

# Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system

Andrew W. Dale<sup>1,2,\*</sup>, Ricardo Prego<sup>1</sup>

<sup>1</sup>Marine Biogeochemistry Research Group, Institute of Marine Research (CSIC), 6 Eduardo Cabello,  
36208 Vigo, Spain

<sup>2</sup>Department of Environmental Sciences, University of Plymouth, Plymouth PL4 8AA, United Kingdom

**ABSTRACT:** Sediment incubation microcosms, multitrapp apparatus and water column variables have been employed to describe the dynamic changes in benthic-pelagic coupling between nutrient pools in the Pontevedra ria, NW Spain, during spring and summer 1998. A comparison of the chemical characteristics of suspended and bed sediment together with sediment nutrient effluxes revealed that particulate organic nitrogen and carbon were progressively depleted upon transit through the nutrient pools. The main fate of particulate organic nitrogen reaching the bed sediment is denitrification, although resuspension is also important. An estimate of net denitrification ( $D_{\text{net}}$ ) was made at 2 muddy sites in the ria with a mass balance at the benthic boundary layer. First-order approximations calculate  $D_{\text{net}}$  to be 178 and 182  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$  at the 2 stations, and agree well with previous modelling estimates. Denitrification is highest when upwelling relaxes and the flux of organic matter to the sediment increases. Regular inputs of offshore water ensure water renewal and re-oxygenation of bottom waters, thus preventing anoxia, particularly in the summer. With upwelling, large quantities of ammonium are effluxed to the water column ( $250 \mu\text{mol NH}_4^+ \text{ m}^{-2} \text{ h}^{-1}$ ), probably as a result of the bed sediment resuspension engendered by upwelling and stirring of phytodetrital fluff held in suspension as neutrally buoyant material above the sediment surface. We hypothesise that hydrodynamical processes play an important role in determining the quantity of nutrients remineralised in the Pontevedra ria and, in the case of nitrogen, the rate of denitrification at the benthic boundary layer.

**KEY WORDS:** Upwelling · Denitrification · Nitrogen · Sediment · Hydrodynamics · Benthic-pelagic coupling · Pontevedra ria · Galicia

Resale or republication not permitted without written consent of the publisher

## INTRODUCTION

At present there is keen interest in deciphering the complex web of sediment nutrient recycling. The awareness that coastal sediments act as a sink for terrestrial nutrient inputs, particularly nitrogen, has led to a concerted effort among researchers to determine the main biochemical driving forces behind the buffering processes. For instance, we know that remineralisation

and mobilisation of chemical species are dependent upon the *in situ* redox environment. Benthic environments efficient at nutrient processing are well oxygenated and able to support high populations of enzymatically mediated microbes, whereas sediment anoxia tends to reduce the remineralisation potential (Kemp et al. 1990). However, evidence suggests that maximum nitrogen removal occurs when anoxic and oxic environments coexist in the superficial sedimentary layer (Jenkins & Kemp 1984). Under such conditions, bacterial nitrification ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ) and denitrification ( $\text{NO}_3^- \rightarrow \text{N}_2$ ) are coupled together across the redox microecosystems. In addition, the extent of

\*Present address: Dept of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, United Kingdom.  
E-mail: a.w.dale@plymouth.ac.uk

nitrification and denitrification may be regulated by dissolved  $O_2$  concentrations in the overlying water when  $NO_3^-$  concentrations are low (Rysgaard et al. 1994). Therefore, under the appropriate conditions, large quantities of nitrogen can be shunted out of the immediate biological cycles, thus creating a buffering effect and perhaps N-limitation in coastal systems (Nixon 1981).

Benthic remineralisation processes strongly influence the functioning of coastal systems (Boynton et al. 1995). Contributions of 30 to 80% of the phytoplanktonic nitrogen requirement in shallow (5 to 50 m) coastal environments have been reported to originate from the sediments (Nixon 1981, Blackburn & Henriksen 1983, Boynton & Kemp 1985). Equally, deposition of algal phytodetritus provokes sediment nutrient exchange by microbial remineralisation and gradient-driven diffusion. While these findings are valuable to coastal resource managers, relatively few workers have considered the potential hydrodynamical role in sediment nutrient processing (Floderus & Håkanson 1989, Vorosmarty & Loder 1994, Nielsen et al. 1995, Sloth et al. 1996, Asmus et al. 1998). Laboratory studies by Christiansen et al. (1997) showed that resuspension changes the diffusive sediment water fluxes of nutrients and oxygen consumption. Similarly, resuspension may give rise to profound modification of the water column nutrient characteristics (Morris et al. 1985). In the absence of resuspension, Li et al. (1997) discussed the influence of the rate of mass transfer across the sediment-water interface on constituent efflux. Changes in river flow may also affect sediment accumulation and redistribution (Bale et al. 1985). Therefore, strictly speaking, the majority of microcosm experiments should be interpreted semi-quantitatively.

The Pontevedra ria is one of 4 large embayments situated on the western coast of Spain collectively termed the 'Rias Bajas'. Northerly trade winds created by latitudinal displacements of the Azores and Greenland atmospheric pressure cells (Wooster et al. 1976, Blanton et al. 1987) favour offshore Ekman transport of surface water from the Rias Bajas and adjacent shelf. The resulting baroclinic pressure gradients in the rias are compensated by intrusions of nutrient-rich East North Atlantic Central Water (ENACW), a water mass normally centred offshore at 100 to 200 m depth (Fraga 1981, Fiuza et al. 1998). The quasi-permanent upwelling inside the Pontevedra ria is dependent on wind strength and direction and, theoretically, can occur at any time of the year, although usually from April to October (Prego et al. 2001). A proportion of the nutrient salts exported during the winter is reintroduced during upwelling in the form of remineralised inorganic nutrients (14 to 30%: Prego 1994) and creates the potential for high primary productivity when

terrestrial nutrient input is low (Tilstone et al. 2000). For this reason, the Rias Bajas are renowned for the intensive mussel raft aquaculture they support (Tenore et al. 1982).

This paper presents a description and analysis of nutrient fluxes ( $NH_4^+$ ,  $NO_3^-$ ,  $NO_2^-$ , Si) in the Galician Rias Bajas. A combination of water column studies, sediment core incubations, sediment trap deployments and sediment-constituent maps are used to describe the nutrient fluxes in terms of the immediate chemical environment (bed sediment and water column) and benthic-pelagic coupling (sedimentation rate and suspended particulate chemical composition). The data are subsequently discussed in terms of the hydrodynamical processes that contribute to the modulation of the nutrient cycling, and their influence on defined biological processes such as denitrification. To our knowledge, there has been no previous work on a similar theme regarding Galician coastal waters.

## MATERIALS AND METHODS

**Study site.** The Pontevedra ria extends 23 km from its head at the River Lérez in the east to the islands of Ons and Onza in the west (Fig. 1). In common with the other rias bajas it has a 'V' formation and gradually widens seawards, whereupon it divides into 2 channels. With a depth of 60 m, the southern channel between Couso Point and Onza island is deeper than the channel between Fagilda Point and Ons island in the north (14 m), and thus provides the main zone for marine and freshwater exchange.

As with the Vigo ria (Prego & Fraga 1992), there are distinguishable zones in the Pontevedra ria defined by the water column stratification, (1) the internal part from the River Lérez to Tambo island, (2) an intermediate section from Tambo island to Udra Cape, and (3) an oceanic zone from Udra Cape to Ons island (Fig. 1). Stratification is a function of river runoff in the winter and ENACW upwelling in the summer (Prego et al. 2001). Acting independently, freshwater runoff and wind-forcing favour either water retention or ria flushing, with the result that Zone 1 is the most estuarine-like and Zone 3 the most oceanic. The mean flow of the River Lérez is  $21.2 \text{ m}^3 \text{ s}^{-1}$ .

The catchment of the Pontevedra ria is dominated by granitic bedrock whose weathered components are transported into the ria. The largest sedimentary fractions, comprising coarse sands and gravel, are found to the south of Onza island and at the mouth of the River Lérez, where the near-bed currents are strongest. The oceanic boundary and the ria head are characterised by high and low sediment carbonate content, respectively, thus differentiating sediment of marine and

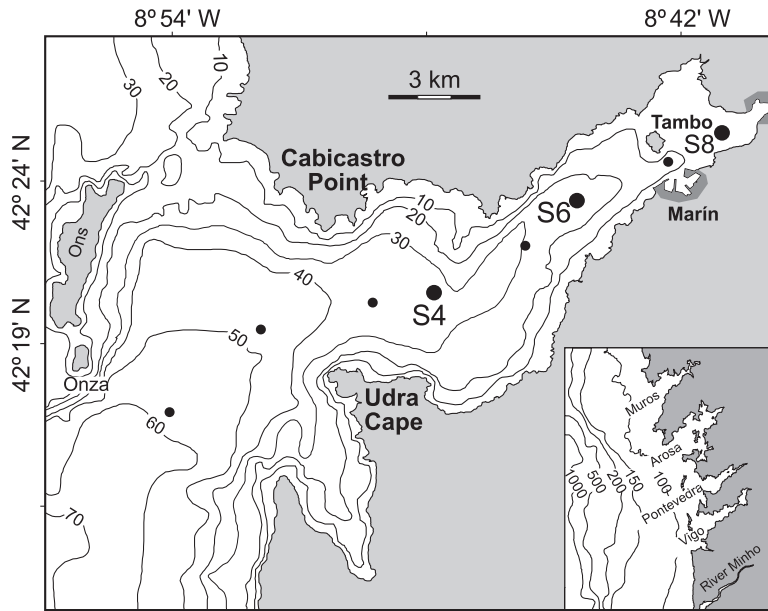


Fig. 1. Map of the Ria Pontevedra on local and regional scales. The city of Pontevedra and the River Lerez mouth are located in the top-right-hand corner. Sampling stations for water column nutrients, chlorophyll *a* and dissolved oxygen along the main axis of the ria are indicated by circles, the larger circles indicating the 3 stations (4,6,8) where sediment cores were taken in addition to samples for water column nutrients. Contour lines show depth (m)

terrestrial origin. The finer fractions, predominated by muds inter-dispersed with sandy patches, are situated along the central axis of the ria from a depth of 50 m in the external ria up to 5 m in the area around Tambo island. Mud banks are located along the northern margin of the internal ria, while the southern shore is notably sandy.

