Nitrogen cycling in coastal marine ecosystems

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Abstract

It is generally considered that nitrogen availability is one of the major factors regulating primary production in temperate coastal marine environments. Coastal regions often receive large anthropogenic inputs of nitrogen that cause eutrophication. The impact of these nitrogen additions has a profound effect in estuaries and coastal lagoons where water exchange is limited. Such increased nutrient loading promotes the growth of phytoplankton and fast growing pelagic macroalgae while rooted plants (sea-grasses) and benthic are suppressed due to reduced light availability. This shift from benthic to pelagic primary production introduces large diurnal variations in oxygen concentrations in the water column. In addition oxygen consumption in the surface sediments increases due to the deposition of readily degradable biomass. In this review the physico-chemical and biological factors regulating nitrogen cycling in coastal marine ecosystems are considered in relation to developing effective management programmes to rehabilitate seagrass communities in lagoons currently dominated by pelagic macroalgae and/or cyanobacteria. © 1999 Federation of European Microbiological Societies. Published by Elsevier Science B.V. All rights reserved.

Keywords: N₂ fixation; Ammonification; Nitrification; Denitrification; Physico-chemical gradient; Eutrophication; Anthropogenic input; Rhizosphere effect; Meiofauna; C/N ratio; Carbon availability

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1. Introduction

Microbial communities in shallow marine sediments play a key role in the oxidation of complex organic compounds and regeneration of nutrients essential for sustaining primary production in the overlying water column [1–4]. The fundamental significance and interdependence of these processes is well exemplified by the biogeochemical cycling of carbon and nitrogen. Since these elements are key constituents of all living matter it is perhaps not surprising that the impact of carbon and nitrogen availability on primary production and mineralisation of organic matter has been the subject of intensive study [5–7]. From a biogeochemical viewpoint the two cycles share many common features. These include the dominance of specialised groups of microorganisms, which carry out specific transformations, and the regulation of these processes by oxygen and the prevailing redox regime. Given that these cycles are inextricably linked due consideration must therefore be given to the complex interactions that exist between them if any meaningful understanding of individual transformations is to be achieved. This is well illustrated by nitrogen transformations such as heterotrophic nitrogen fixation and denitrification that are functionally dependent upon the availability of oxidisable carbon sources [8–10].

It is widely accepted that shallow coastal sediments are important sites for the mineralisation of organic matter [11,12]. These transformations are mediated principally by bacteria and the resulting gradients of nutrients result in their release to the overlying water column or adsorption and burial in deeper sediment layers. Several studies of shallow water coastal ecosystems have indicated that mineralisation of nitrogen mediated by the heterotrophic activity of the microbiota and the larger macrofauna plays an important role in supporting primary production both in phytoplankton dominated systems and those where macrophytes are the dominant primary producers [5,13–16]. The driving force for benthic nitrogen cycling is the degradation of organic matter deposited at the sediment surface or excreted by the roots and rhizomes of rooted macrophytes [17–19].

The major factors controlling the concentrations of inorganic nitrogen species, principally NO$_3^-$ and NH$_4^+$, in the water column of shallow coastal marine ecosystems (water depth 0.5–50 m) are inputs arising from fluvial discharges and those resulting from exchange across the sediment-water interface. Benthic nutrient exchange (benthic flux) is largely determined by the rate of detritus sedimentation and decomposition and the rate at which nutrients are transported to or from the overlying water by diffusion and infauna bioturbation [20]. In addition to playing a key role in nitrogen recycling, the benthic flux can be used as a net measure of the individual processes involved in sediment nitrogen turnover [21]. Thus, the rates of net ammonification (NH$_4^+$ release from organic matter), nitrification (oxidation of NH$_4^+$ to NO$_3^-$) and denitrification (reduction of NO$_3^-$ to N$_2$ and N$_2$O) can all be estimated from net benthic fluxes of NO$_3^-$ and NH$_4^+$ [21,22].

A further factor regulating benthic nutrient regeneration is the quantity, quality and spatial distribution of the deposited organic matter in the sediment. When deposition rates are high, heterotrophic microorganisms are unable to completely degrade the labile components before burial or reworking to depth by the benthic infauna. Aerobic respiration which takes place in the surface sediment layers (typically 0–5 mm depth), results in a rapid depletion of oxygen and alternative e$^-$ acceptors if present, such as nitrate, manganese and ferric oxides, sulfate and carbon dioxide are then sequentially used as oxidants [23,24]. Under these conditions mineralisation proceeds via a sequence of metabolic steps involving coupled fermentation and anaerobic respiration processes, each of which completes a partial oxidation of the organic matter. The result is a spatial and/or temporal succession as successive thermodynamically favourable e$^-$ acceptors are sequentially depleted by the indigenous microflora. The net effect is that a well-defined vertical biogeochemical zonation develops within the sediment except where macrofauna burrows allow lateral diffusion of e$^-$ acceptors from well-irrigated burrow water [25].

Concurrent with the oxidation of organic carbon at these different depth horizons, organic nitrogen is mineralised principally by deaminative fermentation.

It is clearly evident from the foregoing section that nitrogen cycling in marine sediments is subject to a complex array of regulatory mechanisms involving
both physico-chemical and biological factors. The objective of this review is to provide a synthesis of recent developments in our understanding of the processes involved in nitrogen cycling in coastal marine sediments.

In order to gain an understanding of the factors regulating nitrogen cycling in coastal marine sediments there is a need to understand how the individual, microbially mediated processes that make up the nitrogen cycle are controlled. The complexity of the cycle is demonstrated in Fig. 1 which shows that nitrogen undergoes a series of oxidation/reduction reactions and change in valence state from $^3$ to $^+$5. These transformations are mediated by a metabolically diverse range of autotrophic and heterotrophic microorganisms and are strongly influenced by the prevailing physico-chemical conditions.

2. Nitrogen fixation

The availability of fixed nitrogen is considered by many authorities to be a major factor regulating primary production in shallow marine environments [26–28]. Thus, inputs of ‘new’ nitrogen resulting from biological nitrogen fixation may enable the productivity of such ecosystems to increase. Whilst 79% of the earth’s atmosphere is composed of molecular nitrogen ($N_2$), this major nitrogen reservoir is unavailable directly to plants and animals. Biological nitrogen fixation is confined to specialised groups of prokaryotes which possess the enzyme nitrogenase and include both autotrophs and heterotrophs. All major groups of cyanobacteria found in the marine environment have nitrogen fixing representatives, including unicellular and non-heterocystous species [29–31]. The ability to fix nitrogen is also common amongst members of the Chromatiaceae, Chlorobiaceae, Chloroflexaceae and Rhodospirillaceae and a variety of chemoautotrophic bacteria [29,30]. Marine heterotrophic nitrogen fixing bacteria comprise a taxonomically diverse group (see Table 1) and include aerobes, microaerophiles, facultative and strict anaerobes [29,32]. Since the $N_7$ bond is extremely stable the biological reduction of dinitrogen to ammonia is an energy demanding process estimated to

![Fig. 1. The nitrogen cycle showing the chemical forms and key processes involved in the biogeochemical cycling of nitrogen [235].](image-url)
be equivalent to a minimum of 16 ATP per molecule of N₂ fixed [33]. Given the high metabolic cost involved it is not surprising that diazotrophic photoautotrophs such as cyanobacteria have a significant advantage in photic habitats over their heterotrophic counterparts whose nitrogen fixing capacity is limited by the availability of suitable organic carbon sources [34,35]. Thus, in unvegetated shallow coastal lagoons and intertidal sediments where light is not limiting, dense populations of benthic nitrogen fixing cyanobacteria may develop and contribute fixed nitrogen to the local ecosystem. Data presented in Table 2 show that these cyanobacterial mats in both temperate and tropical environments exhibit high nitrogen fixation rates as measured by the acetylene reduction assay (ARA). Whilst the highest rates have been recorded in the tropics those measured in temperate salt marsh sediments in the UK and eastern USA are still significant and substantially greater than those recorded for uncolonised sediments (Table 3). However, whilst nitrogen fixed by cyanobacterial mats is locally important to the mat communities themselves their contribution to the total nitrogen budget in most shallow marine ecosystems is minor due to their restricted areal distribution. For example, Hanson and Gunderson [56] recorded very high nitrogen fixation rates (Table 2) for microbial mats in Kaneohe Bay, Hawaii, yet they are estimated to contribute only 0.3% of the annual nitrogen input to the Bay. Similarly in salt marsh ecosystems N-fixation by cyanobacterial mats is considered to be of less importance as an overall source of fixed nitrogen than heterotrophic fixation [53,67].

