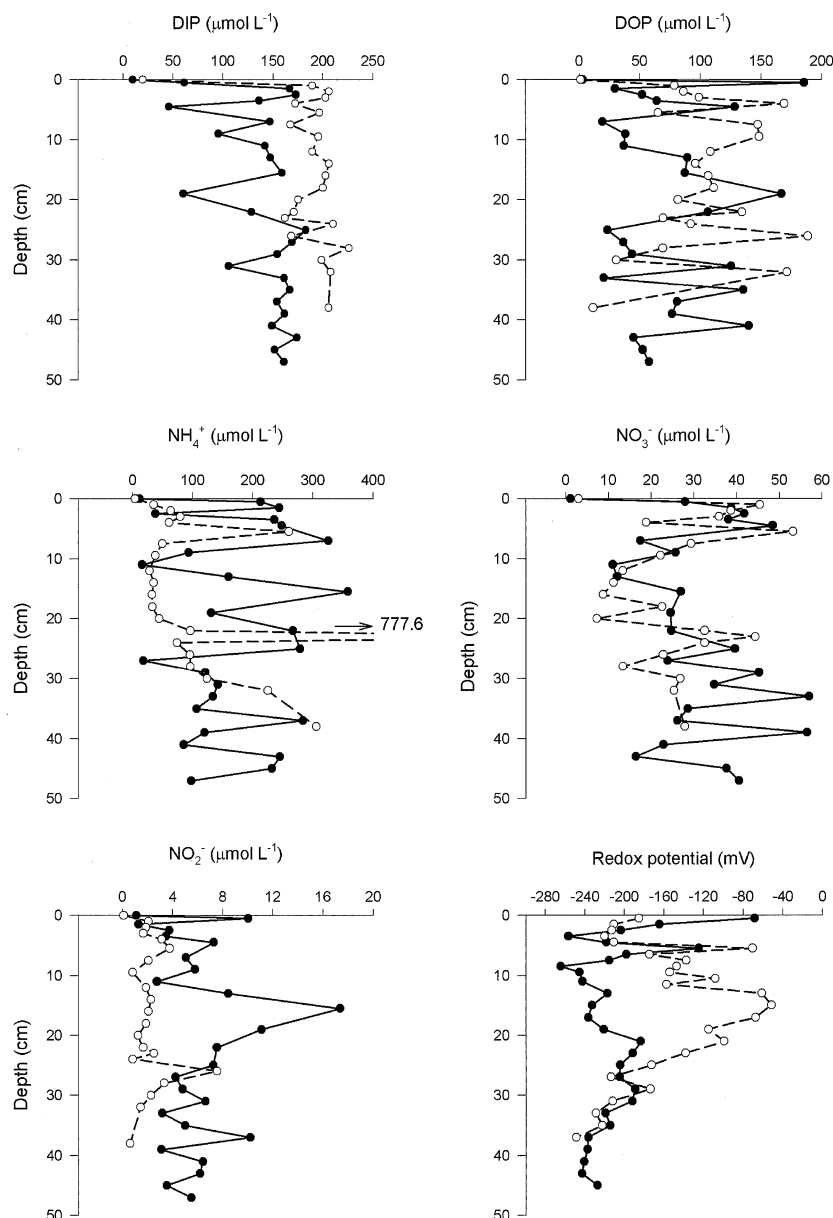
sources of inorganic nutrients to the overlying seawater except at OA, where both cores were a minor sink of NO_2^- (–0.22 and –0.31 μmol m^{-2} h^{-1}, Fig. 6). However, there was a high level of intra-site variability at SM, where there were positive and negative fluxes of NH_4^+ (–104.3 and 643.1 μmol m^{-2} h^{-1}) and a high range of NO_2^- fluxes (1.8–19.0 μmol m^{-2} h^{-1}). Fluxes of DIP across the sediment–seawater interface were greatest from SR (mean ± 1 S.D. = 123.4 ± 14.1 μmol m^{-2} h^{-1}) while the

lowest fluxes of DIP were from OA cores (9.4 and 14.5 μmol m^{-2} h^{-1}). DIP fluxes were comparatively low in both cores from SM (20.5 and 42.5 μmol m^{-2} h^{-1}) and at MR (37.1 ± 10.3 μmol m^{-2} h^{-1}). There were large effluxes of NH_4^+, in both cores at OA (746.0 and 895.4 μmol m^{-2} h^{-1}) that exceeded fluxes of any other nutrient (Fig. 6). The mean DIN flux from the sediments at OA (944.4 μmol m^{-2} h^{-1}) exceeded the DIN flux from any other site by more than double.