**Water column chemistry.** The sampling campaign took place fortnightly between February and October 1998 on board the RV 'Mytilus'. Water samples were collected at 8 stations along the longitudinal ria axis with Niskin 'General Oceanic' bottles at standard depths of 0, 5, 10, 20, 30 and 50 m (depth permitting; Fig. 1). Dissolved  $O_2$  was determined by the Winkler method and chlorophyll *a* by fluorimetric techniques using Whatman GF/F filters and 90% acetic extracts (Parsons et al. 1984). The inorganic nutrients nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), ammonium ( $NH_4^+$ ) and dissolved silicate (DSi) were analysed following the auto-analytical methodology of Hansen & Grasshoff (1983). The precision of 10 replicate analyses of nutrient aliquots of equal concentrations was:  $NO_3^- \pm 0.01 \mu M$  (within the 0–10  $\mu M$  range),  $NO_2^- \pm 0.01 \mu M$  (0 to 2  $\mu M$ ),  $NH_4^+ \pm 0.02 \mu M$  (0 to 2  $\mu M$ ) and  $DSi \pm 0.02 \mu M$  (0 to 65  $\mu M$ ). Hydrographical data (conductivity, temperature, pressure) were collected at 11 stations with a Sea-Bird SEACAT 19 CTD.

**Bed-sediment analysis.** The surface sediment in the ria was analysed for biogenic opal and particulate organic carbon (POC) and nitrogen (PON) by means of a rigorous sampling regime of high spatiality. Over the ria, 33 sediment samples of the whole oxic layer (top 0 to 1 cm) were collected with a Shipek grab and dried in an oven below 40°C. Sediments were size-fractionated into mud, sand and gravel with 63 and 2000  $\mu m$  sieves. Analysis for percentage opal followed the alkaline digestion method described by Mortlock & Froelich (1989). POC and PON were determined with a Carlo Erba CHNS-O 1108 elemental analyser by the Research Support Service at the University of La Coruña. Organic carbon was calculated as the difference between total carbon measured by the analyser, and inorganic carbon as weight loss at 550 and 975°C. In this paper, opal refers to particulate biogenic silica in the bed sediments.

**Suspended particulate matter.** Water column particulate material was collected with a multitrap system (Knauer et al. 1979) anchored to the seafloor at 2 sites in the ria (Stns 4 and 6) for periods of 2 to 3 d.

Trap deployment was intended to span the whole survey period, although logistical problems limited the collection period to 6 mo (February to July 1998). The trap system consisted of 4 bound Plexiglas tubes (6 cm diameter) filled with preservative-free filtered seawater. NaCl (35 g) was added to each tube to raise the salinity and prevent particle loss. POC and PON were analysed as above, and biogenic silica (BSi) following the methodology of Ragueneau & Tréguer (1994). BSi is defined as particulate biogenic silica in the water column.

**Nutrient flux assays.** Sediment cores were regularly sampled from Stns 4 (35 m depth), 6 (25 m) and 8 (9 m) for incubation experiments. Triplicate samples were extracted at each site. Cores of 6 to 8 cm undisturbed sediment and approximately 200 ml of the overlying water were taken with a 'Rouvillois' box-corer fitted with Plexiglas tubes (length 20 cm, diameter 5.4 cm; Fig. 2). The tubes were sealed at the bottom with a rubber bung, inspected for trapped air pockets and to verify that the collection process had not artificially disturbed the sediment structure. A fourth control consisted of seawater only, transferred from the 3 other tubes. The cores were immediately incubated on-board at the *in situ* temperature and in the dark. To help maintain the water column oxic, a loose-fitting lid was placed on each tube permitting gas exchange with

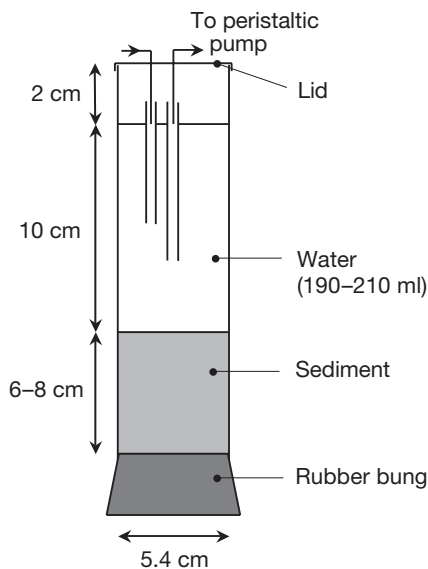


Fig. 2. Experimental incubation design. Triplicate sediment cores and a control of water only were used for nutrient flux assessment. All cores were maintained in a water bath at *in situ* temperature in darkness

the atmosphere, and the supernatant water was continually circulated by means of a peristaltic pump operating at  $4 \text{ ml min}^{-1}$ . At intervals of 0, 1, 2, 3, 4, 5, 6 and 12 h, 10 ml aliquots were taken from each core for analysis of dissolved  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$  and DSI following the methodology described above. Corrections to the fluxes were made for the inclination of the sediment inside the incubation cores. Although this may seem trivial, a slope of 10 to 20° will result in several percent greater sediment-water nutrient exchanges. Further corrections were made to account for the decrease in water volume with removal of aliquots over the incubation period. Finally, the fluxes were corrected against the control when necessary. The concentration-time curves for each analysis were inspected, and those clearly displaying random fluxes were not considered. The mean flux of the remaining cores was then calculated. The correlation coefficients of the nutrient rates in the sediment and control cores were greater than  $r^2 = 0.70$  for >90% of the incubations.

## RESULTS

### Water column characteristics

The temporal change in chl *a* at Stn 4 during the survey period is shown in Fig. 3. February was characterised by long sunshine hours and mild temperatures. At the same time, high nutrient

concentrations and a stable water column created suitable conditions for early phytoplankton growth. Consequently, a sharp decline in nutrients and a simultaneous increase in dissolved  $\text{O}_2$  were noted in the main body of the ria, resulting from a 'mini-phytoplankton bloom', where chlorophyll *a* (chl *a*) concentration increased to  $4 \text{ mg m}^{-3}$  below the surface at Stn 4 (Fig. 3). Other workers have described similar spring blooms as a 'false start' (Owens et al. 1986). Fig. 4a shows the chemical distribution in the ria shortly after the early bloom, when the concentrations of inorganic nitrogen were generally below  $1.0 \text{ } \mu\text{M}$ , reaching maximum values near the ria bed. Surface concentrations were close to detection limits. Maximum DSI concentrations ( $5.0 \text{ } \mu\text{M}$ ) were recorded both near the ria bed and at the ria head close to the River Lérez mouth. Minimum DSI concentrations were recorded in the surface layers ( $1.0 \text{ } \mu\text{M}$ ), concomitant with oxygen supersaturation (>110%). In April and May, favourable meteorological conditions and increasing fluvial nutrient inputs initiated the spring phytoplankton bloom with chl *a* reaching  $1.5 \text{ mg m}^{-3}$  in the central ria (Fig. 3).

In the dry season, nutrient concentrations, emblematic of the August cruise (Fig. 4b), were elevated in comparison with those in spring, enhanced by inputs of nutrient-rich ENACW. In August, nutrient concentrations in the upper 10 m water layers of the inner ria were  $7.3 \text{ } \mu\text{M NO}_3^-$ ,  $0.6 \text{ } \mu\text{M NO}_2^-$ ,  $2.8 \text{ } \mu\text{M NH}_4^+$  and  $5.7 \text{ } \mu\text{M DSI}$ . Chl *a* concentration increased 4-fold to  $3.8 \text{ mg m}^{-3}$  in the external ria (data not shown), and up to  $2.0 \text{ mg m}^{-3}$  at Stn 4 (Fig. 3). Dissolved oxygen saturation in the bottom water layers in summer (70%) was less than in spring (90%).