Table 2
Nitrogen fixation rates reported for cyanobacterial mats

<table>
<thead>
<tr>
<th>System</th>
<th>N-fixation rate (g N m⁻² year⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Island of Mellum, Germany</td>
<td>0.8–1.5</td>
<td>[50]</td>
</tr>
<tr>
<td>Sippewisset salt marsh, Massachusetts</td>
<td>1.42</td>
<td>[51]</td>
</tr>
<tr>
<td>Colne Point marsh, UK</td>
<td>5.99</td>
<td>[35]</td>
</tr>
<tr>
<td>Hiddensee Island, Baltic</td>
<td>7.60</td>
<td>[52]</td>
</tr>
<tr>
<td>Flax Pond salt marsh, New York</td>
<td>13.44</td>
<td>[53]</td>
</tr>
<tr>
<td>Bank End, UK</td>
<td>10.06</td>
<td>[54]</td>
</tr>
<tr>
<td>Enewatak Atoll, Marshall Islands</td>
<td>65.70</td>
<td>[55]</td>
</tr>
<tr>
<td>Kaneohe Bay, Hawaii</td>
<td>76.00</td>
<td>[56]</td>
</tr>
</tbody>
</table>

Table 3
Nitrogen fixation rates reported for uncolonised marine sediments

<table>
<thead>
<tr>
<th>System</th>
<th>Nitrogen fixation rate (g N m⁻² year⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vostok Bay, Japan</td>
<td>0.002</td>
<td>[57]</td>
</tr>
<tr>
<td>Narragansett Bay, Massachusetts</td>
<td>0.03</td>
<td>[58]</td>
</tr>
<tr>
<td>Rhode Island</td>
<td>0.13</td>
<td>[59]</td>
</tr>
<tr>
<td>Rhode River Estuary, Maryland</td>
<td>0.14</td>
<td>[37]</td>
</tr>
<tr>
<td>Lune Estuary, England</td>
<td>0.37</td>
<td>[60]</td>
</tr>
<tr>
<td>Waccasassa Estuary, Florida</td>
<td>0.43</td>
<td>[54]</td>
</tr>
<tr>
<td>Bank End, England</td>
<td>0.60</td>
<td>[56]</td>
</tr>
<tr>
<td>Kaneohe Bay, Hawaii</td>
<td>0.65</td>
<td>[53]</td>
</tr>
<tr>
<td>Flax Pond mud flats, New York</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In contrast to cyanobacterial mats, N-fixation rates in unvegetated marine sediments are low ranging from 0.002–0.65 g N m⁻² year⁻¹ (Table 3). The N₂ fixing community responsible comprises a diverse array of heterotrophic and chemolithoautotrophic bacterial genera with physiologies ranging from strict anaerobes to obligate aerobes (Table 1). The highest rates have been reported in organically rich sediments such as those found in the Waccasassa estuary, Bank End salt marsh and Flax Pond mud flats. This finding is unsurprising given that metabolisable carbon is required to support heterotrophic N-fixation and in oligotrophic marine environments the availability of organic carbon is probably the factor limiting the nitrogen fixing potential of unvegetated sediments. Herbert [34] reported that amending carbon depleted sediments from the Tay estuary, Scotland, with 5 mM glucose stimulated heterotrophic N-fixation rates under both aerobic (×3) and anaerobic (×2.5) conditions. Similarly, Tibbles et al. [68] demonstrated that the plant structural polysaccharides xylan and alginate stimulated nitrogenase activity 5–18-fold when added to salt marsh sediments from the Langebaan Lagoon, South Africa. Even higher levels of stimulation were recorded, 19- to 92-fold respectively, when plant storage polysaccharides, laminarin and glycogen were added to sediment samples compared with untreated controls. These data indicate whilst the potential for high nitrogen fixing activity in unvegetated coastal marine ecosystems exists it is rarely realised due to the lack of
suitable oxidisable carbon substrates. As a consequence, whilst unvegetated sediments are extensive when measured on an areal basis their contribution to the overall nitrogen budgets of temperate estuaries, salt marshes and coastal lagoons is relatively small. Nixon [69] estimated that in Narragansett Bay, sediment nitrogen fixation accounted for \( \sim 4\% \) of the total annual nitrogen input. This is a similar value to that reported by Marsho et al. [59] for the Rhode River estuary in Chesapeake Bay. In tropical coastal marine lagoons however, nitrogen fixation in unvegetated sediments may account for significant inputs of fixed nitrogen. In Kaneohe Bay, Hawaii sediment nitrogen fixation has been calculated to contribute 11\% of the annual nitrogen input [56]. Nitrogen budgets calculated by Smith [70] for Shark Bay, Australia and two Pacific island atolls suggest that nitrogen fixation is the principal nitrogen input into these oligotrophic ecosystems. However, no direct measurements of N-fixation have yet been made to confirm the validity of the estimated rates used to calculate the nitrogen budgets for these lagoons. Hence the values of 56–97\% of the net nitrogen input should be treated with caution. From the foregoing section it is apparent that, with the exception of oligotrophic tropical lagoons, nitrogen fixation contributes a relatively small percentage of the annual nitrogen input to non-vegetated shallow coastal marine environments.

Many shallow coastal marine environments are characterised by the presence of extensive meadows of rooted macrophytes. These include Spartina alterniflora, Zostera marina, Zostera noltii, Zostera capricorni and Thalassia testudinium [61,63,65]. In order to achieve and sustain such high levels of primary production substantial inputs of fixed nitrogen are required [71]. Whilst efficient recycling of organic nitrogen in the sediment can supply a large proportion of this fixed nitrogen [72–74], it is insufficient to meet the growth requirements of these plant communities [71,75]. Data presented in Table 4 show that high rates of nitrogen fixation have been recorded in seagrass colonised sediments. It has been estimated that in tropical seagrass meadows nitrogen fixation can supply up to 50\% of the nitrogen requirements of the plants [36,63,65,76]. In temperate seagrass meadows such as those in the Bassin d’Arcachon, southwest France the contribution from nitrogen fixation to the fixed nitrogen requirements of the plants is markedly lower. Welsh et al. [61] have estimated that in this shallow lagoon system nitrogen fixation provides between 6 and 12\% of the annual nitrogen requirement of the Z. noltii meadow. These values are similar to those recorded for a Z. marina bed in the Limfjorden, Denmark by Risgaard-Petersen and co-workers [77]. These investigators concluded that in this system nitrogen fixation was unimportant due to the high nitrogen availability in the water column and sediment. The high rates of nitrogen fixation associated with salt marsh grass and seagrass colonised sediments have been demonstrated to be intimately associated with the excretion of organic compounds from the plant roots and closely coupled to the photosynthetic activity of the plants [61,64,76]. Several authors have speculated that specific symbiotic associations between the heterotrophic diazotrophs and the macrophyte may exist but to date none have been demonstrated [30,78]. A number of studies have demonstrated that diazotrophic sulfate reducing bacteria are responsible for the bulk of nitrogen fixing activity associated with the roots/rhizomes of S. alterniflora, Z. noltii and Z. marina [30,61,79–81]. When 20 mM sodium molybdate, a specific inhibitor of sulfate reducing bacteria was added to sediment cores nitrogen fixation, measured as acetylene reduction rates, was inhibited by 70 to 90\%. Acetylene reduction rates were always greater in the light than in the dark, indicating a