Fig. 3 Pore water nutrient concentrations and redox profiles from MR (70% $\leq$ 63 μm) cores ($n = 3$) from the Ancão Basin (solid; ± 1 S.E.) and sand/mud (49% $\leq$ 63μm) cores ($n = 2$) collected from outside the Ancão Basin (open/dashed) (OA). Cores were collected up to 30 min before low water within 2 m of the tidal level at time of collection
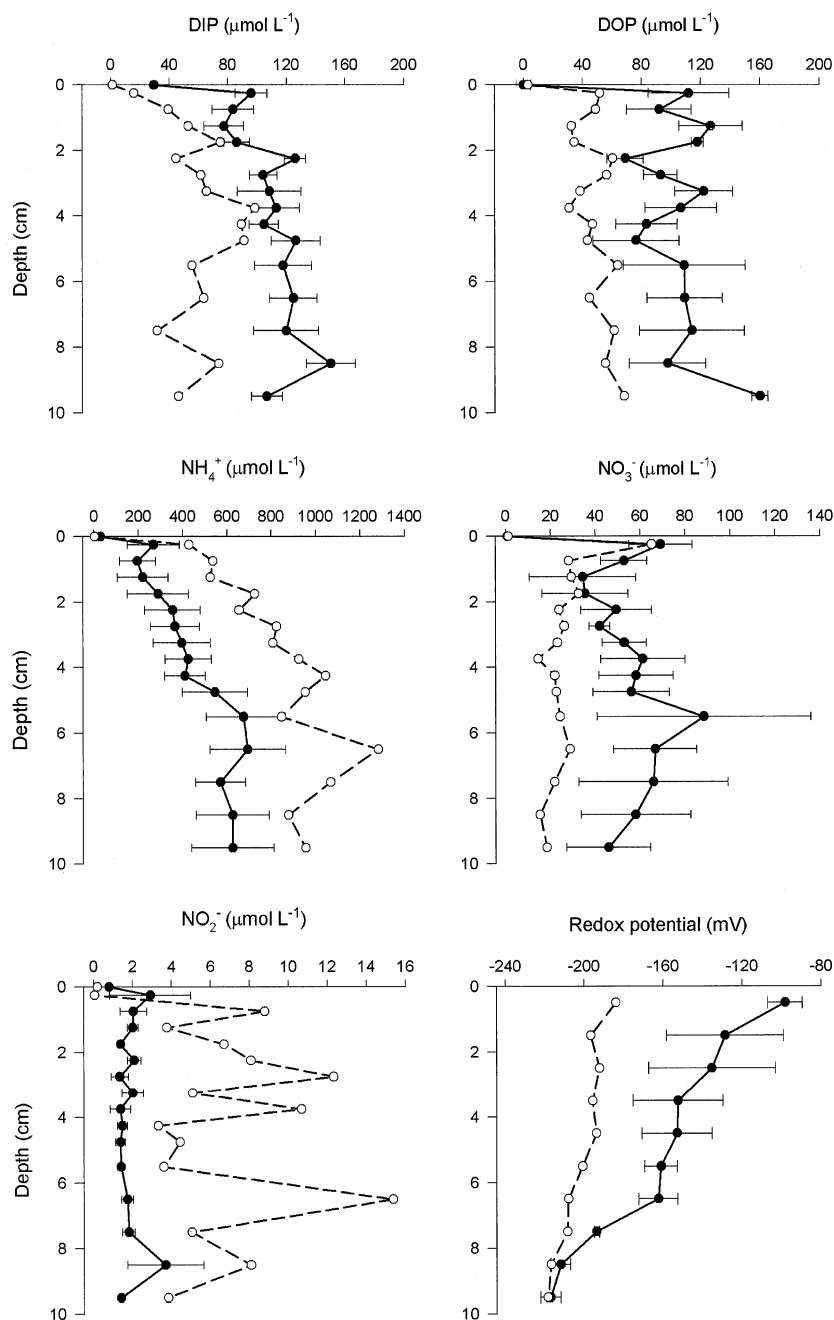

Intertidal pools

Temperature and salinity varied similarly in all pools, although the temperature at low water was slightly higher in the trays (26.4°C) than at SP (23.9°C) and MP (23.5°C). Temperature showed highly significant linear increases with time in all pools ($F_{1,10} \leq 39.16$, $R^2 \geq 0.797$, $P < 0.001$). Seawater salinities were similar at low water, with values of 37.0, 37.2 and 37.5 for SP, MP and trays, respectively. There were highly significant linear increases in salinity with time in all pools ($F_{1,10} \leq 57.95$, $R^2 \geq 0.838$, $P < 0.001$).

Fig. 4 Pore water nutrient concentrations and redox profiles from sites SR (solid; ±1 S.E.) and SM (open/dashed) (*n* = 3 and *n* = 2, respectively) in the Ancão Basin, both in sand (22% and 26% ≤ 63 μm, respectively). Cores were collected up to 30 min before low water within 2 m of the tidal level at time of collection
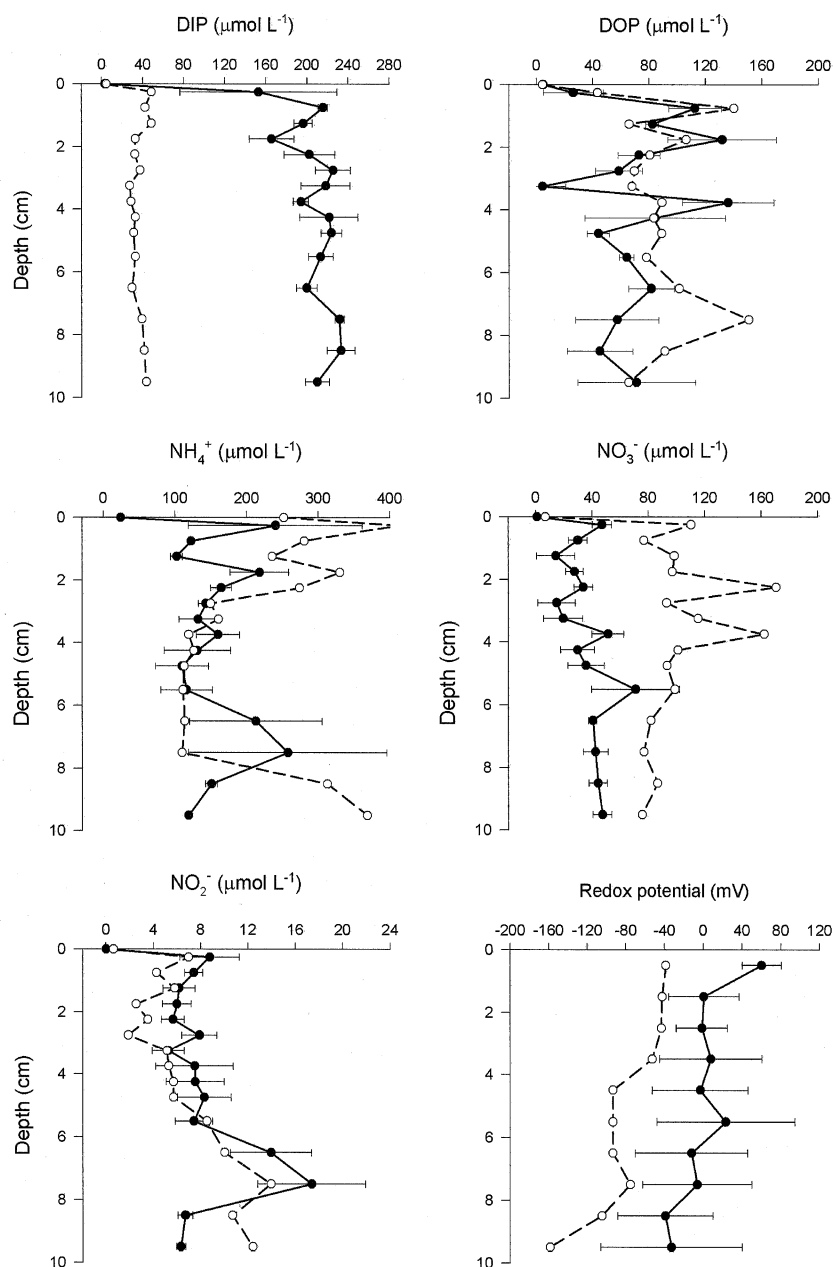