### Opal, POC and PON distribution in the sediment

The percentage opal, POC and PON and the sediment-sorting in the upper 1 cm of the sediment in the

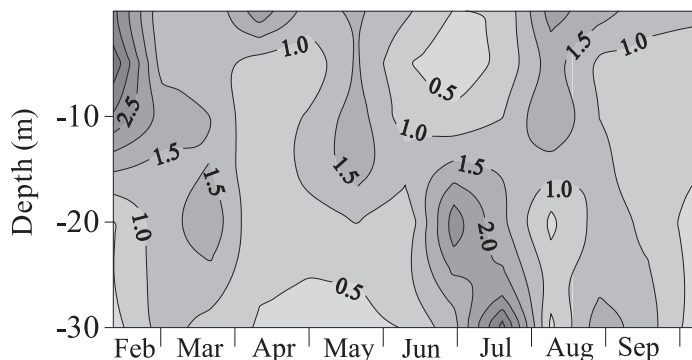


Fig. 3. Temporal variability of chlorophyll *a* ( $\text{mg m}^{-3}$ ) with depth, measured at Stn 4 during 1998

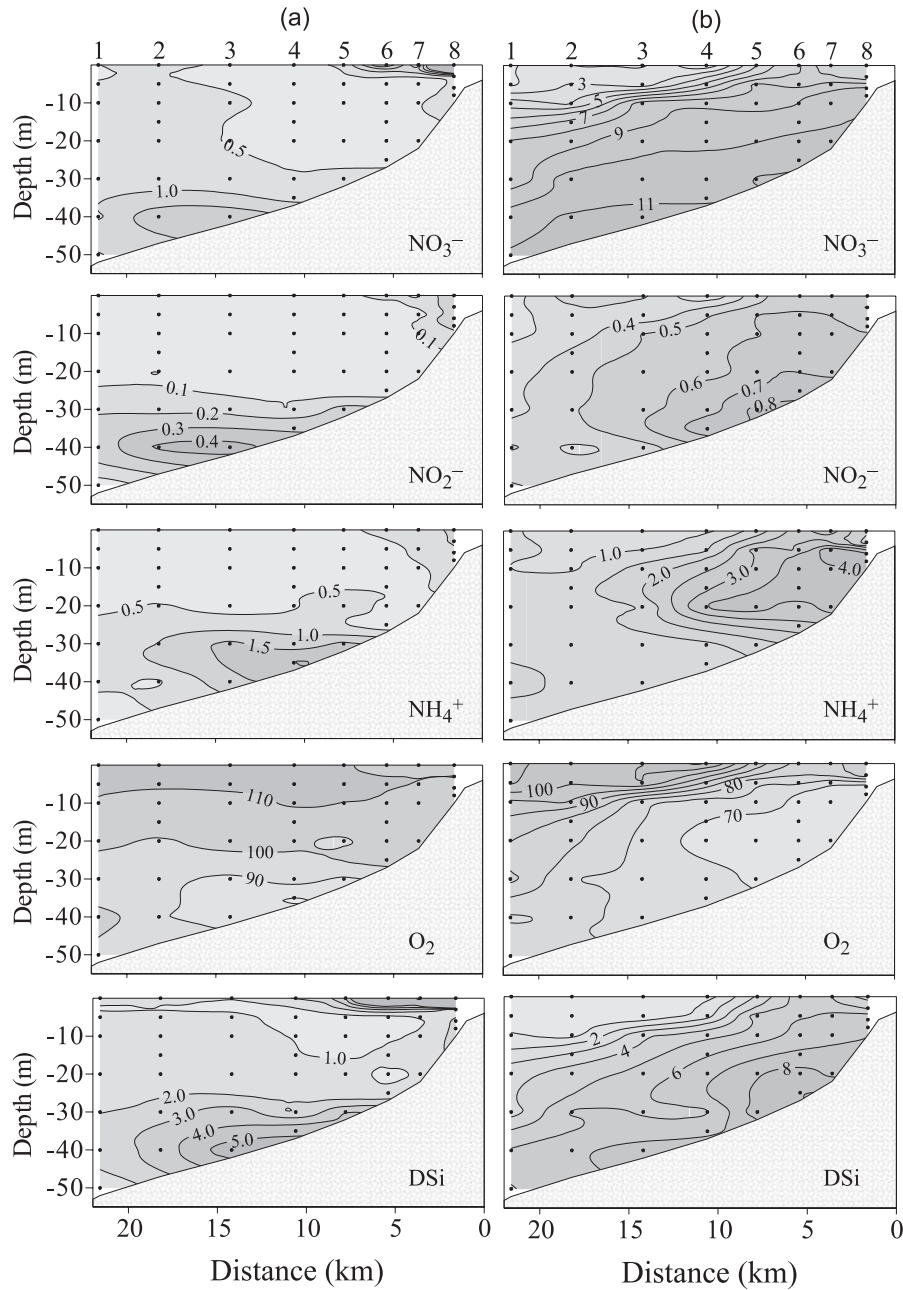


Fig. 4. Isoplots of nutrients ( $\mu\text{M}$ )  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , DSi and dissolved  $\text{O}_2$  (% saturation) along the main axis of the Pontevedra ria during 1998 in (a) spring (March 10), and (b) summer (August 1). Stns 1 to 8 (Fig. 1) are indicated on the top horizontal axes. The mouth of the River Lérez is located upstream of Stn 8

Pontevedra ria are presented in Fig. 5. Table 1 provides further data on the size-fractionated sediment.

The highest percentage of opal in the Pontevedra ria sediments (5.0%) was found in the internal ria adjacent to the northern coast, concentrated behind Tambo island (Fig. 5a). At the ria head, coarse terrestrial material dominated the sediment structure and the opal fraction decreased to <0.5%. At Stn 4 the opal content was ~2.0%, a value representative of the adjacent continental shelf (Prego & Bao 1997).

Total POC and PON generally showed a similar geographical distribution, with the highest fractions (4.7 and 0.7% respectively) close to the northern coast in the internal ria (Fig. 5b,c). Total organic material in the inner ria may be as high as 10% (López-Jamar et al. 1992), and is enhanced by sedimentation of faecal material from the intensive aquaculture of the mussel *Mytilus edulis* in this area. In contrast to opal, a second zone of high POC (7.4%) and PON (0.7%) was located behind Tambo island close to the mouth of Marín

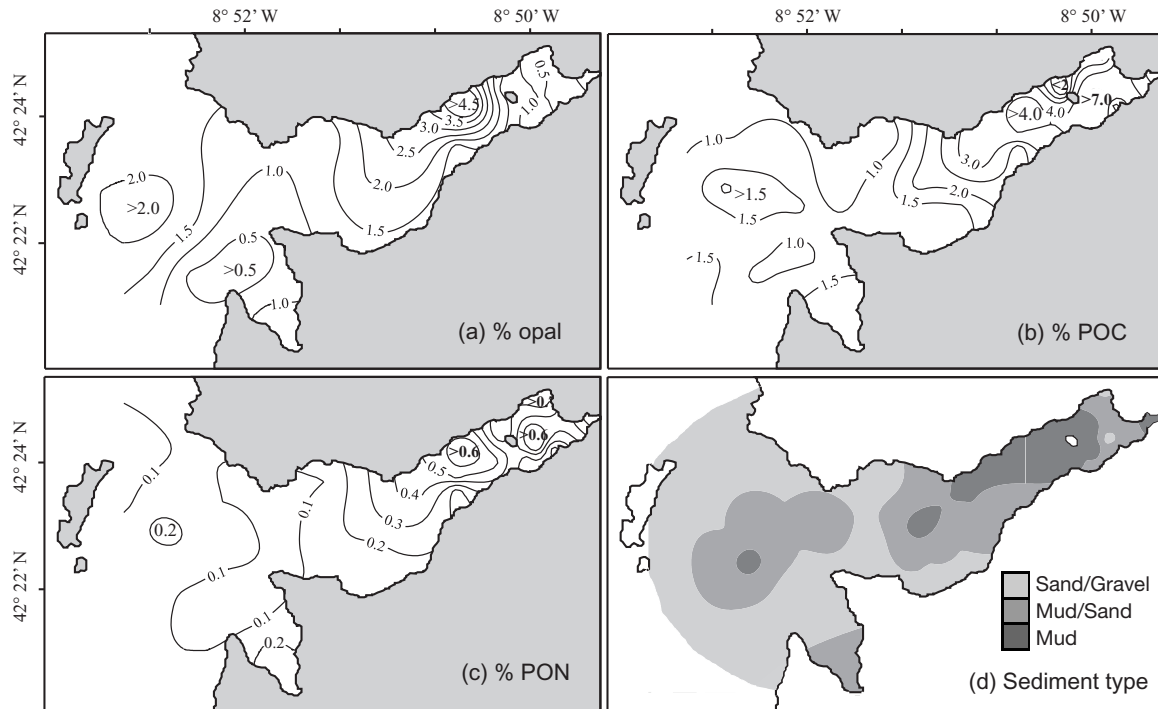


Fig. 5. Total fractions of opal (a), POC (b), PON (c) and the superficial sediment structure (d) in the Pontevedra ria. Samples were taken from the uppermost oxic layer (0 to 1 cm)

Table 1. Characteristics of the sediment at the 3 sites (determined in incubation microcosms) where sediment cores were taken. Total sediment represents the oxic layer in the upper 1 cm. All values other than molar C:N ratios are percentage dry weight

Site	Description	Total sediment			Fraction <63 mm			Fraction >63 mm		
		Opal	POC	PON	POC	PON	C:N	POC	PON	C:N
4	Mud/sand	1.91	2.16	0.24	3.74	0.40	10:1	1.87	0.22	9:1
6	Mud	2.73	4.02	0.53	5.27	0.55	10:1	3.41	0.52	7:1
8	Sand	1.34	7.42	0.66	6.28	0.55	11:1	8.11	0.72	12:1

harbour. This area is likely to be impacted by discharges of particulate organic material from a nearby paper mill (Mora et al. 1989, Arbones et al. 1992) and urban wastewater from the Pontevedra urbanisation. The upshot of this is maximum POC and PON fractions in the coarse and fine sediments at Stn 8 (Table 1).