<table>
<thead>
<tr>
<th>Seagrass species</th>
<th>Nitrogen fixation rate (mg N m(^{-2}) day(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zostera noltii (winter)</td>
<td>0.1–0.2</td>
<td>[61]</td>
</tr>
<tr>
<td>Zostera noltii (summer)</td>
<td>2.0–7.3</td>
<td>[61]</td>
</tr>
<tr>
<td>Zostera marina</td>
<td>5</td>
<td>[30]</td>
</tr>
<tr>
<td>Zostera marina</td>
<td>1–6</td>
<td>[62]</td>
</tr>
<tr>
<td>Thalassia hemprichii (summer)</td>
<td>16</td>
<td>[63]</td>
</tr>
<tr>
<td>Enhalus acoroides (summer)</td>
<td>25</td>
<td>[63]</td>
</tr>
<tr>
<td>Zostera capricorni (summer)</td>
<td>25–40</td>
<td>[64]</td>
</tr>
<tr>
<td>Zostera capricorni (winter)</td>
<td>10</td>
<td>[64]</td>
</tr>
<tr>
<td>Thalassia testudinium</td>
<td>27–140</td>
<td>[36]</td>
</tr>
<tr>
<td>Thalassia testudinum</td>
<td>5–24</td>
<td>[65]</td>
</tr>
<tr>
<td>Hadodule beaudetti</td>
<td>28</td>
<td>[66]</td>
</tr>
</tbody>
</table>
photosynthetically driven input of organic carbon to the sediment as the driving force for heterotrophic nitrogen fixation in the rhizosphere. Under oxygen limiting conditions \textit{Z. marina} roots switch to fermentative metabolism producing ethanol, CO$_2$ and lactate with the latter accumulating in the root tissue [82]. Lactate accumulated in the plant roots represents a significant pool of organic carbon. Capone [30] elegantly demonstrated that following the exposure of \textit{Z. marina} roots to $^{15}$N$_2$ there was a rapid translocation of the fixed nitrogen to the distal leaf tissues. These data suggest a mutualistic relationship between \textit{Zostera} and sulfate reducing bacteria in the rhizosphere: the bacteria benefitting from the supply of organic carbon by the plant roots and in turn the plant is provided with a supply of fixed nitrogen. By adopting such a strategy the diazotrophs are able to overcome the constraint of carbon availability and thus contribute to the overall productivity of these seagrass and salt marsh grass communities.

In addition to carbon availability a broad range of physico-chemical parameters can also influence nitrogen fixation activity in benthic sediments. These include temperature, light, pH, O$_2$, inorganic nitrogen, salinity and trace metal availability [30,83,84]. None of these factors have been systematically investigated in situ to determine how they regulate/influence nitrogen fixation in coastal marine systems. Whilst molecular oxygen is inhibitory to nitrogenase it is unlikely to be a major factor modulating nitrogen fixing activity in marine sediments, since oxygen concentrations decrease rapidly with depth and even within a few millimetres of the sediment surface, oxygen is undetectable [85]. Porewater ammonium concentrations of 50–100 $\mu$M have been shown to severely inhibit nitrogen fixation in salt marsh sediments [30,51,86] but it is still not clear whether ammonium is a major factor modulating nitrogen fixation in these systems. Capone and Carpenter [87] showed that the removal of interstitial ammonium by perfusion stimulated nitrogen fixation 7–8-fold. However, in a recent study Welsh et al. [88] showed that the addition of 1 mM ammonium chloride to \textit{Z. noltii} colonised sediments only reduced nitrogen fixation to 30% of the rate in the unamended control sediment [88]. The authors concluded that photosynthetically driven release of carbon from the plant roots was the dominant factor regulating nitrogen fixation in this system. Similar results have been reported by McGlathery et al. [62] for \textit{Z. marina}. These results highlight the difficulty in unequivocally establishing the role of porewater ammonium in regulating nitrogen fixation and stem in part from the difficulty in accurately measuring in situ concentrations of this nitrogen species. In shallow marine sediments ammonium released from sedimented organic matter by ammonification can be assimilated by the seagrass/salt marsh grass roots and the indigenous microflora. Alternatively ammonium may be adsorbed onto sediment particles or diffuse upward into the surface oxic zone where it is oxidised by autotrophic nitrifying bacteria to nitrate. Given the complexity of these interactions it is perhaps not surprising that the role of ammonium in regulating heterotrophic nitrogen fixation in these systems still remains equivocal.

3. Ammonification

In shallow coastal marine environments benthic nutrient regeneration and metabolism are regulated by the quantity and quality of the organic matter supplied to the sediment. As a result of the close proximity of the sediment to the productive photic zone the time-scale of benthic-pelagic coupling is short compared to oceanic systems except where organic matter is advected away from the area of production. Deposition of organic matter in these ecosystems can result from episodic events such as the rapid sedimentation of annual phytoplankton blooms or in systems where rooted macrophytes are dominant deposition of moribund plant material occurs throughout the year [22,95]. The quality of the deposited organic matter i.e. whether it is labile or highly refractory determines how rapidly it is mineralised and this in turn is dependent upon its origin [96,97]. Seagrass detritus consists of 25–30% fibre with a lignin content of $\sim$ 8% and its mineralisation rate is low compared to phytoplankton cells which contain more labile nitrogenous material. Irrespective of its origin, all living matter contains nitrogenous macromolecules, such as nucleic acids, proteins and polyamino-sugars as well as low molecular mass compounds and these become available upon death of the cells to decomposer organisms. The release of
ammonium from this nitrogenous matter is termed ammonia
cation. Depending upon the structural complexity of the organic matter ammonia
cation can be either a simple deamination reaction or a
complex series of metabolic steps involving a number of hydrolytic enzymes during which N-containing
colours are broken down to their soluble monomer
sub-units. The low molecular mass forms of organic N forming the dissolved organic nitrogen
good (DON) are still poorly characterised. The identified components comprise amino acids, short poly-
peptides, amines, nucleic acids and urea [98–102]. Components such as amino acids, purines, pyrimidines and urea are rapidly degraded by the indigenous bacterial flora [94,100,102–104]. Boon et al. [94] demonstrated that between 35 and 65% of 15N-gly-
cine added to sediment cores containing intact Z. capricorni was deaminated within 12 h. These observations are consistent with those of Jorgensen et al. [104] who reported amino acid deamination accounted for up to 25% of the ammonium regenerated in sediments colonised by Posidonia oceanica and Cymodocea nodosa. Urea is another important organic nitrogen compound present in coastal marine sediments and is produced as a degradation product of nucleic acids [103,105,106]. Therkildsen et al. [103] showed that urea production was stimulated when AMP, CMP and 16S ribosomal RNA were added to an anoxic, defaunated marine sediment. Subsequent laboratory studies using enriched cultures of aerobic, fermentative and sulfate reducing bacteria showed that urea could be produced from RNA under both oxic [106] and anoxic conditions (Lyng-
aard, unpublished results). Whilst few studies have been undertaken it is now recognised that urea ef-
uxing from the sediment may be an important source of regenerated nitrogen available to primary producers in the overlying water column [106–109]. Urea, since it can be rapidly hydrolysed by bacterial ureases is also an important source of ammonium in sediments particularly those with a high macrofaunal biomass. Lomstein et al. [109] showed that in sediments of the productive Bering Sea Shelf urea hydrolysis could be responsible for up to 80% of the gross production of ammonium. Urease activity is a widely distributed property of many Gram-negative and Gram-positive bacteria, including aerobes, fac-
tulative anaerobes and obligate anaerobes [110,111] and would account for the rapid hydrolysis of urea and ammonium production observed in these sediments.

The mineralisation of complex nitrogenous macromolecules in sediments is still poorly understood. The initial step in the degradation of these complex polymers is hydrolysis to their monomeric components. Proteins are hydrolysed by proteinases and peptidases to their constituent amino acids which in turn are deaminated to release ammonium. The overall reaction can be summarised as:

\[
\text{Protein} \xrightarrow{\text{proteinases}} \text{Peptides} \xrightarrow{\text{peptidases}} \text{Amino acids} \xrightarrow{\text{deamination}} \text{Organic acid} + \text{NH}_4^+ 
\]

A diverse range of microorganisms which produce active proteinases are present in marine sediments. These include representatives of the genera Pseudo-
monas, Vibrio, Proteus, Serratia, Bacillus and Clo-
tridium as well as many actinomycetes and fungi [110,112,113]. Donnelly and Herbert [114] showed that in the shallow northern Adriatic populations of ammonifying bacteria increased rapidly to 4.7 × 10^9 ml sediment^{-1} in the surficial sediment layer following the collapse of the spring phyto-
plankton bloom and was correlated with a marked increase in proteolytic activity as measured using azocasein as a model substrate. These data show that in this dynamic shallow marine system strong benthic-pelagic coupling was occurring with a rapid release of ammonium to the water column. Whilst there have been a limited number of studies inves-
tigating the mineralisation of proteins in marine sedi-
ments our knowledge of the degradation of other nitrogen containing macromolecules such as DNA, RNA and chitin is almost unknown. There is an urgent need for a systematic investigation of the processes involved.