Mean redox potential (±1S.D.) decreased from 202.7 ± 1.2 to 197.7 ± 0.6 mV in the trays of seawater, compared to a decrease from 210 to 174 mV at MP and 189 to 146 mV at SP. There were significant correlations between time and E_h in trays ($F_{1,10}$ = 10.93, R^2 = 0.522, P = 0.008), at SP ($F_{1,10}$ = 162.80, R^2 = 0.942, P < 0.001) and MP ($F_{1,10}$ = 265.08, R^2=0.964, P < 0.001). Residuals of redox potential data were normally distributed (Anderson–Darling = 0.649, P = 0.083) and

variances were approximately equal. There were highly significant differences (Analysis of covariance, P < 0.001 using time as covariate) between the change in redox potential with time in trays and in the intertidal pools.

Observed concentrations of DIP were greater than predicted by volume change alone in all pools (Fig. 7a). The differences between observed and predicted DIP concentrations were greatest at SP (0.4–4.1 μmol l^{-1}) for most of the sampling period.

Fig. 5 DIN profiles and regression lines at (**a**) sites DM (crosses) and DS (squares) and (**b**) MR (crosses), SR (solid squares), SM (open circles) and OA (solid diamond)
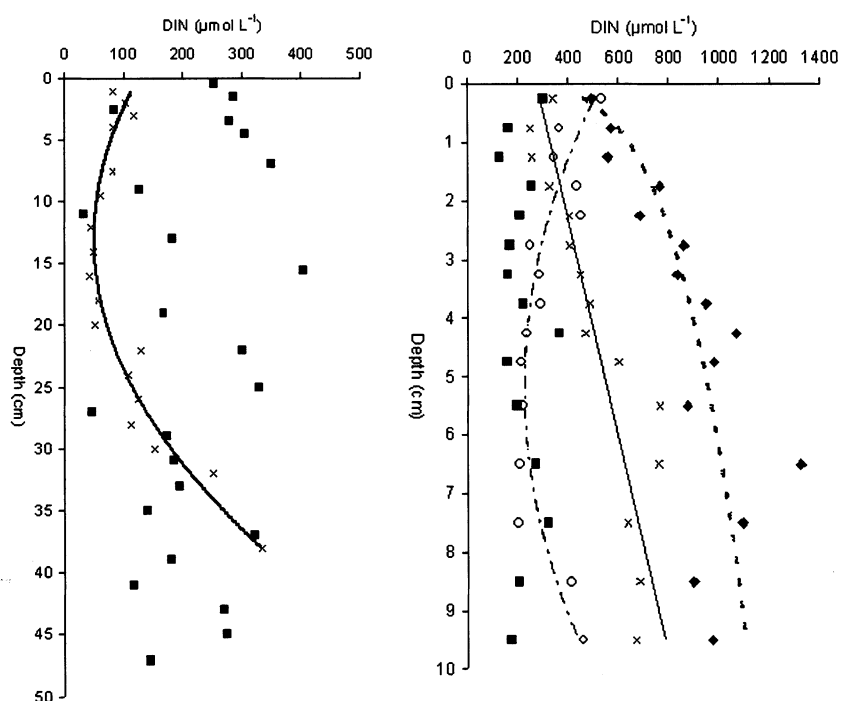
There was a mean DIP flux into the sediments at MP (-37.98 μmol m^{-2} h^{-1}) and an efflux at SP (79.52 μmol m^{-2} h^{-1}, Fig. 7a).

Predicted DOP concentrations due to evaporation were generally greater than those observed and were highly variable in all pools (Fig. 7b). SP exhibited the greatest range of observed DOP concentrations relative to the predicted values (-5.4–2.0 μmol l^{-1}). The mean flux was -7.29 μmol m^{-2} h^{-1} at MP compared to 40.20 μmol m^{-2} h^{-1} at SP (Fig. 7b).

Observed DIN concentrations generally exceeded predicted concentrations in the trays of seawater (Fig. 7c); the difference ranged from -1.2 to 4.3 μmol l^{-1} in the trays. In the tidepools the predicted concentrations were greater than the observed values. Both tidepools were sinks for DIN (Fig. 7c). The mean DIN flux at SP was -47.3 μmol m^{-2} h^{-1} and -490.8 μmol m^{-2} h^{-1} at MP.