Suspended and bed sediment pools are closely coupled in dynamic coastal systems. The material caught in the multitrap apparatus at the sediment surface can be used to gauge the extent of the coupling between the 2 reservoirs. The temporal variability in the elemental N:Si and C:N molar ratio of particulate material collected in traps at Stns 4 and 6 is shown in Fig. 6 a,b respectively, together with the mean sedimentation rates of particulate Si and PON at Stns 4 and 6. A decrease in C:N is observed to coincide with an increase in PON sedimentation, and similar trends can be seen with regard to N:Si and particulate Si sedimentation rate. The N:Si composition of the cap-

tured sediment was consistently below the diatom N:Si composition of ~1 (Nelson et al. 1995), and averaged 0.56. The C:N ratio (Fig. 6b) of local phytoplankton was determined to be 7 to 8 by Rios & Fraga (1987). This is consistent with our multitrap data, with notable deviations in early February (C:N ≈ 10) and in April and early May (C:N ≈ 4 to 5). The sediment maps in Fig. 7 show further evidence for PON loss throughout the ria. The C:N ratios were notably higher along the southern margins of the internal ria (Fig. 7a), and increased toward the inner ria (C:N ≈ 12). On the northern coast, C:N approximated more closely the local phytoplanktonic composition of 7 to 8 (Rios & Fraga 1987). The N:Si ratio in the sediment surface was approximately 0.2 over the ria, except in the areas of industry and urbanisation in the inner ria (Fig. 7b). C:Si ratios were consistently lower than in the phytoplankton (7 to 8), with increasing to >10 at the ria head (Fig. 7c).

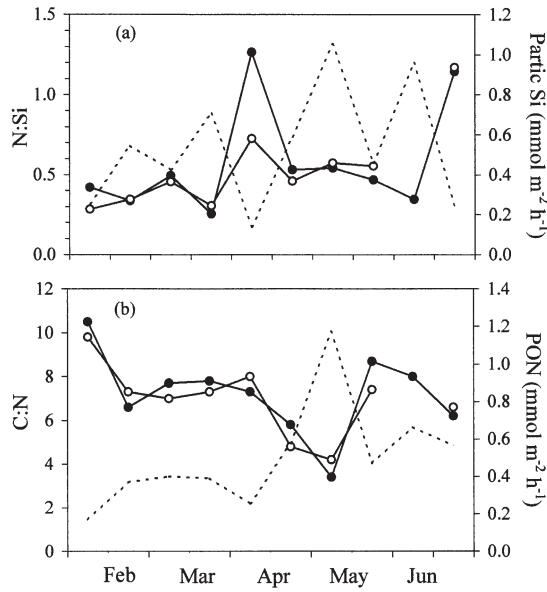


Fig. 6. N:Si (a) and C:N (b) molar composition of particulate material caught in sediment traps between February and June 1998 at Stns 4 (●) and 6 (○) in the Pontevedra Ria. Dotted line in (a) represents the mean sedimentation rate of particulate Si at Stns 4 and 6, and that in (b) the mean sedimentation rate of particulate organic nitrogen (PON) at Stns 4 and 6

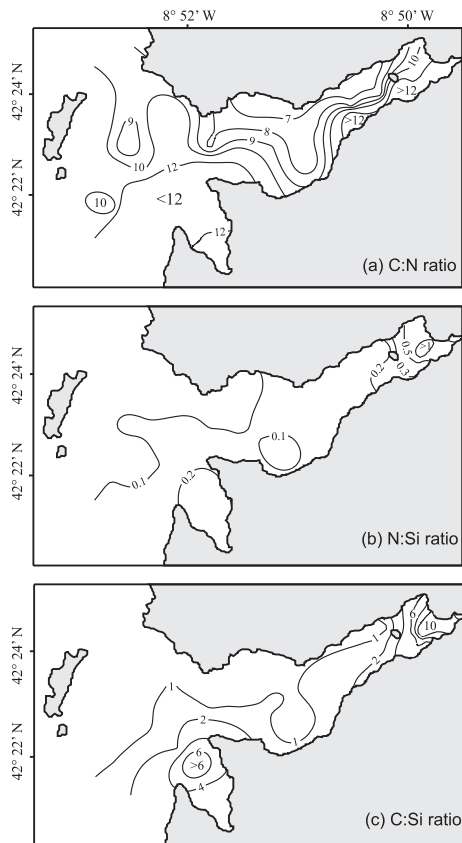


Fig. 7. Nutrient elemental molar ratios in the oxic upper 1 cm of the sediment in the Pontevedra ria

**Sediment fluxes**

The seasonal variation in the fluxes of DSi,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are shown in Fig. 8. The fluxes follow the general trend of  $\text{DSi} > \text{NH}_4^+ > \text{NO}_3^- > \text{NO}_2^-$ . The fluxes were generally higher at Stns 4 and 6 than at Stn 8. DSi was always released from the sediment, and

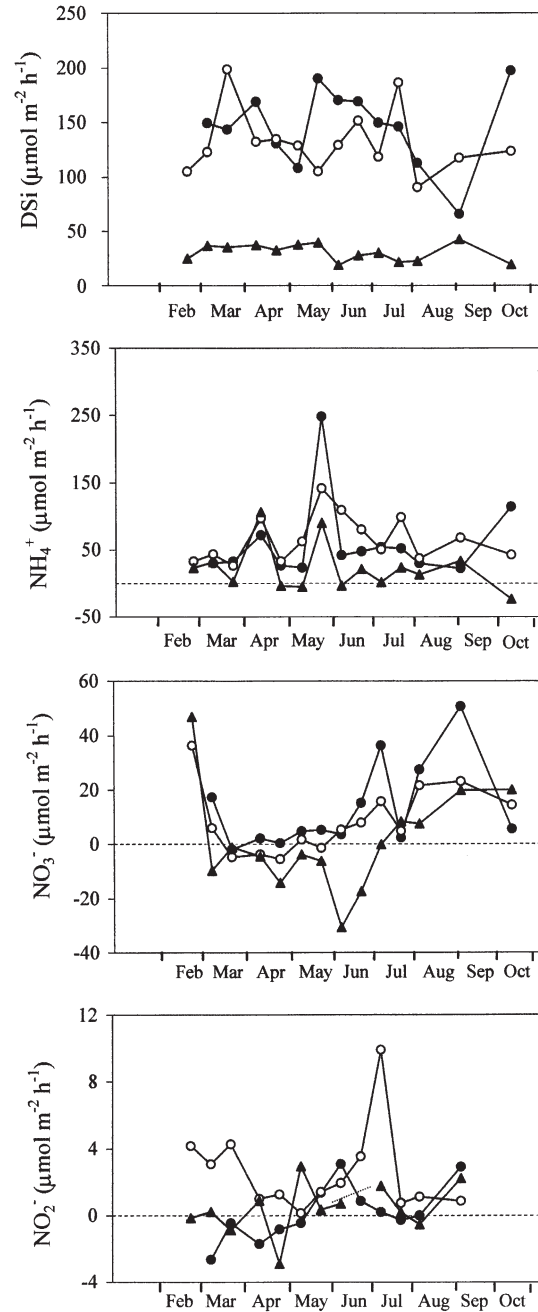


Fig. 8. Seasonal variation in the fluxes of DSi,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  across the sediment-water interface at Stns 4 (●), 6 (○) and 8 (▲). Each flux is the mean of triplicate analyses. Positive fluxes indicate release to the water column and negative fluxes indicate sediment nutrient uptake

the mean effluxes were 4-fold higher at Stns 4 and 6 than at Stn 8, with rates of 149, 137 and 37  $\mu\text{mol m}^{-2} \text{h}^{-1}$  respectively.  $\text{NH}_4^+$  effluxed the sediment at Stns 4 and 6, but  $\text{NH}_4^+$  was occasionally taken up at Stn 8. The  $\text{NH}_4^+$  efflux at Stn 6 reached a maximum on May 26, when the efflux was almost 250  $\mu\text{mol m}^{-2} \text{h}^{-1}$ . The direction of the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  fluxes was variable. Net  $\text{NO}_3^-$  fluxes were small and directed into the sediment during spring at a rate of 1  $\mu\text{mol m}^{-2} \text{h}^{-1}$ . In summer (June 9 to September 1) the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  efflux rates were up to 50  $\mu\text{mol NO}_3^- \text{m}^{-2} \text{h}^{-1}$  and 4  $\mu\text{mol NO}_2^- \text{m}^{-2} \text{h}^{-1}$  at Stn 4, and up to 20  $\mu\text{mol NO}_3^- \text{m}^{-2} \text{h}^{-1}$  and 10  $\mu\text{mol NO}_2^- \text{m}^{-2} \text{h}^{-1}$  at Stn 6.

## DISCUSSION

### Hydrographical influence on benthic-pelagic coupling

Offshore water input creates friction on the seabed and determines the flushing time, both of which processes indirectly regulate ria ventilation, the phytoplankton nutrient availability and, therefore, the particulate organic material deposited and resuspended from the sediments. Accordingly, we hypothesise that hydrodynamical processes ultimately dominate the sediment biogeochemistry in the Pontevedra ria.

One important aspect of the hydrodynamical influence on sediment composition is highlighted in Fig. 5, where high opal, PON and PON fractions were observed seaward of Tambo island and along the northern coast. A 3D hydrodynamical model of the Pontevedra ria (Taboada et al. 2000) revealed that seaward-flowing surface-water currents are deflected behind Tambo island, weakened, downwelled and cycled landwards. This circulation is thus presumably partly responsible for the size-distribution of particulates (Fig. 5d) and the spatial variability of opal, POC and PON in the sediment (Fig. 5a–c, Table 1). Similar trends have been observed in the adjacent Vigo and Arosa rias (Barciela et al. 2000).