In the absence of specific methods to determine the mineralisation of nitrogenous organic matter most investigators have used ammonium production as a measure of organic N mineralisation rates. These methods range from simple sediment incubation experiments in which ammonium accumulation is measured over time [115,116] to more sophisti-
cated methods such as the 15N-NH_4^+ isotope dilution
technique in which intact sediment cores or mixed anoxic slurries are injected with $^{15}$N-NH$_4^+$ [117]. The advantage of this method is that it enables both gross and net rates of mineralisation to be calculated. Other methods that have been extensively used include measuring the exchange of ammonium, nitrate and nitrite across the sediment/water interface. In shallow lagoons and intertidal sediments these measurements can be performed in situ using benthic chambers and provide a more realistic estimate of whole community activity than laboratory incubated sediment cores [118]. This method can also be used to determine the effects of seasonal inputs of organic matter on the magnitude of N-fluxes to the overlying water column. Data presented in Table 5 show reported rates of ammonification in a range of unvegetated and vegetated coastal marine sediments. As might be anticipated ammonification rates in seagrass colonised sediments are substantially higher than for bare sediment due to continual deposition of plant detritus to the sediment surface. Dennison et al. [74] showed that the rapid regeneration of ammonium in Great Harbour, Massachusetts, ensured that nitrogen was always available in excess of the eelgrass requirements. Similarly, Iizumi et al. [72] demonstrated that ammonium regeneration in the sediments of the Izembek Lagoon, Alaska, balanced the nitrogen requirements of the eelgrass community present in this shallow marine environment.

Whilst ammonification rates are substantially lower in uncolonised sediments this is probably attributable to the lower organic nitrogen input these environments receive. Laboratory studies by Hansen and Blackburn [119] show that the addition of the marine diatom *Ditylum brightwellii* to sediment cores from Aarhus Bay stimulated ammonification with 62 to 68% of the ammonium fluxes occurring in the first five days. These workers estimated that the ‘half-life’ of the added algal material was 2 to 3 weeks and are similar to those reported by Graf et al. [120] and Gaber [121]. Although the processes whereby ammonium is released from organic N are still poorly defined it is clearly evident that ammonification plays a central role in nitrogen recycling in coastal marine environments. In these shallow water ecosystems (< 50 m depth) benthic recycling may account for between 20–80% of the nitrogen requirements of the phytoplankton [22,69,119]. However, not all the ammonium produced during the deamination of organic N in sediments is available to the primary producers. A proportion, which will vary depending upon the physico-chemical characteristics of the sediment, may be oxidised to nitrate in the surficial oxic zone. This process of ammonia oxidation, termed nitrification, is mediated by specialist chemolithotrophs. Nitrification provides a link between the reduced and oxidised sides of the nitrogen cycle and is therefore of fundamental importance in all ecosystems.

### Table 5
Ammonification rates reported for unvegetated and vegetated coastal sediments

<table>
<thead>
<tr>
<th>System</th>
<th>Ammonification rate (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unvegetated sediments</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aarhus Bay, Denmark</td>
<td>7</td>
<td>[22]</td>
</tr>
<tr>
<td>Kaltegat, Denmark (summer)</td>
<td>34</td>
<td>[22]</td>
</tr>
<tr>
<td>Limfjorden, Denmark</td>
<td>30–95</td>
<td>[89]</td>
</tr>
<tr>
<td>Southern North Sea</td>
<td>11–74</td>
<td>[90, 91]</td>
</tr>
<tr>
<td>Narragansett Bay, USA</td>
<td>106</td>
<td>[92]</td>
</tr>
<tr>
<td>Patuxent Estuary, USA</td>
<td>157</td>
<td>[93]</td>
</tr>
<tr>
<td>Chesapeake Bay, USA</td>
<td>120–430</td>
<td>[73]</td>
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<tr>
<td><strong>Vegetated sediments</strong></td>
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</tr>
<tr>
<td>Oyster Bay, Jamaica</td>
<td>229</td>
<td>[66]</td>
</tr>
<tr>
<td>Izembek Lagoon, Alaska</td>
<td>396</td>
<td>[72]</td>
</tr>
<tr>
<td>Crane Cove, Alaska</td>
<td>508</td>
<td>[72]</td>
</tr>
<tr>
<td>Mangoku-Ura Bay, Japan</td>
<td>644</td>
<td>[72]</td>
</tr>
<tr>
<td>Moreton Bay, Australia</td>
<td>50–490</td>
<td>[94]</td>
</tr>
<tr>
<td>Great Harbour, Woods Hole</td>
<td>225–1125</td>
<td>[74]</td>
</tr>
</tbody>
</table>

*aAverage daily rate.

4. Nitrification

Our understanding of the significance of nitrification in shallow coastal sediments has advanced considerably over the past decade. It is now recognised that oxidation of ammonium plays a pivotal role in generating a source of nitrate for denitrifying bacteria. The coupling of this obligately aerobic process (nitrification) with an anaerobic process (denitrification) leads to the loss of nitrogen to the atmosphere as nitrous oxide and/or dinitrogen.

Ammonia oxidation to nitrate is a two stage process. The first step mediated by ammonia oxidising...
bacteria produces nitrite which in turn is oxidised to nitrate catalysed by nitrite oxidisers. Until recently the classification of nitrifying bacteria was based primarily on morphological characteristics. *Nitrosomonas, Nitrosococcus, Nitrosospira, Nitrosolobus* and *Nitrosovibrio* are generally accepted as ammonia oxidisers and *Nitrobacter, Nitrosococcus, Nitrosospira* and *Nitrosovibrio* as nitrite oxidising genera [122,123]. Recent phylogenetic analysis of pure cultures, based on 16S and RNA sequence data has demonstrated that ammonia oxidising bacteria can be sub-divided into two distinct groups. The first contains *Nitrosococcus oceanus* and forms a deep branch within the γ-proteobacteria [124]. The second group forms a tight cluster within the β-proteobacteria and can be sub-divided into two clades corresponding to *Nitrosomonas* spp. and *Nitrosospira* spp. [125,126]. Since ammonia oxidisers previously classified as *Nitrosovibrio* sp., *Nitrosolobus* sp. and *Nitrosospira* sp. exhibit very high levels of 16S and RNA gene sequence homology they are now accommodated within a single genus for which the name *Nitrosospira* has priority. Phylogenetic analysis of nitrite oxidising species of the genus shows that they form a group within the ε-sub-division. In shallow coastal systems *Nitrosomonas* spp. and *Nitrobacter* spp. are the principal organisms responsible for the two steps, respectively, of nitrification although recently Stephen et al. [127] have provided the first evidence for the existence of marine *Nitrosospira* spp.

Nitrifying bacteria are notoriously difficult to isolate and grow and this has prevented, until recently, a meaningful study of their community structure and diversity. Most probable number methods have been widely used to enumerate nitrifying bacteria [128,129]. The efficiency of this technique is low and it has an inherently low statistical precision. Typically population densities range from $10^2$ to $10^4$ per ml$^{-1}$ sediment and exceptionally may be as high as $10^7$ per ml$^{-1}$ sediment using this method [129–131]. The introduction of improved enumeration techniques based on immunofluorescence has yielded population densities substantially higher than MPN counts [132]. Whilst immunofluorescence is a considerable improvement on conventional MPN methods it nonetheless underestimates the true abundance of nitrifiers because of the specificity of fluorescent antibodies [133]. As yet it is not proved possible to obtain a true estimate of the abundance or diversity of nitrifiers in marine environments. The recent development of specific gene probes for different ammonia oxidisers will however provide a powerful tool to elucidate the community structure of nitrifying bacteria in marine sediments [127,134].

A number of different methods have been developed to estimate nitrification rates in marine sediments. One of the most widely used is the $^{15}$N isotope dilution technique which can be employed with either sediment slurries or intact cores [135]. Nitrification rates have also been determined by measuring $^{15}$N-N$_2$ production from sediment cores amended with $^{15}$N-NH$_4^+$ [130]. This technique has the advantage that it enables both nitrification and denitrification rates to be measured and the degree of coupling between the two processes determined.