Discussion

Seawater nutrient concentrations

In the current study, at all sites except SM, concentrations of NO_3^- were <3 μmol l^{-1} in seawater, while all coring sites had seawater concentrations of NO_2^- <1 μmol l^{-1}. Asmus et al. (2000) found similarly low NO_3^- and DIP concentrations of 1.1–3.5 μmol l^{-1} and 0.5–1.64 μmol l^{-1}, respectively inside the Ancão Basin. DIP concentrations measured in the present study within the Ancão Basin were comparatively high, with a mean of 11.2 ± 11.1 μmol l^{-1}, and a maximum of 29.5 μmol l^{-1}. Newton et al. (2003) reported higher concentrations of DIN in the western Ria Formosa, just outside the Ancão Basin, from <10 μmol l^{-1} in May increasing to over 20 μmol l^{-1} in August; DIP concentrations decreased from 1.1 to <0.4 μmol l^{-1} during the summer months, also much lower than found in the current study.

N:P ratios in seawater at the six coring sites in the present study ranged from 0.34 at site DM to 61.42 at site SM, this being the only site with an N to P ratio $> 16:1$. In a recent study, Newton and Mudge (2005) recorded highly variable seawater N:P ratios immediately outside the Ancão Basin; during the summer months N:P rations were often <16 while DIP concentrations were high ($\sim$0.7–2.3 μmol l^{-1}) relative to flood tide water, indicative of P enrichment. The large range of
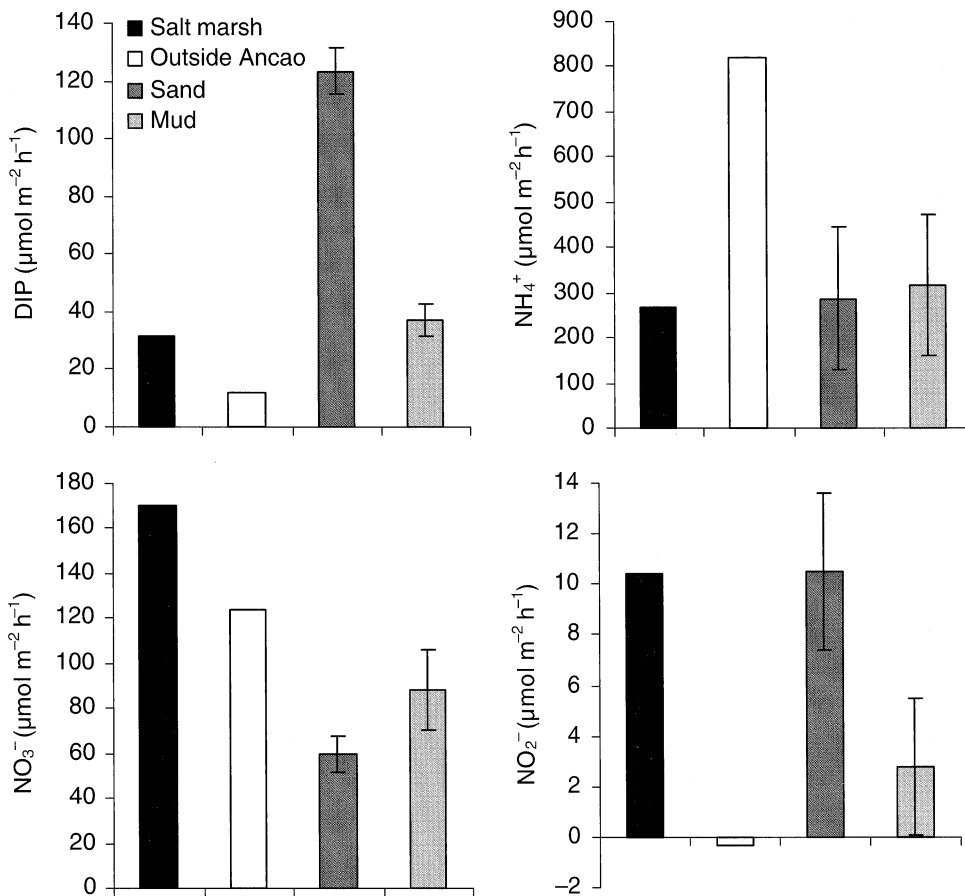
Fig. 6 Fluxes of nutrients across the sediment–seawater interface in the Ria Formosa on the ebb tide. Cores were collected on mud ($n = 3$) and sand ($n = 3$) and from a salt marsh channel ($n = 2$) in the Ancão Basin, and approximately 50 m outside of the Ancão Basin ($n = 2$), in August 2004. Error bars indicate ±1 S.E of the mean where $n = 3$

N:P ratios found in the Ancão Basin suggests that N:P ratios are not dominated by remineralization of organic matter (e.g. Redfield et al. 1963; Farias 2003) and, therefore, there are likely to be other sources of N and P.

Duarte (1990) reported a mean N:P ratio of 8:1, and a median of 24:1, in 30 sea-grass species, while Kamer et al. (2001) reported N:P ratios to be lower in *Enteromorpha intestinalis* (22.9) than in *Ulva expansa* (26.3) or *Ceramium rubrum* (32.5). Therefore, algae may cause N:P ratios to vary around the 16:1 ratio. However, the range measured in the present study extends beyond the range of N:P ratios found in algae and aquatic vegetation. Thus it appears that other sources or sinks for N and P dominate nutrient concentrations in the Ancão Basin during the ebb tide.