Given the hydrographical importance of offshore inputs of cold, nutrient-rich East North Atlantic Central Water in the Pontevedra ria (Prego et al. 2001), it is reasonable to assume that upwelling also plays an important role in the sediment biogeochemistry. However, little is known about the impact of upwelling stress and relaxation cycles on sediment regimes. The incoming water flux ( $Q_{\text{in}}$ ) to the Pontevedra ria over the sampling period has been quantified (A. W. Dale & T. R. Prego unpubl. data) using a non-stationary-state water and salt-budget model (Gordon et al. 1996 and present Fig. 9). In spring, it can be seen that the  $\text{NH}_4^+$  effluxes on April 13 and May 26 in Fig. 8 are concomitant with discrete upwelling events (Fig. 9), with up to

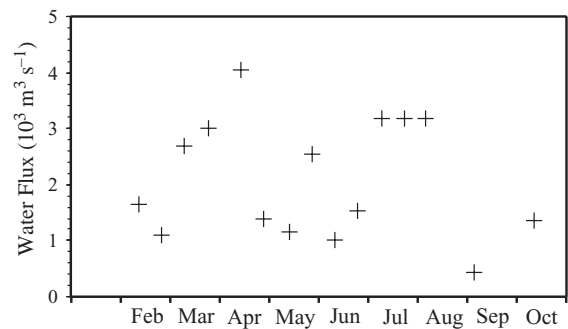


Fig. 9. Temporal change in incoming water flux to the ria,  $Q_{\text{in}}$ , through the cross-section between Udra Cape and Cabcastro Point (Fig. 1) between February and October 1998, quantified with a non-steady-state water and salt budget

250  $\mu\text{mol m}^{-2} \text{h}^{-1}$  at Stn 4 alone. DSi showed a similar efflux increase on May 26 at Stn 4, close to the ria mouth. Literature evidence (Hansen & Blackburn 1992, Conley & Johnstone 1995, Sloth et al. 1995) suggests that these observations of the  $\text{NH}_4^+$  efflux on April 13 and May 26 may result from 2 separate detrital deposition events after spring blooms. Delayed remineralisation of the spring phytoplankton blooms is also conceivable, with  $\text{NH}_4^+$  fluxes possibly taking up to 15 d to return to steady state levels (Hansen & Blackburn 1992). However, SCUBA divers working in the narrow inner zone of the Rias Bajas have observed resuspension of bed sediment. The idea of decaying biological fluff of low settling velocity held in suspension above the sediment surface in response to tidal currents has been discussed as part of the recent North Sea Sediment Resuspension Experiment (SERE: Jago & Jones 1998, Millward et al. 1998). Furthermore, the mineralisation of algal material results in an increased concentration of  $\text{NH}_4^+$  in the porewater (Conley & Johnstone 1995), which may be effluxed by advective flushing (Asmus et al. 1998). The results of these workers led us to the hypothesis that the incoming water flux may have played an important role in generating the large  $\text{NH}_4^+$  effluxes throughout the ria on April 13 and May 26 by stirring of bottom waters. In support of this theory, the tongue of water characterised by oxygen undersaturation and near-bed emanation of  $\text{NH}_4^+$  in March (Fig. 4a) resembles remineralisation of quasi-benthic, neutrally buoyant phytodetritus immediately above the sediment surface. This biological fluff is an important niche for microbial processes and was almost certainly incorporated in the sediment core extractions. Therefore, the spring  $\text{NH}_4^+$  efflux on April 13 and May 26 may have had 2 sources: (1) porewater infusions of  $\text{NH}_4^+$  accumulated from the 2 spring blooms, and (2) 'fluidised-bed' microbial remineralisation and dissimilatory  $\text{NO}_3^-$  reduction mediated by bacteria adsorbed to the suspended particulate matter,



in a similar way to the *in situ* nitrification noted by Owens (1986) and Uncles et al. (1998) in turbid estuaries.

In summer, the lower  $\text{NH}_4^+$  and higher  $\text{NO}_3^-$  effluxes (Fig. 8) and the  $\text{NH}_4^+$  and  $\text{NO}_2^-$  isoplots (Fig. 4b) were evidence of nitrification of phytoplankton material, in contrast to other areas where summer is characteristically a period of low sediment nitrification potential, mainly due to depressed  $\text{O}_2$  concentrations or high oxygen consumption (Seitzinger et al. 1983, Jenkins & Kemp 1984). The prominent oxygen decrease (Fig. 4b) and high chl *a* concentration above the bed sediment ( $3.5 \text{ mg m}^{-3}$ ; Fig. 3) lend further support to this premise. An important feature of the data is a decrease in  $\text{NH}_4^+$  efflux (Fig. 8) despite high  $Q_{\text{in}}$  (Fig. 9) and sediment loading of fresh biogenic material (Fig. 3). An explanation for low  $\text{NH}_4^+$  efflux may be found in the laboratory resuspension experiments of Sloth et al. (1996), who highlighted the importance of the natural frequency of resuspension. In other words, regular summer upwelling in the Pontevedra ria may impede accumulation of  $\text{NH}_4^+$  at the benthic boundary layer by continual reworking of the sediment and fluff in suspension. Essentially, a similar sequence of events has been discussed by Álvarez-Salgado et al. (1996) regarding rapid dispersal of  $\text{NH}_4^+$  at the benthic boundary during upwelling in the Arosa ria and also by Christensen et al. (2000), who observed a 'wash out' of sedimentary organic material by bottom water currents. Consequently, it is likely that resuspension is a likely fate of PON in summer, when high rates of PON export have also been observed in the adjacent Arosa and Vigo rias (Prego 1994, Álvarez-Salgado et al. 1996).

### Sediment nutrient processing

The rate of nutrient processing in the sediment can be assessed by first considering the DIN:DSi ratio of the nutrient effluxes at Stns 4, 6 and 8 during the spring and summer (Fig. 10), whereby DIN is the sum of the  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$  fractions. An increase in DIN:DSi was noted at all stations when water input was high on April 13 and May 26 ( $Q_{\text{in}}$ ; Fig. 9), mainly due to the  $\text{NH}_4^+$  efflux. The sediment flux data on the dates of multitraps deployment (February to July; Fig. 6), reveal that the mean DIN:DSi ratios of the nutrients effluxed at Stns 4 (0.46) and 6 (0.57) were higher than those of the particulate material bed sediment (0.13 Stn 4, 0.19 Stn 6) but similar to those of the particulate material collected in the multitraps (0.58 Stn 4, 0.54 Stn 6). This suggests that most material remineralised and effluxed from the sediments is recently deposited algal matter. Low N:Si in the bed sediment commonly arises from *in situ* oxidation of

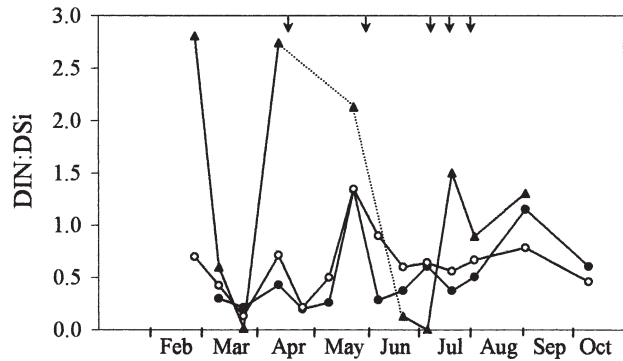


Fig. 10. DIN:DSi molar ratio of the effluxed nutrients between February and October 1998 at Stns 4 (●), 6 (○) and 8 (▲) where DIN is equal to the sum of the  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  fluxes. Arrows represent periods of high water influx into the ria

labile POC and PON in the water column and sediments, which will increase the proportion of opal and refractive C in the particulate matter (Westrich & Berner 1984). Opal appears to be more resistant to microbial attack than POC and PON, since dissolution is partially impeded by the organic matrix surrounding diatom tests (Bidle & Azam 1999). Furthermore, as the porewaters become saturated with DSi, further opal dissolution is debilitated (Hurd 1983), ultimately leading to sediment opal preservation and burial and low particulate DIN:DSi ratios (Fig. 7).

The amount of a particular nutrient ( $Nu$ ) sequestered by the sediments is a function of the nutrient sedimentation rate ( $dS_{Nu}/dt$ ) and the net nutrient efflux rate ( $dE_{Nu}/dt$ ) across the sediment-water interface. In addition, particulate detrital algal fluff may be resuspended. We have no direct measurements of resuspension and, crucially, our data have shown that this is an important process in the Pontevedra ria. Resuspension would lead to an overestimation of PON sedimentation. Consequently, we can introduce a resuspension factor into Eq. (1) based on the assumption that 50% of the apparent  $Nu_{\text{storage}}$  is resuspended. Thus the estimated apparent  $Nu_{\text{storage}}$  data is quantified using the following mass balance equation, and is shown graphically in Fig. 11:

$$\text{apparent } Nu_{\text{storage}} = 0.5 \times \frac{dS_{Nu}}{dt} - \frac{dE_{Nu}}{dt} \quad (1)$$

We assume steady state in bacterial biomass for Eq. (1) over the study period, despite the possibility of some N storage within this pool. With isolated upwelling (April 13 and May 26), both  $N_{\text{storage}}$  and  $Si_{\text{storage}}$  were low, even for N at Stns 4 and 6 and for Si at Stn 6, indicating a sediment net nutrient loss. The bottom sediments sequestered Si and N throughout the sampling period, with mean rates of  $126 \mu\text{mol m}^{-2} \text{ h}^{-1}$  (Stn 4) and  $130 \mu\text{mol m}^{-2} \text{ h}^{-1}$  (Stn 6) for Si, and  $194 \mu\text{mol m}^{-2} \text{ h}^{-1}$