Alternatively, non-isotopic methods using specific nitrification inhibitors can be employed. Three inhibitors (nitrapyrin, allylthiourea and chlorate) have been widely used to measure nitrification rates in coastal marine sediments [20,129,136,137]. Inhibitors such as nitrapyrin (also called N-serve) and allylthiourea prevent the oxidation of ammonia to hydroxylamine by inhibiting ammonia monooxygenase, the enzyme catalysing this reaction [138]. The nitrification rate is determined by measuring the difference in ammonium accumulation in the presence and absence of the inhibitor. A variation on this technique is to measure the dark incorporation of $^{14}$C-bicarbonate into the cells of nitrifying bacteria in the presence and absence of N-serve [139]. The nitrification rate is calculated by relating CO$_2$ incorporation to ammonium oxidation using an N:C ratio of 8.3. A particular problem of this method is that N:C ratio can vary from 4 to 40 depending upon the growth conditions and oxygen tension thus making interpretation of the results difficult [141].

All the above methods for determining nitrification rates have inherent limitations and assumptions built into them and these have been excellently reviewed by Henriksen and Kemp [140] and Ward [141]. Data presented in Table 6 show that irrespective of the geographical location, different sediment types and methods used to measure nitrification, the rates are remarkably similar. However, when ana-
lysed on a seasonal basis a different pattern emerges. In Danish coastal waters nitrification rates show a minimum during the summer months and similar observations have also been reported for the Providence river station in Narragansett Bay [136,142] and the upper reaches of Chesapeake Bay. These minima have been attributed to a combination of reduced O2 penetration into the sediment, greater competition for ammonium and elevated sulfide levels which are inhibitory to nitrifying bacteria [136]. In other marine systems such as the Tay Estuary, Scotland and the middle reaches of Narragansett Bay, USA the converse has been observed and summer maxima for nitrification have been recorded [92,136]. In both these cases seasonal patterns of nitrification follow the annual temperature cycle with maximum rates in June-July. In these systems temperature rather than O2 diffusion into the sediment appears to be a more important factor regulating nitrifying activity.

A number of physico-chemical and biological factors are important in regulating nitrifying activity in coastal marine sediments. These include temperature, NH3 concentration, O2 tension, pH, dissolved CO2 concentration, salinity, presence of inhibitory compounds, light, macrofaunal activity and presence of macrophyte roots. Most of the data reported in the literature are derived from pure culture studies and therefore extrapolation of how these parameters affect in situ nitrifying activity must be interpreted with care.

The optimum temperature for the growth of pure cultures of nitrifying bacteria isolated from temperate environments is in the range 25–35°C [143] and below 15°C growth rates decline sharply. Hansen [131] showed that nitrification rates in Danish coastal sediments increased 5-fold when the sediment temperature increased from 2°C in spring to 22°C in autumn. However, shallow coastal sediments, particularly intertidal sediments are subject to both seasonal and diurnal changes in temperatures and hence it may be expected that nitrifying bacteria would exhibit optimal growth and/or activity during the summer months when temperatures are maximal. The little quantitative evidence that is available is contradictory. MacFarlane and Herbert [129] reported that in the Tay estuary, Scotland maximal nitrification rates were recorded in summer when sediment temperatures reached 19–21°C. Similar seasonal patterns have been reported for the middle region of Narragansett Bay [92]. However, temperature also affects other parameters, most notably O2 solubility and this coupled with increased benthic respiration during the summer months, as a result of higher ambient temperatures, means that the downward diffusion of oxygen is limited to the top 1–2 mm of the sediment. Thus, in organically rich sediments oxygen availability rather than temperature per se is the factor most probably limiting nitrifying activity, and would explain the recorded summer nitrification minima recorded in Danish coastal sediments and Chesapeake Bay [130,136].

Nitrifying bacteria are obligate aerobes and thus the depth distribution of nitrifying bacteria is ultimately constrained by the limits of downward O2 diffusion which is typically 1–6.5 mm depending upon sediment type, organic matter content, temperature and degree of mixing and bioturbation [85]. Nitrifying bacteria therefore have to compete with other heterotrophs for the limited supplies of dissolved oxygen. Laboratory studies show that heterotrophic bacteria have a much higher affinity for oxygen ($K_m < 1 \mu M$ O2) and are likely to outcompete nitrifying bacteria at low oxygen concentrations. The reported dissolved oxygen concentrations at which ammonium oxidation is inhibited range from 1.1 to 6.2 $\mu M$ O2 [146–148]. At low oxygen concentrations (< 10 $\mu M$ O2) ammonia oxidisers produce nitrous oxide in addition to nitrate [147,148]. Laboratory

<table>
<thead>
<tr>
<th>System</th>
<th>Nitrification rate (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Sea sediments</td>
<td>2–9</td>
<td>[20]</td>
</tr>
<tr>
<td>Kingoodie Bay, UK</td>
<td>20</td>
<td>[129]</td>
</tr>
<tr>
<td>Limfjorden sediments, Denmark</td>
<td>38</td>
<td>[11]</td>
</tr>
<tr>
<td>Normsinde Fjord, Denmark</td>
<td>112</td>
<td>[144]</td>
</tr>
<tr>
<td>Ochlockonee Bay, Florida</td>
<td>84</td>
<td>[145]</td>
</tr>
<tr>
<td>Southern North Sea sediments</td>
<td>26</td>
<td>[90]</td>
</tr>
<tr>
<td>Narragansett Bay, USA</td>
<td>23</td>
<td>[92]</td>
</tr>
<tr>
<td>Chesapeake Bay, USA</td>
<td>14–23</td>
<td>[140]</td>
</tr>
<tr>
<td>Patuxent River Estuary, USA</td>
<td>26</td>
<td>[130]</td>
</tr>
<tr>
<td>Kysing Fjord, Denmark</td>
<td>23–27</td>
<td>[136]</td>
</tr>
<tr>
<td>Odawa Bay, Japan</td>
<td>38–42</td>
<td>[135]</td>
</tr>
</tbody>
</table>
studies have shown that under conditions of oxygen limitation *Nitrosomonas europaea* functions as a denitrifier, using nitrite generated as the end-product of ammonium oxidation as terminal e\(^{-}\) acceptor [148,149]. In coastal marine sediments dissolved O\(_2\) concentrations undergo very sharp diel cycles: from super-saturating conditions resulting from benthic microalgal photosynthesis during daytime to complete anoxia at night as a consequence of high respiratory demand [150]. The ability of ammonia oxidisers to grow at low dissolved O\(_2\) tensions using nitrite as terminal e\(^{-}\) acceptor may be a mechanism whereby these bacteria survive such rapidly changing conditions. At the other end of the spectrum almost nothing is known about the effect of elevated oxygen concentrations on nitrifying activity. Yet in shallow water sediments oxygen levels can reach 2–3 times air saturation values during daytime as a result of benthic primary production [85]. Henriksen and Kemp [140] reported that increasing O\(_2\) concentrations to 2 and 2.6 times air saturation values resulted in a 15% and 25% inhibition of nitrifying activity in estuarine sediment slurries. However, no systematic investigations have been undertaken to evaluate the effects of elevated oxygen concentrations on nitrifying activity.

In sediment systems colonised by emergent and submersed vascular plants the release of oxygen into the rhizosphere zone may stimulate nitrification activity [151,152]. However, few direct measurements of nitrification rates have been made in macrophyte colonised sediments. Kemp et al. [153] reported that nitrification rates in sediments colonised by *Potamogeton perfoliatus* were 20-fold higher than in uncolonised sediments. Equally, discontinuities arising from the effects of macrofaunal activity significantly alter the spatial gradients of O\(_2\) and NH\(_4^+\) in sediments. Several studies have demonstrated higher nitrification activity in the lining of infauna burrows than in defaunated sediments [154–156]. This may be explained by the higher ammonium concentrations found in the deeper parts of burrows which together with ammonium excreted by their macrofauna inhabitants provides a higher substrate availability. The downward transport of oxygen into the burrows is dependent on the ventilation activity of the burrow inhabitants. Whilst burrows are different from surface sediment they can in some respects be considered as an extension of the sediment-water interface. Kristensen [156] estimated that an estuarine population of the polychaete *Nereis virens* (700 individuals per m\(^{-2}\)) increased the contact zone between sediment and water by \(~\)150% and oxic sediment volume by 30–50%. Kristensen et al. [157] estimated that in sediments colonised by *N. virens* nitrification in the burrows accounted for between 10 and 70% (mean value 40%) of the bulk sediment nitrification. These data are similar to these reported by Henriksen et al. [158] and Blackburn and Henriksen [21]. Thus, oxygenated burrows increase the potential for nitrification in a sediment by providing additional sites for ammonium oxidation and stimulating bacterial activity. Nitrate produced by the oxic sediment layers can either diffuse into the overlying water column as a source of ‘regenerated’ nitrogen or enter the anoxic sediment where it can be reduced to nitrogen and/or dinitrogen by denitrification or NH\(_4^+\) by nitrate ammonifying bacteria.