Sediment characteristics

The sediments of the Ria Formosa are subject to inputs of organic matter from salt marsh vegetation, sea-grasses and sewage, together with local and Atlantic Ocean-borne phytoplankton. Rocha et al. (2000) measured an organic matter content of between 0 and 2.3% by mass in sand sediments from the Ancão Basin. In the current study, organic matter content ranged from 0 to 9% on sand and mud sediments, respectively, while in sand the maximum organic matter content in any single core was 3.1%. Thus organic matter inputs to the mud sites (DM and MR) seem to be high, possibly due to transport of sea-grass and salt marsh detritus, with deposition occurring in the lower tidal energy muddy areas. Sediment from all sites consisted of at least 23% sand reflecting
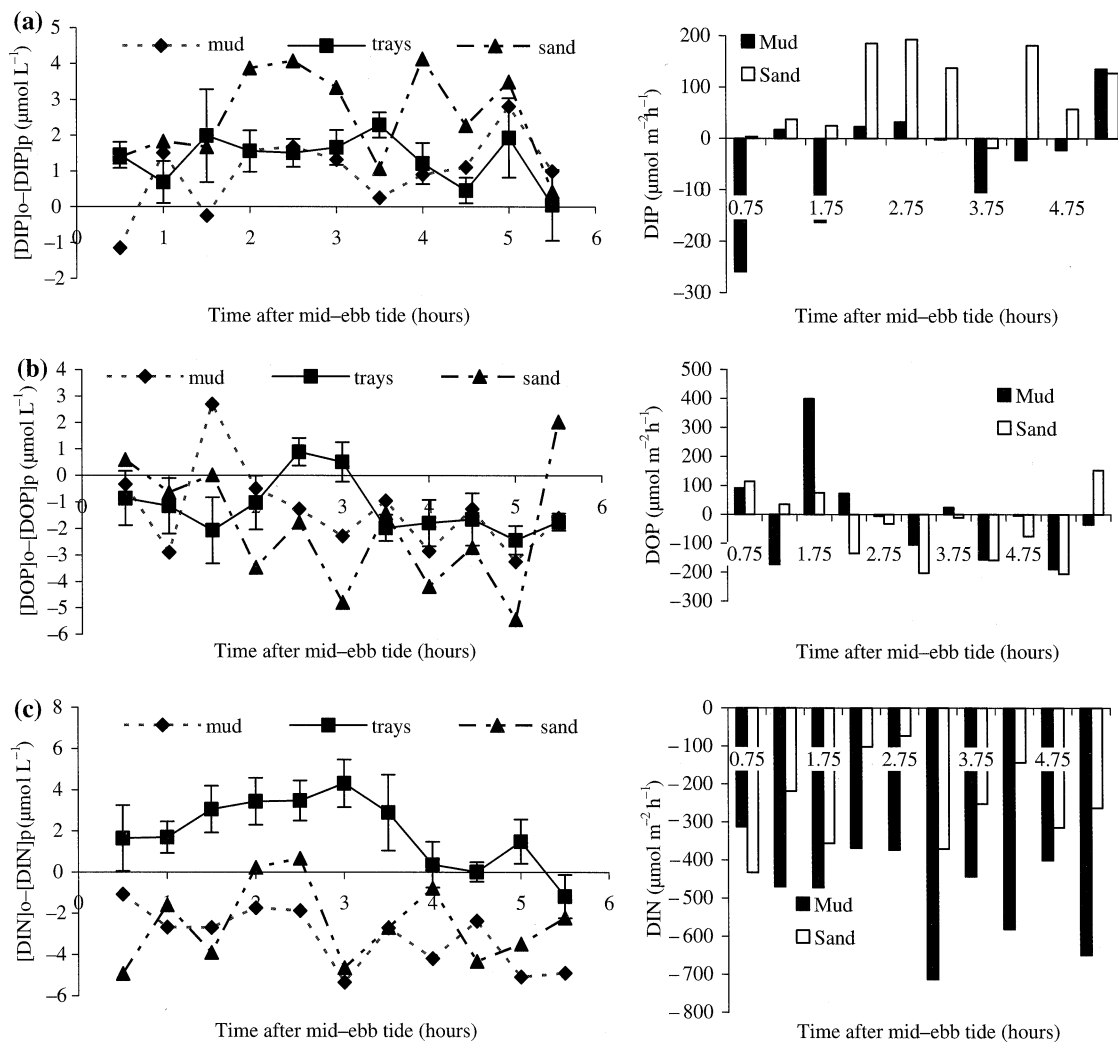
Fig. 7 Difference between observed (o) and predicted (p) DIP (**a**), DOP (**b**) and DIN (**c**) concentrations in the trays of seawater and intertidal pools; and sediment–seawater fluxes of dissolved nutrients in the intertidal pools. Positive values indicate a flux from sediment to seawater. Predicted concentrations are based on the effect of evaporation, calculated from the change in salinity between samples Error bars for seawater in trays indicate ±1 S.E. of mean difference ($n = 3$)

the proximity of all sites to sand beaches. The sand content of the sediments may have reduced the capacity of the sediments to bind PO_4^{3-} as P is more readily bound to the <63 μm sediment fraction (Stumm 1973; Selig 2003).

Redox potential

Only site SR exhibited oxic sediments, probably due to the greater particle size (Lohse et al. 1996). Oxygen penetration at other sites may have been poor due to limited bioturbation and

finer sediments, while bacterial respiration may have been high and seawater oxygen concentrations low (Burke 1999). The proportion of mud to sand was not the dominant factor in controlling redox potential, as both site DS and SM appeared entirely anoxic. No micro-oxic sites were detected at the sampling resolution used.

Paludan and Morris (1999) found that estuarine salt marsh sediments were reducing ($E_h < 0$ mV) due to the organic matter supply from the surface (–70 mV) to 1 m depth (–150 mV), with a redox potential of –110 mV at

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10.5 cm. A similar range of redox potentials at SM was found in the current study, ranging from −158 mV at 10 cm deep to −39 mV at the surface (0–0.5 cm deep). At sites MR, DM, SM and OA sediments showed some black colouration, indicative of iron sulphides (FeS and FeS_2, Ferdelman et al. 1997). DM and OA exhibited the most obvious black colouration, corresponding with the low redox potentials at these sites. Furthermore, *Enteromorpha* sp. detritus was visible at OA, and remineralization of this organic material may have contributed to the low redox potentials at this site (Fig. 3). In addition, Farias (2003) noted the presence of bacterial mats that appeared to cause an increase in surface NH_4^+ concentrations by dissimilatory NO_3^- reduction.