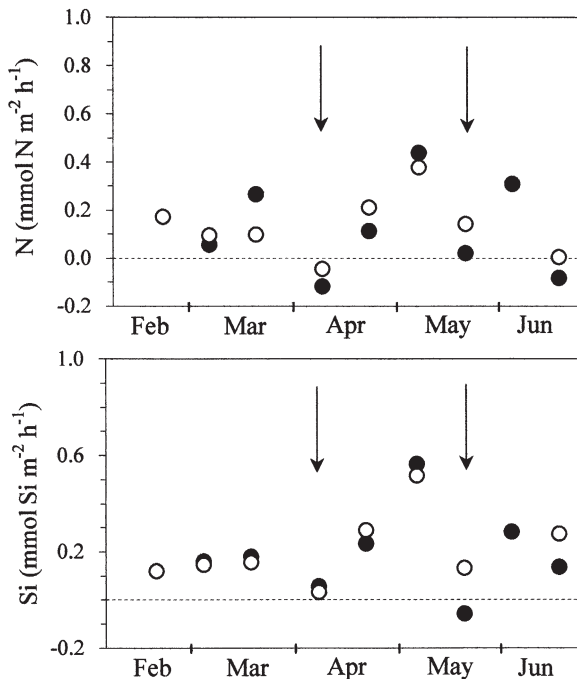


Fig. 11. Apparent storage of N and Si for the Pontevedra ria sediments at Stns 4 (●) and 6 (○) between February and June 1998 calculated from the particulate Si and PON caught in sediment traps and the rate of DIN and Si efflux from the sediments (Eq. 1). Arrows represent periods of high water influx into the ria

(Stn 4) and  $208 \mu\text{mol m}^{-2} \text{h}^{-1}$  (Stn 6) for N. Employing the whole data set, there was a linear relationship between  $N_{\text{storage}}$  and  $Si_{\text{storage}}$  ( $N_{\text{storage}} = 0.89 \times Si_{\text{storage}} + 39$ ;  $r^2 = 0.69$ ,  $p < 0.01$ ). The sediment N:Si sequestration ratio is equal to 1.55 at Stn 4 and 1.58 at Stn 6, and so there appears to be a greater capacity for N removal compared to Si removal if the particulate material is considered phytoplanktonic (N:Si = 1).

Clearly then, additional N must have been lost from the sediments in order to preserve the surface sediment N:Si ratio of ~0.1 to 0.2 (Fig. 7). Organic N reaching the sediment will be buried, resuspended, remineralised, and either effluxed or denitrified. The sediments at Stns 4 and 6 were located below the 1% light level throughout the experiment, and so benthic algal nutrient assimilation was presumed negligible. Burial is also ignored as this takes place over very long timescales. A resuspension factor has been included in Eq. (1), and so assuming that denitrification was the remaining dominant N-cycling process, a first-order estimate of net denitrification ( $D_{\text{net}}$ ) can be calculated with a constituent flux balance across the benthic boundary (Kamp-Nielsen 1992). Here we employ the sedimentation rate inferred from the multitrap deployment, opal and PON fractions in bed and suspended sediment, together with the net flux of N and Si across

the benthic boundary layer. Assuming apparent  $Si_{\text{storage}}$  is equal to true  $Si_{\text{storage}}$ :

$$D_{\text{net}} = \text{apparent } N_{\text{storage}} - \text{true } N_{\text{storage}} \quad (2)$$

where

$$\text{true } N_{\text{storage}} = \left[ \frac{N}{Si} \right]_{\text{sediments}} \times \text{apparent } Si_{\text{storage}} \quad (3)$$

N:Si in Eq. (3) is calculated from the particulate material contained in the top 0 to 1 cm of sediment, representing many years of sedimentation. The mean N:Si of the sediment trap material (0.56) is substantially higher than the uppermost 0 to 1 cm of bed sediment (0.13 to 0.19), and implies that the upper sediment is well degraded, although we acknowledge that a small amount of unremineralised organic material was included, which will tend to increase the  $D_{\text{net}}$  estimate.

The time-series results for  $D_{\text{net}}$  and PON deposition at Stns 4 and 6 are shown in Fig. 12. After examining many combinations, we found no significant correlation between  $D_{\text{net}}$  and other physical (temperature: Brunt-Väisälä water-column stability) or chemical (water column  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{O}_2$ ) parameters. An interesting feature of Fig. 12 is the notable decrease in PON sedimentation and  $D_{\text{net}}$  when upwelling stress is high (arrows in Fig. 12). Between upwellings,  $D_{\text{net}}$  showed a 5-fold increase from  $100 \mu\text{mol N m}^{-2} \text{h}^{-1}$  in early April to  $500 \mu\text{mol N m}^{-2} \text{h}^{-1}$  in May. Mean  $D_{\text{net}}$  values were  $178 \mu\text{mol N m}^{-2} \text{h}^{-1}$  at Stn 4 and  $182 \mu\text{mol N m}^{-2} \text{h}^{-1}$  at Stn 6. An independent box-model  $D_{\text{net}}$  estimate of  $220 \mu\text{mol N m}^{-2} \text{h}^{-1}$  has been made by Dale & Prego for the Pontevedra ria. The difference between the 2 estimates presumably arises from the 2 contrasting approaches for calculating denitrification (Nielsen et al. 1995). Regional denitrification estimates include  $11.3 \mu\text{mol N m}^{-2} \text{h}^{-1}$  for North Sea sediments (Lohse et al. 1996) and  $700 \mu\text{mol N m}^{-2} \text{h}^{-1}$  for the North Atlantic continental shelf (Seitzinger

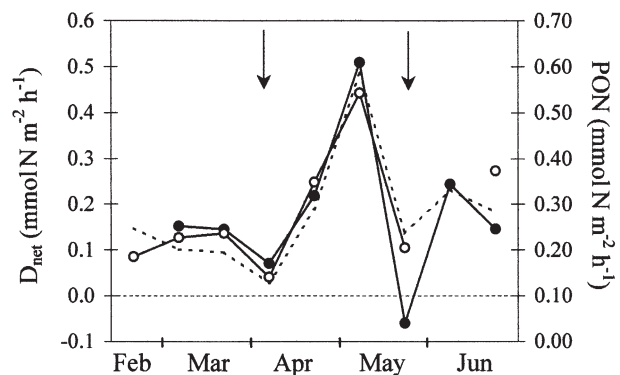


Fig. 12. Time-series net denitrification at Stns 4 (●) and 6 (○). Dotted line is the mean rate of particulate organic nitrogen (PON) flux to the sediment at Stns 4 and 6. Arrows represent periods of high water influx into the ria

& Giblin 1996). Higher rates are generally observed in estuaries, with up to  $10\,000\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  in the muddy reaches of the Thames Estuary, UK (Trimmer et al. 2000). A more conservative range for temperate coastal sediments frequently quoted in the literature is 50 to  $250\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  (Seitzinger 1988), and the Pontevedra ria  $D_{\text{net}}$  falls well within this range.

The conceptual balance in Fig. 13 summarizes the benthic N cycling in the Pontevedra ria during spring 1998. The imbalance of  $D_{\text{net}}$  and benthic DIN effluxes ( $71\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  Stn 4,  $77\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  Stn 6) demonstrates that the sediments were a sink for N and consumed 34% of the sedimented PON at Stn 4 and 33% PON at Stn 6. Elsewhere, denitrification from  $\text{NO}_3^-$  diffusing into the sediments (commonly termed  $D_w$ ) may act as a buffering mechanism for high  $\text{NO}_3^-$ -loading from rivers (Trimmer et al. 1998). In the Pontevedra ria, the small positive spring  $\text{NO}_3^-$  fluxes ( $6\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  Stn 4,  $5\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$  Stn 6) suggest coupling of nitrification and denitrification and sedimentary  $\text{NO}_3^-$  buffering (Jenkins & Kemp 1984). It must be noted, however, that Eq. (1) overlooks several uncertainties, including denitrification outside the period of mass balance application, bioturbation (Aller 1988), effluxes of dissolved organic N (Enoksson 1993), and possible anaerobic conditions during microcosm N-incubations. A mass balance more finely tuned to the temporal variability of upwelling would also be desirable (Álvarez-Salgado et al. 1996). A sensitivity analysis of the independent terms in Eqs. (1) to (3) showed that by far the greatest uncertainty was the resuspension term, which we arbitrarily proposed to represent 50% of the sedimented material. It is entirely conceivable, however, that resuspension of algal fluff may provide a larger or smaller sink for PON, thus creating an error in  $D_{\text{net}}$  of  $\pm 70\ \mu\text{molN m}^{-2}\ \text{h}^{-1}$ . Further investigation of this hypothesis is required, however, and for the present study we consider  $D_{\text{net}}$  estimate to be in satisfactory agreement with the previous box-model estimate.