### 5. Denitrification and nitrate ammonification

Whereas nitrification involves the oxidation of reduced nitrogen mediated by obligate aerobes, denitrification is a reductive process, whereby heterotrophic bacteria utilise nitrate as a terminal e\(^{-}\) acceptor in respiration and reduce it to either gaseous products (denitrification) or ammonium (nitrate ammonification). Denitrification is a key process in the sediment nitrogen cycle since it decreases the amount of nitrogen available to the primary producers as the gaseous end-products (N\(_2\)O and N\(_2\)) diffuse into the atmosphere. It also provides a mechanism, in coastal marine systems that receive large quantities of nitrogen from anthropogenic sources, to remove excess nitrogen and therefore help control the rate of eutrophication of these environments [172,173, 180,181]. The ability to denitrify is widely distributed amongst different taxonomic groups of heterotrophic bacteria [182–184]. In the presence of molecular oxygen these bacteria grow aerobically but under oxygen depleted conditions they are able to maintain respiratory activity using nitrate as the terminal e\(^{-}\) acceptor. The most frequently isolated denitrifying bacteria belong to the genus *Pseudomonas* which produce dinitrogen as the end-product of nitrate re-
piration [185,186]. In addition to denitrification, a number of studies have shown that nitrate can be reduced to ammonium by a number of fermentative and strictly anaerobic bacteria [185–189]. In contrast to denitrification where nitrogen is lost from the ecosystem nitrate ammonification results in the conservation of nitrogen in an available form. A further aspect of denitrification that has been intensively studied is the coupling of nitrification to denitrification since this provides a mechanism whereby substantial quantities of nitrogen can be removed from marine ecosystems [130,140,144].

A wide range of experimental methodologies have been developed to estimate denitrification rates in shallow marine environments. These include mass balance methods which estimate denitrification rates on the difference between N-inputs and outputs [102,145,181,190], the acetylene inhibition technique [191,192], N₂ production measurements [92,130,171], diagenetic models of pore water profiles [92], nitrate consumption measurements [193], microelectrode methods using either acetylene inhibition in conjunction with O₂/N₂O microelectrodes or by calculating denitrification rates from nitrate profiles measured using a nitrate microsensor [144,194,195] and ¹⁵N-tracer techniques [4,130,174,176,196,197]. The acetylene inhibition technique (AIT) is based on the inhibition of nitrous oxide reductase by acetylene and is a simple, sensitive and inexpensive method [180,192]. However, it suffers a number of disadvantages, most notably that at the low nitrate concentrations often found in marine sediments (< 10 μM) inhibition is incomplete [180,192]. As a consequence of the incomplete inhibition of nitrous oxide reductase by acetylene, denitrification rates may be underestimated by as much as 30–50% [198]. The limitations of the AIT method have been clearly demonstrated by Lohse et al. [91]. These investigators simultaneously measured denitrification rates in the southern North Sea by the AIT technique and isotope pairing method (IPM) and showed that rates recorded using acetylene inhibition were 45% lower than those obtained by the IPM method (see Table 7 for details). Furthermore acetylene severely inhibits nitrifying activity [199] and in marine sediments sulfide reverses the acetylene block of nitrous oxide reductase activity [180,192]. As a consequence of these experimental limitations direct measurements using ¹⁵N-tracer techniques are now the preferred method for measuring denitrification rates. The recently developed ¹⁵N isotope pairing method is a powerful analytical technique which not only enables the rate of denitrification to be accurately determined but also the proportion arising from nitrate in the water column and that produced by nitrification in the sediment [176,177,196]. This experimental approach has the major advantage that no inhibitor is required and that nitrification, denitrification, nitrate ammonification and N-mineralisation rates can all be determined in a single experiment if the nitrate and ammonium fluxes have been measured [91,177].

Data presented in Table 7 show reported denitrification rates for a range of coastal and estuarine sediments using ¹⁵N isotope and acetylene inhibition techniques. The sediments show a wide range of activities with a trend to higher rates in shallow nearshore waters e.g. Lendrup Vig, Kysing Fjord, Norsminde Fjord, Chesapeake Bay and Narragansett Bay where the supplies of organic carbon and nitrate runoff are higher. High denitrification rates have also been recorded in Z. marina colonised sediments in Chesapeake Bay (Table 7). These probably arise as a result of the macrophytes increasing the organic content of the sediment by trapping detritus and/or excreting organic carbon from the roots [200,201].

A number of studies have shown in temperate marine environments that denitrification rates show distinct seasonal patterns governed principally by temperature, supply of nitrate and availability of organic carbon [172,179,202]. In systems where there is a substantial input of nitrate throughout the year there is a good correlation between denitrification activity and ambient temperature [202–204]. However, in other shallow inshore environments nitrate inputs are more episodic events such as increased agricultural run-off during winter and spring. In Norsminde Fjord, Jorgensen and Sorensen [162] showed that there were two seasonal maxima of denitrifying activity, one in May attributed to the deposition and decomposition of a microalgal bloom and presence of high nitrate concentrations in the water column and one in the late autumn associated with increased inputs of nitrate into the water column. In this system, nitrate concentrations in the sediment were controlled by the nitrate load in the overlying water column. Where external nitrogen inputs are small
nitrification is the principal source of nitrate for denitrification. Jenkins and Kemp [130] showed that in the Patuxent Estuary there was a strong coupling between nitrification and denitrification. In this estuary > 99% of the nitrate produced by nitrification was reduced to dinitrogen during the spring. However, during the summer this coupling decreased by two orders of magnitude, even though the denitrification potential was similar to that recorded in the spring, due to reduced nitrification rates resulting from low O2 concentrations in the surface sediments. This seasonal pattern of high denitrification rates in spring followed by lower rates in summer has also been reported for Ochlockonee Bay in Florida [92].