Site DM exhibited a sub-surface increase in redox potential at 15 cm depth (Fig. 2). It is possible that water in the fresh water marshes reached the study sites through groundwater flow that may have caused variation in the deeper cores. Groundwater flow has been detected in the Baltic Sea in both sand and mud (Viventsova and Voronov 2003; Schlueter et al. 2004) but there have been no studies of groundwater flow in the Ria Formosa. It is essential that all sources of nutrients to sediments are ascertained in the future if nutrient inputs to the Ria Formosa are to be reduced.

Pore water nutrient profiles

NO_3^- was found in all cores despite sediments being reducing. When submerged in oxic seawater nitrification of the generally high levels of NH_4^+ (Table 1, Figs. 2–4) may have occurred in seawater and possibly in surface sediments. The presence of NO_3^- at low water may reflect sediments with a reducing capacity insufficient for complete denitrification of NO_3^- to occur. Sørensen (1978) showed that the reduction rate of NO_3^- to NH_4^+ ranged from 0.75 μmol N cm^{-3} sediment day^{-1} in oxidized (75 mV) surface sediments (0–3 cm) to 0.12 μmol N cm^{-3} sediment day^{-1} in deeper reducing (−275 mV) sediments (9–12 cm); even after 76 h incubation 0.5 μmol NO_3^- cm^{-3} remained of the 1.5 μmol NO_3^- cm^{-3} at 0 h in reducing sediments. In addition, high NH_4^+ concentrations, as found in this study, repress

assimilatory NO_3^- reduction in *Aquaspirillium magnetotacticum*, a microaerophillic denitrifier (Bazylinski and Blakemore 1983). In consequence, concentration gradients of NO_3^- may exist, even under reducing conditions, and therefore cause fluxes of NO_3^-, which, as evident from the tidepools, are high in the Ancão Basin.

Thus the presence of NO_3^- in reducing, NH_4^+ rich sediments is quite possible and will be influenced by bacterial population composition and abundance, as well as redox conditions and NH_4^+ concentrations. Furthermore, due to high evaporation in the study area leading to elevated nutrient concentrations (as found in the intertidal pools) diffusion of NO_3^- deeper into the sediments is likely to occur, perhaps even from pore water in surface sediments as well as from tidepools.

The lack of any trend in DIN concentrations with depth at DS and SR is perhaps attributable to advection of seawater at these sites, which would prevent any diffusion equilibrium being reached. The polynomial correlation between depth and DIN exhibited at DM indicates an input of N deeper in the sediments (>20 cm), possibly from groundwater flow below 35 cm depth, while the slight surface increase may be attributed to degradation of the higher surface organic matter concentrations (Table 2). The polynomial correlation between DIN and depth at SM is thought to be due to the remineralization of organic matter, which was elevated at the surface and bottom of the cores, thus preventing equilibrium being reached. The more linear correlations between DIN and depth at MR and OA are suggestive of diffusion dominated movement of N originating from either groundwater flow or organic matter deposits deeper in the sediments; the latter being the most likely cause of the high concentrations of NH_4^+ at OA given the observed *Enteromorpha* sp. mats. The drop in DIN concentrations at the surface of OA is indicative of the high NH_4^+ sediment–seawater concentration gradient and consequent effluxes.

Desorption of P from sediment into higher salinity water (Carrit and Goodgal 1954) may have occurred in the Ancão Basin, explaining the higher DIP concentrations measured in seawater passing out of the basin by Fletcher (2002) and low summer N:P ratios (Newton and Mudge

2005). However, DOP may also exist in refractory and leachable forms, with the refractory component acting as a sink for DIP, and the leachable form providing a source of DIP (Lopez 2004). Therefore, such differences in the proportion of each component could account for the spatial variation found in the present study.

DIP concentrations were similar to DOP concentrations at the muddy sites, DM and MR, but DIP concentrations tended to be higher than DOP concentrations at the sandy sites, DS and SR, probably due to binding of P to finer sediment particles (Stumm 1973; Selig 2003). Furthermore, Andrieux-Loyer and Aminot (2001) showed that exchangeable Fe and Al bound P are also associated with the ≤ 63 μm sediment fraction, which would account for the higher sand pore water concentrations of DIP found in the current study.

NH_4^+ concentrations at SM, like DOP, showed a mid-depth decrease, from around 400 μmol l^{-1} at the surface to 120 μmol l^{-1} from 3–7 cm depth, indicating that NH_4^+ at SM may be derived predominantly from organic matter which also decreased in content (~2–1%) at mid-depth. Organic matter content was relatively low at SM (Table 1); however, this may be attributable to high rates of decomposition. The high range of NH_4^+ and NO_2^- fluxes between cores at SM may also be attributable to variation in organic matter content between cores. NO_3^- concentrations showed little variation with depth, other than at 2 and 4 cm, where there were peaks of over 160 μmol l^{-1}, most probably due nitrification of NH_4^+ having occurred in sediments which may well have been oxic when submerged. An increase in NO_2^- concentrations between 5 and 8 cm supports this suggestion.

The lack of variation in DIP concentration with depth at SM, unlike DOP, suggests DIP is not derived from organic matter, but possibly from terrestrial runoff.

Variability in nutrient concentrations with depth was high at DS, whereas at DM profiles showed much more gradual change except for a few spikes, which are likely to be due to microniches with high organic content and distinct bacterial populations (Sørensen, 1978). DOP concentrations are likely to vary as function of historical organic inputs and remineralization rates, thus affecting DIP concentrations.