### Upwelling enhancement of sediment biogeochemistry

First-order approximations suggest that the principal fate of benthic PON in the Pontevedra ria is resuspension and denitrification, both of which appear to be influenced by positive upwelling stress. Water advection over the sediments will have an impact on disturbance and transport of sediment and hence the sediment nutrient source-sink term (Li et al. 1997). At the outset, upwelling is intermittent and dependent on wind-induced offshore water transport, leading to cycles of high and low primary productivity (Rosón et al. 1999) and thus sedimentation. It seems further probable that

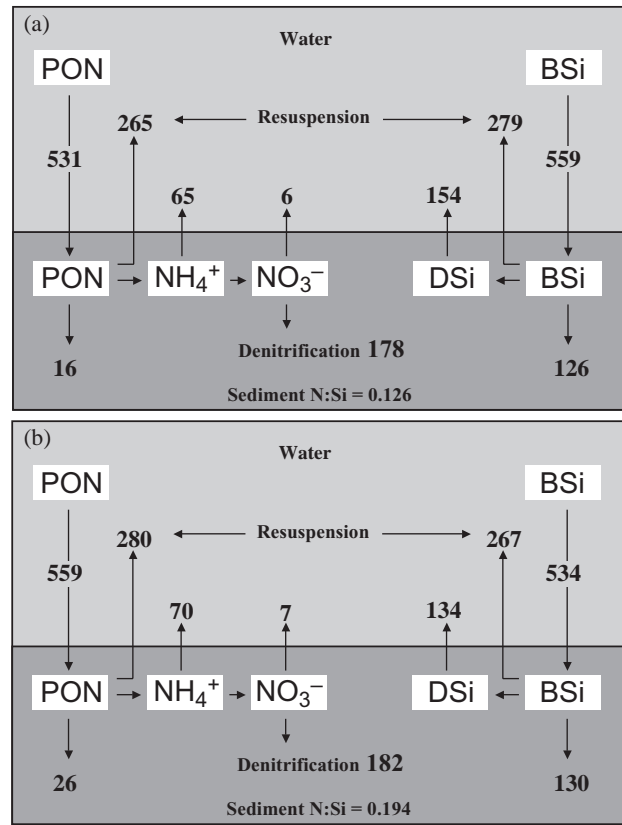


Fig. 13. Conceptual diagram for particulate organic N and Si benthic-pelagic coupling ( $\mu\text{mol m}^{-2}\ \text{h}^{-1}$ ) in the Pontevedra ria during spring 1998 at Stns 4 (a) and 6 (b). Denitrification is estimated to be correct within  $\pm 50\%$  (see 'Discussion'). Denitrification and storage do not add up exactly, since the values in the figure are the means of individually calculated rates from particulate deposition and nutrient efflux data on each sampling date rather than the mean particulate deposition and nutrient efflux

a significant quantity of detrital material in the Pontevedra ria is held in suspension above the bed sediment as neutrally buoyant fluff. The specific role of the quasi-benthic algal fluff in nutrient recycling remains unclear. We hypothesise that regular organic matter deposition between upwelling cycles and the superficial fluff provide the substrate for coupled nitrification-denitrification across zones of distinct oxygen potential (termed  $D_n$  in the literature), in a similar fashion to faecal pellets in the sediment (Jenkins & Kemp 1984). Many areas of high denitrification are based on high concentrations of  $\text{NO}_3^-$  in the bottom water (e.g. Nielsen et al. 1995, Trimmer et al. 1998). However, when dissolved  $\text{NO}_3^-$  is low, such as in the Pontevedra ria, experiments by Rysgaard et al. (1994) have shown that denitrification is favoured by high dissolved  $\text{O}_2$  concentrations in the bottom waters. Upwelling maintains high  $\text{O}_2$  saturation in the Pontevedra ria, and this

could be an important consideration in further denitrification studies. Moreover, nitrification will be promoted by the ventilating effect of offshore water input (Jenkins & Kemp 1984, Koike & Sørensen 1988, Kemp et al. 1990), and there is further evidence to suggest that water column bacterial activity (Wainright 1987), water phase denitrification ( $D_w$ ) and coupled nitrification-denitrification ( $D_n$ ) increase after resuspension (Nielsen et al. 1990, Sloth et al. 1996).

Many recent advances in the field of sediment POC and PON recycling have been reported in the literature. In this paper, we have shown that it is also advantageous to consider the hydrodynamical characteristics of the system. This is important, since well-defined biological processes such as denitrification are intricately related to estuarine hydrodynamics via alteration of the dissolved oxygen concentrations by resuspension and, in the case of the Pontevedra ria, stirring of quasi-benthic biogenic fluff. Accordingly, using mean net denitrification ( $D_{net}$ ) at Stns 4 and 6 and triplicate core data in order to reduce data dispersion,  $D_{net}$  and incoming water flux ( $Q_{in}$ ) are significantly related ( $r^2 = 0.71$ ,  $p < 0.05$ ) by an exponential relationship. However, in the absence of resuspension data and direct analysis of denitrification (isotope pairing method), the  $D_{net}$ - $Q_{in}$  relationship is qualitative only, that is to say,  $D_{net}$  decreases as  $Q_{in}$  increases. The basis of this relationship is a complex function of benthic-pelagic particulate coupling, and remains to be fully rationalised, although the rate of PON deposition appears to be important. For the reasons outlined in the previous paragraph, the direct effect of water advection on sediment nutrient cycling ought to be considered alongside the more obvious physico-biogeochemical processes which modify nutrient fluxes in the Galician Rias Bajas.

*Acknowledgements.* We would like to thank Captain Jorge Alonso and the crew of the RV 'Mytilus' and all those who participated in the sampling campaign, Dr. Carmen Barciela, Victor Ferreiro and Montserrat Martinez for the nutrient analyses, and Juan R. González and Luis Freites for their technical assistance. Thanks also to Dr. Manuel Varela for the chlorophyll *a* and particulate organic data, and to Professor Geoff Millward and 2 anonymous referees, whose constructive comments improved this paper. This work was supported by CICYT under the project 'The hydrodynamics and biogeochemical cycle of silicon in the Pontevedra ria', ref. MAR96-1782. A.W.D. was supported by a research grant jointly funded by CSIC (Spain) and the University of Plymouth (UK).

#### LITERATURE CITED

- Aller RC (1988) Benthic fauna and biogeochemical processes in marine sediments: the role of burrow structures. In: Blackburn TH, Sørensen J (eds) Nitrogen cycling in coastal marine environments. John Wiley & Sons, Chichester, p 207–249
- Álvarez-Salgado XA, Rosón G, Pérez FF, Figueiras FG, Pazos Y (1996) Nitrogen cycling in an estuarine upwelling system, the Ría de Arosa (NW Spain). I. Short-time-scale patterns of hydrodynamic and biogeochemical circulation. *Mar Ecol Prog Ser* 135:259–273
- Arbones FMB, Andrade CML, Marcet MP, Montero VMJ (1992) Levels of organic material, nitrogen and phosphorus deposited by effluents in the coastal zone of the Pontevedra Ria. *Thalassas* 10:59–69 (in Spanish)
- Asmus RM, Jensen MH, Jensen KM, Kristensen E, Asmus H, Wille A (1998) The role of water movement and spatial scaling for measurement of dissolved inorganic nitrogen fluxes in intertidal sediments. *Estuar Coast Shelf Sci* 46: 221–232
- Bale AJ, Morris AW, Howland RJM (1985) Seasonal sediment movement in the Tamar estuary. *Oceanol Acta* 8:1–6
- Barciela MC, Bao R, Prego R, Herbello P (2000) Opal in the superficial sediment of the Pontevedra Ria: distribution and comparison with the ria (Arosa and Vigo) and adjacent shelf. In: Duarte A, Vale C, Prego R (eds) Biogeochemical studies in the Iberian coastal zone. IXth Iberian Seminar of Marine Chemistry, University of Aveiro, Aveiro, p 153–158 (in Spanish)
- Bidle KD, Azam F (1999) Accelerated dissolution of diatom silica by marine bacterial assemblages. *Nature* 379:508–512
- Blackburn TH, Henriksen K (1983) Nitrogen cycling in different types of sediments from Danish waters. *Limnol Oceanogr* 28:447–493
- Blanton JO, Tenore KR, Castillejo F, Atkinson LP, Schwing FB, Lavín A (1987) The relationship of upwelling to mussel production in the rias on the western coast of Spain. *J Mar Res* 45:497–511
- Boynton WR, Kemp WM (1985) Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. *Mar Ecol Prog Ser* 23:44–55
- Boynton WR, Garber JH, Summers R, Kemp WM (1995) Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* 18: 285–314
- Christiansen C, Gertz F, Laima MJC, Lundhansen LC, Vang T, Jurgensen C (1997) Nutrient (P,N) dynamics in the southwestern Kattegat, Scandinavia: sedimentation and resuspension effects. *Environ Geol* 29:66–77
- Christensen PB, Rysgaard S, Sloth NP, Dalsgaard T, Schwaerter S (2000) Sediment mineralization, nutrient fluxes, denitrification and dissimilatory nitrate reduction to ammonium in an estuarine fjord with sea cage trout farms. *Aquat Microb Ecol* 21:73–84
- Conley DJ, Johnstone RW (1995) Biogeochemistry of N, P and Si in Baltic Sea sediments: response to a simulated deposition of a spring diatom bloom. *Mar Ecol Prog Ser* 122: 265–276
- Enoksson V (1993) Resuspension, ephemeral mud blankets and nitrogen cycling in Laholmsbukten, south east Kattegat. *Hydrobiologia* 176/177:61–75
- Fiuzza AFG, Hamann M, Ambar I, Diaz del Rio G, González N, Cabanas JM (1998) Water masses and their circulation off western Iberia during May 1993. *Deep-Sea Res* 45: 1127–1160
- Floderus S, Håkanson L (1989) Resuspension, ephemeral mud blankets and nitrogen cycling in Laholmsbukten, south east Kattegat. *Hydrobiologia* 176/177:61–75
- Fraga F (1981) Upwelling off the Galician Coast, Northwest Spain. In: Richards FA (ed) Coastal upwelling. American Geophysical Union, Washington, DC, p 176–182
- Gordon DC Jr, Boudreau PR, Mann KH, Ong JE and 5 others (1996) LOICZ (Land-Ocean Interactions in the Coastal