Table 7

<table>
<thead>
<tr>
<th>System</th>
<th>Denitrification rate (mg N m(^{-2}) day(^{-1}))</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Randers Fjord</td>
<td>20–141</td>
<td>[159](^a)</td>
</tr>
<tr>
<td>Kysing Fjord</td>
<td>3–1109</td>
<td>[159](^a)</td>
</tr>
<tr>
<td>Delaware Inlet</td>
<td>20–40</td>
<td>[160](^a)</td>
</tr>
<tr>
<td>Lendrup Vig</td>
<td>40–715</td>
<td>[161](^a)</td>
</tr>
<tr>
<td>Norsminde Fjord</td>
<td>278–1401</td>
<td>[162](^a)</td>
</tr>
<tr>
<td>Norsminde Fjord</td>
<td>14–224</td>
<td>[163](^a)</td>
</tr>
<tr>
<td>Newport River Estuary</td>
<td>14–42</td>
<td>[164](^a)</td>
</tr>
<tr>
<td>Tomales Bay sub-tidal</td>
<td>14–98</td>
<td>[165](^a)</td>
</tr>
<tr>
<td>Tomales Bay mud flat</td>
<td>10–100</td>
<td>[166](^a)</td>
</tr>
<tr>
<td>Torridge River mud flat</td>
<td>2–19</td>
<td>[167](^a)</td>
</tr>
<tr>
<td>Torridge River marsh</td>
<td>8–198</td>
<td>[167](^a)</td>
</tr>
<tr>
<td>Chesapeake Bay, Z. marina</td>
<td>225–702</td>
<td>[168](^a)</td>
</tr>
<tr>
<td>Chesapeake Bay, non-vegetated</td>
<td>20–739</td>
<td>[168](^a)</td>
</tr>
<tr>
<td>Great Ouse Estuary</td>
<td>7–32</td>
<td>[169](^a)</td>
</tr>
<tr>
<td>Texel, Wadden Sea</td>
<td>3–185</td>
<td>[170](^a)</td>
</tr>
<tr>
<td>Southern North Sea</td>
<td>2–3</td>
<td>[91](^a)</td>
</tr>
<tr>
<td>Narragansett Bay</td>
<td>50–655</td>
<td>[171](^a)</td>
</tr>
<tr>
<td>Guadalupe Estuary</td>
<td>15–116</td>
<td>[172](^a)</td>
</tr>
<tr>
<td>Boston Harbour</td>
<td>&lt;10–412</td>
<td>[173](^a)</td>
</tr>
<tr>
<td>Massachusetts Bay</td>
<td>&lt;10–128</td>
<td>[173](^a)</td>
</tr>
<tr>
<td>Patuxent River Estuary</td>
<td>259–299</td>
<td>[130](^a)</td>
</tr>
<tr>
<td>Tokyo Bay</td>
<td>54–111</td>
<td>[174](^a)</td>
</tr>
<tr>
<td>Colne Point salt marsh</td>
<td>13–44</td>
<td>[175](^a)</td>
</tr>
<tr>
<td>Aarhus Bay</td>
<td>40–71</td>
<td>[176](^a)</td>
</tr>
<tr>
<td>Southern North Sea</td>
<td>3–4</td>
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</tr>
<tr>
<td>Arcachon Bay</td>
<td>0–59</td>
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</tr>
<tr>
<td>Etang de Prévoit</td>
<td>1–153</td>
<td>[177](^a)</td>
</tr>
<tr>
<td>Colne Estuary</td>
<td>1–154</td>
<td>[178](^a)</td>
</tr>
<tr>
<td>Gulf of Finland</td>
<td>1–9</td>
<td>[179](^a)</td>
</tr>
<tr>
<td>Northern Baltic Proper</td>
<td>0–4.2</td>
<td>[179](^a)</td>
</tr>
</tbody>
</table>

\(^{a}\) Acetylene block method. 
\(^{b}\) N\(_2\) flux method. 
\(^{c}\) 15 N isotope pairing method.

In addition to seasonal changes in denitrification rate, rates in intertidal and sub-tidal environments are also subject to significant change on a diel basis due to the growth of benthic microalgae at the sediment surface. During daylight hours O\(_2\) produced during photosynthesis can diffuse into the surface sediments and inhibit dissimilatory nitrate reduction. Jorgensen and Sorensen [162] showed that inhibition of denitrification was most pronounced in early spring when rates were reduced by as much as 60% in the light compared to dark controls. However, when calculated on an annual basis denitrification rates were reduced by only 13% due to light inhibition. Similar findings have been reported for Lendrup Strand sediment by Andersen et al. [161].

As described earlier in this review (Section 4) the presence of macrophytes and infauna can exert a profound influence on processes such as nitrification and denitrification. For example, Kemp and Murray [205] have calculated that oxygen released from the roots of \(P. perfoliatus\) was sufficient to support \(V\(_5\) times the rate of nitrification in unvegetated sediments. Equally macrophytes may stimulate denitrification by trapping readily degradeable organic detritus in the water column or releasing labile organic carbon from the roots [200]. The exchange of nitrate between the overlying water and sediment is also significantly influenced by the burrow-dwelling infauna. In the presence of different infaunal species the nitrate flux either increases or decreases. This has been attributed to the substantial variation in the degree of coupling and rates of nitrification and denitrification occurring in the burrows. For example, Henriksen et al. [154] showed that shallow burrowers such as \(C. volutator\) which have a higher ventilation activity and large burrow volume compared to size stimulate nitrification because oxygen is able to penetrate deeper into the burrow walls. In contrast, deep burrowers such as \(N. virens\) usually show a nitrate flux into the burrow inferring a high rate of denitrification. The infauna not only influence nitrogen cycling in marine sediments by producing burrows they also selectively concentrate organic material as faecal pellets. Faecal pellets have long been recognised as sites of intense microbial activity which result in a high oxygen demand with the formation of reduced microniches [206,207]. These anoxic microsites enable anaerobic processes such as

*FEMSRE 662 5-10-99*
denitrification to take place in what are ostensibly oxic surface sediments and may explain how these two processes can occur in close proximity. These data show that the infauna play an important role in stimulating nitrogen cycling in coastal marine sediments.

Denitrification is widely accepted as being the dominant process of nitrate reduction in most shallow marine sediments [129,135,144,160,167]. However, the alternative pathway of nitrate reduction, nitrate ammonification may also be important under certain conditions. Few systematic studies of nitrate ammonification have been undertaken and hence it is not possible to evaluate how significant this process is in coastal marine systems. A number of studies have demonstrated that heterotrophic bacteria with the capacity to respire nitrate to ammonium are widely distributed in marine sediments. They are predominantly fermentative bacteria and include members of the genera Aeromonas, Vibrio [129,185], Clostridium [187,189] and Desulfovibrio [188]. Macfarlane and Herbert [129] showed that in the Tay estuary, Scotland, populations of nitrate ammonifying bacteria in the surface sediments were in the order of $10^6$--$10^7$ g dry wt. sediment$^{-1}$. Similar population densities of nitrate ammonifiers have been reported for other shallow marine ecosystems [208]. In organically rich sediments, such as those found in Mangoku-Ura Bay, Japan, nitrate ammonification accounted for $\sim 50\%$ of the total nitrate reduced whereas in sediments with a low C:N ratio the rates were lower (4--35%) and denitrification was the dominant process [129,135,177,209,210]. Jorgensen [209] showed that in Norsminde Fjord, Denmark nitrate ammonification was only a significant process during the late summer when the sediment was reduced all the way to the surface. Under these conditions, nitrate ammonification was maximal in the surface layer whereas at all other times activity was restricted to the deep sediment layers and denitrification was the predominant process of nitrate reduction. Laboratory studies by Herbert and Nedwell [3] demonstrated that nitrate concentration plays a key role in determining whether nitrate is reduced to gaseous products or conserved as ammonium. These workers showed that at low nitrate concentrations denitrifiers were outcompeted by nitrate ammonifying bacteria whereas at high nitrate concentrations the converse was true. These observations are consistent with field data obtained from the Colne estuary, England, which show that as the nitrate concentration increased denitrification became the dominant process [211,212]. Similarly, Smith and co-workers [204] demonstrated that nitrate ammonification in a salt marsh sediment decreased from $> 50\%$ to $\sim 4\%$ of the total nitrate reduced when nitrate concentrations increased. These observations reflect the different competitive abilities of denitrifiers and nitrate ammonifying bacteria and hence selection of different nitrate reducing communities under changing C:N conditions in the field [213].