Diffusive nutrient fluxes

Anoxic conditions promote the release of DIP from sediment (Ingall and Jahnke 1994; Wallmann 2003). Micro-organisms accumulate and store P under aerobic conditions due to oxidative phosphorylation; under anoxic conditions this P is released as DIP after use in anaerobic respiration (Ingall and Jahnke 1994). However, in the current study, site SR exhibited the greatest DIP flux despite the lowest redox potential of any site, suggesting bacterial P storage was not the main factor controlling DIP fluxes.

Niencheski and Jahnke (2002) suggested that sediment nutrient concentrations reflect longer term conditions rather than water column nutrients levels. The burial of organic matter in sediments, P binding to clays and Fe, nutrient uptake by microphytobenthos and subsequent consumption by benthic invertebrates may all cause the sediments to act as a sink for nutrients. Bacterial remineralization of organic matter and diffusive fluxes from buried nutrients may cause sediments to act as a source of nutrients. Table 3 shows nutrient fluxes measured and calculated at a selection of study sites including the Ria Formosa. The fluxes calculated in the current study fall within the ranges found in other studies of nearshore sediments.

Rates of NH_4^+ uptake are high in *Enteromorpha intestinalis* compared to other macro-algae (Hein et al. 1995; Taylor et al. 1999). Organic matter derived from *Enteromorpha* sp. (as observed in the current study at OA) may then contribute to NH_4^+ fluxes as remineralization occurs. OA exhibited increasing NH_4^+ concentration with depth, reaching the highest concentration found at any site (~1350 μmol l^{-1}), combined with decreasing E_h and elevated NO_3^- concentrations in surface sediments (Fig. 3), indicative of organic matter remineralization. Redox potentials have been found to be up to 199 mV lower in bare sediments compared to those in which macrophytes are present, with the effect extending to 10 cm depth (Aldridge and Ganf 2003). Thus, ammonification of remineralized N is more

Table 3 Nutrient fluxes from selected studies including the current study (June–August, 2004)

Source	Site	DIP	NO$_3^-$	NO$_2^-$	NH$_4^+$	Method
Falcão and Vale (1990)	Ria Formosa, Portugal	-6 to 96	-175 to 25	–	0 to 911	M
Current study (Cores)	Ria Formosa, Portugal	11.9 to 123.4	59.7 to 169.9	-0.27 to 10.5	269.4 to 820.7	C
Mortimer et al. 1998	Humber Estuary, UK	-45.8 to 91.7	-1791.7 to 625	-62.5 to 58.3	-279.2 to 1079.2	C
Mortimer et al. 1998	Humber Estuary, UK	-37.5 to 37.5	-950 to -79.0	-1.0 to 7.0	-73.8 to 58.9	M
Forja and Gómez-Parra (1998)	Bay of Cádiz, Spain	104.2 to 262.5	–	–	629.2 to 833.3	C
Clavero et al. 1999	Palmones River Estuary, Spain	0.42 to 1.13	–	–	–	M
Clavero et al. 1999	Palmones River Estuary, Spain	0.05 to 0.13	–	–	–	C
Hopkinson et al. 1999	Plum Island Sound Estuary, USA	-10.8 to 60.8	DIN: -12.5 to 2712.5	–	–	M
Lillebø et al. 2004	Mondego Estuary, Portugal	-0.024 to 0.183	–	–	–	M
Hopkinson (1987)	Georgia Bight. Continental shelf, USA	2.0 to 50.0	1.3 to 35.4	–	25 to 102.1	M
Denis and Grenz (2003)	Gulf of Lions. Continental shelf, France	0 to 1.50	5.79 to 19.79	-1.79 to 1.08	1.42 to 4.21	M

Fluxes measured using benthic flux chambers or core incubations are noted as 'M'. Fluxes calculated using Fick's First Law of Diffusion or other means are noted as 'C'. All fluxes are given in units of $\mu mol\ m^{-2}\ h^{-1}$

likely to occur on bare sediments than on those with macrophytes. At site OA, *Enteromorpha* sp. may have acted as an additional source of N, but without actually being present directly above the cores to take up NH$_4^+$.

Scouring by clam digging may increase nitrification in sediments (Rocha et al. 2000) and short-term effects of shellfish dredging have been described by Falcão and Vale (1990), Falcão et al. (2003) and Warnken et al. (2003). However, it is uncertain how rapidly nutrient profiles return to the pre-disturbed state and whether clam digging alters sediment–seawater fluxes in the Ancão Basin. The sites sampled in the current study had not been recently disturbed. However, the long-term effects of clam digging on nutrient profiles are uncertain and investigation into the possibly of long lasting effects of clam digging would be of value.

Intertidal pools

As water temperature increases, redox potential decreases due to a loss of dissolved oxygen. However, the total decrease in redox potential was much greater in the intertidal pools (–50 mV) than in the trays of seawater (–5 mV). Thus, there is an impact of the sediments on redox potential, either due to an oxygen flux into the sediments, bacterial activity or oxygen consumption by benthic fauna.

Both sand and mud appear to be sinks for DIN. Concentrations predicted based on the effect of evaporation exceeded observed concentrations (adjusted for seawater biological uptake and remineralization in the water column) in all but two seawater samples in the sand and mud pools, indicating that there was a loss of DIN from the pools that must have been due to a flux into the sediments, uptake by microphytobenthos or settlement and burial of phytoplankton. Thus, intertidal pools are a route for N into the sediments. Total tidepool coverage must, therefore, be considered in any assessment or modelling of nutrient dynamics within a water body.

DIP and DOP tended to vary inversely in concentration in the sand and mud pools but not in the trays (Fig. 7), suggesting that microphytobenthos including cyanobacteria and benthic

bacteria are dominant in assimilation and remineralization of P. There were decreases in DIP between 5 and 5.5 h after mid-ebb tide in all pools, while DOP increased in all pools during this period, indicative of phytoplankton uptake of DIP.