- Zone) biogeochemical modelling guidelines. Reports & Studies No. 5, LOICZ Core Project, Texel
- Hansen HP, Grasshoff K (1983) Automated chemical analysis. In: Grasshoff K, Ehrhardt M, Kremling K (eds) *Methods of seawater analysis*, 2nd edn. Verlag Chemie, Weinheim, p 368–376
- Hansen LS, Blackburn TH (1992) Effect of algal bloom deposition on sediment respiration and fluxes. *Mar Biol* 112: 147–152
- Hurd DC (1983) Physical and chemical properties of siliceous skeletons. In: Aston SR (ed) *Silicon geochemistry and biogeochemistry*. Academic Press, New York, p 187–244
- Jago CF, Jones SE (1998) Observation and modelling of the dynamics of benthic fluff resuspended from a sandy bed in the southern North Sea. *Contin Shelf Res* 18:1255–1282
- Jenkins MC, Kemp WM (1984) The coupling of nitrification and denitrification in two estuarine sediments. *Limnol Oceanogr* 29:609–619
- Kamp-Nielsen L (1992) Benthic-pelagic coupling of nutrient metabolism along an estuarine eutrophication gradient. *Hydrobiologia* 235/236:457–470
- Kemp WM, Sampou P, Caffrey J, Mayer M (1990) Ammonium recycling versus denitrification in Chesapeake Bay sediments. *Limnol Oceanogr* 35:1545–1563
- Knauer GA, Martin JH, Bruland KW (1979) Fluxes of particulate carbon, nitrogen and phosphorus in the upper water column of the northeast Pacific. *Deep-Sea Res* 26:97–108
- Koike I, Sørensen J (1988) Nitrate reduction and denitrification in marine sediments. In: Blackburn TH, Sørensen J (eds) *Nitrogen cycling in coastal marine environments*. John Wiley & Sons, Chichester, p 251–273
- Li YG, Mehta AJ, Hatfield K, Dortch MS (1997) Modulation of constituent release across the mud-water interface by water waves. *Water Resour Res* 33:1409–1418
- Lohse L, Kloosterhuis KT, van Raaphorst W, Helder W (1996) Denitrification rates as measured by the isotope pairing method and the acetylene inhibition technique in continental shelf sediments of the North Sea. *Mar Ecol Prog Ser* 132:169–179
- López-Jamar E, Cal RM, González G, Hanson RB, Rey J, Santiago G, Tenore KR (1992) Upwelling and outwelling effects on the benthic regime of the continental shelf off Galicia, NW Spain. *J Mar Res* 50:465–488
- Millward GE, Morris AW, Tappin AD (1998) Trace metals at two sites in the southern North Sea: results from a sediment resuspension study. *Cont Shelf Res* 18:1381–1400
- Mora J, Planas M, Silva R (1989) Impact of organic contamination in the Lourizán inlet: the physical environment and benthic macrofauna. *Cah Biol Mar* 30:181–199 (in Spanish)
- Morris AW, Howland RJM, Woodward EMS, Bale AJ, Mantoura RFC (1985) Nitrite and ammonia in the Tamar Estuary. *Neth J Sea Res* 19:217–222
- Mortlock RA, Froelich PN (1989) A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Res* 36:1415–1426
- Nelson DM, Tréguer P, Brzezinski MA, Leynaert A, Quéguiner B (1995) Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. *Global Biogeochem Cycles* 9:359–372
- Nielsen K, Nielsen LP, Rasmussen P (1995) Estuarine nitrogen retention independently estimated by the denitrification rate and mass balance methods: a study of Norsminde Fjord, Denmark. *Mar Ecol Prog Ser* 119:275–283
- Nielsen LP, Christensen PB, Niels PR, Sørensen J (1990) Denitrification and photosynthesis in stream sediment studied with microsensor and whole-core techniques. *Limnol Oceanogr* 35:1135–1144
- Nixon SW (1981) Remineralisation and nutrient cycling in coastal marine systems. In: Neilson BJ, Cronin LE (eds) *Estuaries and nutrients*. Humana Press, Clifton, NJ, p 111–138
- Owens NJP (1986) Estuarine nitrification: a naturally occurring fluidized bed reaction? *Estuar Coast Shelf Sci* 22: 31–44
- Owens NJP, Mantoura RFC, Burkhill PH, Howland RJM, Pomroy AJ, Woodward EMS (1986) Nutrient cycling studies in Camarthen Bay: phytoplankton production, nitrogen assimilation and regeneration. *Mar Biol* 93:329–342
- Parsons TR, Maita Y, Lalli CM (1984) *A manual of chemical and biological methods for seawater analysis*. Pergamon Press, Oxford
- Prego R (1994) Nitrogen interchanges generated by biogeochemical processes in a Galician ria. *Mar Chem* 45: 167–176
- Prego R, Bao R (1997) Upwelling influence on the Galician coast: silicate in shelf water and underlying surface sediments. *Cont Shelf Res* 17:307–318
- Prego R, Fraga F (1992) A simple model to calculate the residual flows in a Spanish ria. Hydrographic consequences in the ria of Vigo. *Estuar Coast Shelf Sci* 34:603–615
- Prego R, deCastro M, Gómez-Gesteira M, Dale AW, Taboada JJ, Montero P, Villareal MR, Pérez-Villar V (2001) Hydrography of the Pontevedra Ria: intra-annual spatial and temporal variability in a Galician coastal upwelling system (NW Spain). *J Geophys Res* 106(9):19845–19857
- Ragueneau O, Tréguer P (1994) Determination of biogenic silica in coastal waters: applicability and limits of the alkaline digestion method. *Mar Chem* 45:43–51
- Rios AF, Fraga F (1987) Elemental chemical composition of marine plankton. *Investig Pesq (Barc)* 51:619–632 (in Spanish)
- Rosón G, Álvarez-Salgado XA, Pérez FF (1999) Carbon cycling in a large coastal embayment, affected by wind-driven upwelling: short-time-scale variability and spatial differences. *Mar Ecol Prog Ser* 176:215–230
- Rysgaard S, Risgaard-Petersen N, Sloth NP, Jensen K, Nielsen LP (1994) Oxygen regulation of nitrification and denitrification in sediments. *Limnol Oceanogr* 39:1643–1652
- Seitzinger SP (1988) Denitrification in fresh water and coastal marine ecosystems: ecological and geochemical significance. *Limnol Oceanogr* 33:702–724
- Seitzinger SP, Giblin AE (1996) Estimating denitrification in North Atlantic continental shelf sediments. *Biogeochemistry* 35:235–260
- Seitzinger SP, Pilson MEQ, Nixon SW (1983) Nitrous oxide production in nearshore marine sediments. *Science* 222: 1244–1246
- Sloth NP, Blackburn H, Hansen LS, Risgaard-Petersen N, Lomstein BA (1995) Nitrogen cycling in sediments with different organic loading. *Mar Ecol Prog Ser* 116:163–170
- Sloth NP, Riemann B, Nielsen LP, Blackburn TH (1996) Resilience of pelagic and benthic microbial communities to sediment resuspension in a coastal ecosystem, Knebel Vig, Denmark. *Estuar Coast Shelf Sci* 42:405–415
- Taboada JJ, Ruiz-Villarreal M, Gómez-Gesteira M, Montero P, Santos AP, Pérez-Villar V, Prego R (2000) Study of the transport in the Pontevedra Ria (NW Spain) using a 3D model. In: Duarte A, Vale C, Prego R (eds) *Biogeochemical studies in the Iberian coastal zone*. IXth Iberian Seminar Mar Chem, University of Aveiro, Aveiro, p 285–291 (in Spanish)
- Tenore KL, Boyer LF, Cal RM, Corral J and 15 others (1982) Coastal upwelling in the Rias Bajas, NW Spain: contrast-

- ing the benthic regimes of the Rias de Arosa and Muros. *J Mar Res* 40:701–772
- Tilstone GH, Míguez BM, Figueiras FG, Fermín EG (2000) Diatom dynamics in a coastal ecosystem affected by upwelling: coupling between species succession, circulation and biogeochemical processes. *Mar Ecol Prog Ser* 205:23–41
- Trimmer M, Nedwell DB, Sivyer DB, Malcolm SJ (1998) Nitrogen fluxes through the lower estuary of the Great Ouse, England: the role of the bottom sediments. *Mar Ecol Prog Ser* 163:109–124
- Trimmer M, Nedwell DB, Sivyer DB, Malcolm SJ (2000) Seasonal benthic organic matter mineralisation measured by oxygen uptake and denitrification along a transect of the inner and outer River Thames estuary, UK. *Mar Ecol Prog Ser* 197:103–119
- Uncles RJ, Howland RJM, Easton AE, Griffiths ML and 5 others (1998) Concentrations of dissolved nutrients in the tidal Yorkshire Ouse River and Humber Estuary. *Sci Total Environ* 210:377–388
- Vorosmarty CJ, Loder TC (1994) Spring-neap tidal contrasts and nutrient dynamics in a marsh dominated estuary. *Estuaries* 17:537–551
- Wainright SC (1987) Stimulation of heterotrophic microplankton production by resuspended marine sediments. *Science* 238:1710–1712
- Westrich JT, Berner RA (1984) The role of sedimentary organic matter in bacterial sulfate reduction: the G-model tested. *Limnol Oceanogr* 29:236–249
- Wooster WS, Bakun A, McClain DR (1976) The seasonal upwelling cycle along the eastern boundary of the north Atlantic. *J Mar Res* 34:131–141

*Editorial responsibility: Otto Kinne (Editor), Oldendorf/Luhe, Germany*

*Submitted: April 24, 2001; Accepted: November 20, 2001  
Proofs received from author(s): May 13, 2002*