The flux of DIP into the sediments in both pools may be caused by four mechanisms. Firstly, an increase in the DIP concentration gradient due to evaporation, and possibly bacterial remineralization of organic matter; secondly, due to a downward flux of DIP within the sediment by diffusion or advection causing a decrease in surface concentrations. Thirdly, due to uptake of DIP by microphytobenthos; and fourthly, due to settlement and burial of phytoplankton.

The necessary concentration gradient for the effluxes calculated may have been generated by phytoplankton uptake of DIP in the seawater, increasing DIP concentrations at the sediment–seawater interface due to an upward flux from deeper in the sediments, and remineralization of P by benthic bacteria. The variability in the fluxes may be due to bioturbation, which would not necessarily occur continuously and could be driven by a single species (Lohrer et al. 2004).

The positive mean flux of DIP in the pool on sand was 0.03 μmol m^{-2} h^{-1}. The efflux of nutrients to the intertidal pools decreases with a concomitant decrease in the sediment–seawater concentration gradient; this is due to the seawater being static in the pools and not being replaced by tidal flow. Overall, DIP exchange within the intertidal pools is small relative to diffusive fluxes on other intertidal sediments, probably due to the equilibrium reached across the sediment–seawater interface with time. Exchange of N is reversed and greater in magnitude than diffusive fluxes calculated from sediment seawater gradients. Concentration gradients may be maintained by oxidation and reduction of N species. Furthermore, microphytobenthos may be a major route of N into the sediment, leading to the large fluxes of DIN into the sediments of the intertidal pools (Fig. 7c). Therefore, tidepools provide a mechanism by which DIN can be temporarily "fixed" within the sediments to be released into the water column once sediments are covered by new seawater.

Theoretical nutrient transport

Ebb-tide seawater nutrient concentrations measured in the present study were higher than mean seawater nutrient concentrations in flood tide seawater (DIP: 0.19 μmol l^{-1}, NO$_2^-$: 0.09 μmol l^{-1}, NO$_3^-$: 0.57 μmol l^{-1}, NH$_4^+$: 0.03 μmol l^{-1}) measured at the Barra Nova inlet by Fletcher (2002). Fluxes calculated based on these lower nutrient concentrations (using Fick's First Law) are slightly greater than fluxes calculated based on ebb tide seawater nutrient concentrations (Table 1; Fig. 6), with a 5 μmol m^{-2} h^{-1} mean difference in DIP fluxes across all sites. However, over the salt marsh, the diffusive fluxes of NH$_4^+$ and NO$_3^-$ are 424 μmol m^{-2} h^{-1} and 10 μmol m^{-2} h^{-1} greater, respectively, on the flood tide. Thus, it appears that lower nutrient flood tide seawater may be enriched by DIN and DIP fluxes from the sediments, causing decreased diffusive fluxes on the ebb tide, particularly around the salt marsh. Based on observations, tidepools cover between 10 and 20% of the Ancão Basin at low water. Assuming intertidal pools covered 20% of the Ancão Basin with 50% each of mud and sand, the average mass of DIP contained in this water would only be 0.19 kg, 1.2% of the 15.41 kg DIP export from the Ancão Basin on each tidal cycle found by Fletcher (2002).

There was an average of 648.9 μg DIN in the intertidal pools despite the sediments being a sink for DIN. Therefore, if it were assumed that 20% of the Ancão Basin was covered by intertidal pools (on sand and mud) then the seawater contained with the pools would contribute 41.9 g of DIN to seawater once the pools were re-immersed; however, this DIN is derived from seawater from the previous ebb tide water rather than from the sediments, which were a sink for DIN in the pools.

If sediment seawater fluxes were as calculated from the sediment–seawater concentration gradients in the current study over a 12 h tidal cycle, assuming equal coverage of sand, mud and salt marsh sediment, within the Ancão Basin there would be average transports from the sediments to seawater of 1.89 kg DIP, 0.12 kg NO$_2^-$, 2.07 kg NO$_3^-$ and 1.65 kg NH$_4^+$. Thus, the DIN transport (3.84 kg) exceeds the DIP transport. The

sediments both within and outside of the Ancão Basin are a source of DIP during low water. However, the DIP efflux is not sufficient to account for the 15.41 kg DIP export from the Ancão Basin found by Fletcher (2002). Thus there must be terrestrial inputs of P to the Ancão Basin. Furthermore, N is buffered by the sediments to a greater extent than P, leading to lower N to P ratios in seawater exiting the Ancão Basin than in flood tide seawater.

Conclusions

The sediments of the Ancão Basin are a source of N and P on the ebb and flood tides and appear to act as a buffer of terrestrial nutrient inputs. Fluxes of DIP are greatest from sand sediments, attributable to P binding with fine sediments, but are insufficient to account for the flux of P from the Ancão Basin, suggesting terrestrial P inputs are higher in the Ancão Basin than elsewhere in the western Ria Formosa. High NH_4^+ effluxes were evident outside the Ancão Basin, possibly due to *Enteromorpha* sp. mats. Elevated NH_4^+ concentrations in salt marsh sediments are probably due to organic matter supply but DIP appears to be derived from other sources, possibly terrestrial runoff. Tidepools are an important route of N to the sediments at low water and, therefore, may increase the residence time of N within the Ancão Basin. Further investigations into groundwater flow, terrestrial nutrient inputs and sub-tidal sediments are recommended in the Ancão Basin. Thus it is apparent that nutrient concentrations in seawater exiting semi-isolated bodies of water do not necessarily reflect the magnitude of nutrient inputs due to sediment–seawater fluxes, which may also change N to P ratios, potentially leading to changes in the composition of the primary producer community. Future nutrient fluxes from sediments must be considered where a long-term reduction in nutrient concentrations is desired in the water column and quantification of tidepool coverage and consequent nutrient fluxes is desirable when calculating nutrient budgets, as tidepools may act as important routes for dissolved nutrients to enter the sediments, especially in areas where evaporation levels are high.

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