In addition to dinitrogen and ammonium, nitrous oxide can also be produced as an end-product of dissipatory nitrate reduction. In denitrification, nitrous oxide is a true intermediate whereas in nitrate ammonification it is a side reaction [180]. As discussed previously (Section 4) nitrous oxide is also produced as a side reaction of nitrification. The recognition that this gas plays a key role in both the stratospheric ozone and tropospheric heat budget has stimulated research to identify the sources of nitrous oxide production [214,215]. Estuarine and coastal marine environments have been identified as sources of atmospheric nitrous oxide on the basis that in situ concentrations in the water are supersaturated relative to atmospheric levels [216,217]. The production of nitrous oxide is controlled by several factors of which oxygen is considered the most important. Jorgensen et al. [147] demonstrated that at low O$_2$ partial pressures (0--0.2 kPa) nitrous oxide production increased rapidly and was maximum under anoxic conditions. These workers concluded that denitrification was the principal source of nitrous oxide production. In a follow-up study, Jensen et al. [218] showed that nitrous oxide production followed a diel cycle in a manner analogous to that observed for denitrification [162]. They recorded maximum emissions of nitrous oxide at night (0.4 to 4 $\mu$mol N$_2$O-N m$^{-2}$ h$^{-1}$) whereas during the day rates decreased to between --0.4 to 0.4 $\mu$mol N$_2$O-N m$^{-2}$ h$^{-1}$. Nitrous oxide production, resulting from denitrification, was maximum in the surface to 1 cm depth horizon and thus the emission pattern was inversely related to the presence of oxygen at the sediment surface. In the dark lack of oxygen production by the benthic microalgae enabled denitrifica-
tion to occur close to the sediment-water interface thereby facilitating the release of nitrous oxide to the water. Daily average nitrous oxide emissions from this sediment were \( \sim 40 \mu \text{mol N}_2\text{O-N m}^{-2} \text{day}^{-1} \) during the winter months and early spring whereas no significant production was recorded in summer when the sediments were nitrate depleted. Robinson et al. [217] in a comprehensive study of atmospheric N\(_2\)O emissions from the hypernutri\(f\)ed Colne estuary similarly concluded that benthic denitrification and not nitrification was the principal source of N\(_2\)O in this high nitrate estuary. Although the estuarine water was always super-saturated with N\(_2\)O no production could be demonstrated in the water column. They elegantly demonstrated that N\(_2\)O emission fluxes from the surface of the tidally exposed sediments decreased with time. This was a result of the rapid turnover (< 40 min) of the sedimentary nitrate pool and its depletion when it was no longer being recharged by nitrate from the overlying water column. These workers estimated that whilst benthic N\(_2\)O production was < 2% of the nitrate denitrified in the Colne estuary it nevertheless represented a significant export of N\(_2\)O to the atmosphere. A further factor influencing nitrous oxide emissions from coastal marine sediments is nutrient loading. Seitzinger and Nixon [219] showed that increased dissolved inorganic nitrogen loading to marine mesocosms significantly increased nitrous oxide emissions. Similar results were obtained by Middelburg et al. [220] for the Scheldt estuary. These workers showed that in the Scheldt estuary sediments nitrous oxide fluxes appeared to respond linearly to an increasing nitrogen load. Highest nitrous oxide fluxes were recorded at the tidal freshwater member sites where total dissolved nitrogen may reach a concentration of 600 \(\mu\)M, whereas emissions were almost zero at the high salinity stations where nitrogen levels are low. At the most saline sites influxes of nitrous oxide into the tidal flats were recorded. Similar observations have been recorded for other coastal sediments and have been attributed to the utilisation of nitrous oxide as a terminal e\(^{-}\) acceptor during organic matter degradation in the absence of nitrate [170,178,221,222]. This consumption of nitrous oxide in anoxic marine sediments is consistent with their overall high denitrification activity [180].

In summary the preceding sections of this review have amply demonstrated the complexity of nitrogen cycling in shallow marine sediments and how individual microbiologically mediated processes are modulated by physico-chemical and biotic factors. The complex nature of benthic nitrogen cycling is shown schematically in Fig. 2. The driving force

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**Fig. 2.** Schematic representation of nitrogen cycling in coastal marine sediments.
for nitrogen mineralisation is the quality (C:N ratio), quantity, spatial distribution of the degradable organic matter in the sediments and the diffusability of the decomposition products. These factors are not only the major determinants of the amount of organic nitrogen mineralised but also the respective quantities of ammonium, nitrate, dissolved organic N and nitrous oxide/dinitrogen released from the sediment into the overlying water column. The presence/absence of rooted macrophytes and infauna together with concentrations of oxygen, ammonium and nitrate in the overlying water also play a role in determining the ratios of these products by stimulating or inhibiting individual mineralisation processes. These often opposing stimulations and inhibitions of the individual processes which make up the nitrogen cycle result in complex patterns of nitrogen mineralisation that are difficult to interpret. As a consequence a number of investigators have employed mathematical models to examine the interrelationships between these different processes in order to identify the parameter(s) which exert the greatest control on the nitrogen cycle.

6. Modelling of nitrogen cycling in coastal marine systems

A number of models have been developed to simulate benthic nitrogen mineralisation [223–227]. Many of the early models were constrained by the number of components that could be used and this limited the spatial resolution of these systems. In recent years more complex models have been developed. Blackburn [225] developed a systems dynamic model which linked reactants and products by diffusion equations. However, this model also suffered from limited spatial resolution. More sophisticated versions, based on the Cellmatics system, have now been developed which yield a high spatial and temporal resolution [226,227]. Such models have been used to simulate the effects of increased rates of organic matter loading to the surface of a marine sediment on the efflux of nitrate, ammonium, DON and dinitrogen gas as well as nitrification and denitrification rates [226]. The data obtained show that modest increases in organic matter loading (21.6 mmol C m$^{-2}$ day$^{-1}$) stimulated nitrification by increasing ammonium availability whereas at higher loading (> 64.6 mmol C m$^{-2}$ day$^{-1}$) nitrification rates decreased as a consequence of reduced oxygen penetration into the surface sediment layer resulting from stimulated respiratory demand. Since nitrification was reduced under these conditions denitrification rates also declined due to nitrate limitation even though the prevailing anoxic conditions were optimum for nitrate respiration. A further consequence of the decrease in ammonium oxidation rate at high organic matter loadings (107 mmol m$^{-2}$ day$^{-1}$) was that ammonium efflux from the sediment increased by ~50%. In contrast at low organic matter loading rates (7.2 mmol m$^{-2}$ day$^{-1}$) denitrification rates were limited by the availability of organic matter.

Simulations such as these are a valuable tool for testing hypotheses and predicting the outcome of mineralisation processes in sediments. A further example of the power of this experimental approach has been the use of mathematical models to simulate the effects of the distribution of organic matter and different organic matter loadings on nitrification and denitrification rates [227–229]. Three distribution patterns were simulated via surface deposition, linear depth distribution and completely mixed to mimic active bioturbation. Additional factors examined in the model included different concentrations of O$_2$, NO$_3^-$ and NH$_4^+$ in the overlying water column and the presence and absence of sulfide diffusion. It was predicted that the mixed distribution of organic matter would result in high rates of sulfate reduction, nitrification and denitrification in the absence of sulfide diffusion (iron excess conditions) and this was confirmed by the model. The explanation for this is that organic matter oxidation in the deep sediment was coupled to sulfate reduction. Ammonium released during this process was able to diffuse upwards into the oxic surface layer where it was oxidised to nitrate and then denitrified by downward diffusion into the underlying anoxic zone. Under these conditions carbon and nitrogen mineralisation processes are decoupled and since there was relatively little carbon in the oxic zone and sulfide was sequestered as iron sulfide and pyrite more oxygen was available for ammonium oxidation: hence the high nitrification rates. When sulfide was allowed to diffuse freely, simulating iron limiting conditions, it diffused into the oxic zone and competed with the
nitrifiers for oxygen. As a consequence the depth of oxygen penetration into the surface sediment was limited and nitrification and denitrification rates were correspondingly lower. These data have subsequently been confirmed experimentally using sediment cores amended with different organic matter loadings [4].

Further runs of the model investigated the effects of different concentrations of oxygen, ammonium and nitrate in the overlying water column in order to quantify the proportion of nitrification and denitrification arising from the efflux of ammonium and nitrate from the sediment (Ns and Ds) and these nitrogen species in the water column (Nw and Dw). The simulations demonstrated that increased water column nitrate concentrations did not influence coupled nitrification-denitrification reactions in the sediment. However, increased ammonium levels in the overlying water stimulated coupled nitrification-denitrification in the sediment as did elevated oxygen concentrations. The converse was true when sulfide was allowed to diffuse freely in the sediment. This is to be expected since increased ammonium and oxygen availability stimulates nitrifying activity in the surface sediment and this in turn leads to increased sediment denitrification activity. Diffusion of sulfide into the oxic zone reduces oxygen availability and inhibits nitrification hence decreasing the amount of ammonium oxidised, and concomitantly the rate of sediment denitrification (Ds). However, when nitrate concentrations in the water column are high it diffuses into the sediment stimulating denitrification (Dw). Since denitrification is an anaerobic process it is not surprising that rates should be maximal under such conditions. These data highlight both the complexity and apparent contradictions of the different processes involved in benthic nitrogen cycling.

Thus, total rates of denitrification are dependent upon diametrically opposing environmental conditions, viz sediment denitrification (Ds) is dependent upon ammonium oxidation in the surface oxic zone whilst denitrification of water column nitrate (Dw) is dependent upon sediment anoxia and high nitrate concentrations. The value of computer simulations such as those described above is that they may enable environmental conditions that are conducive to high denitrification rates to be identified thereby reducing the amount of recycled nitrogen available to the primary producers.

7. Effects of anthropogenic inputs on nitrogen cycling

Littoral ecosystems such as salt marshes, estuaries and inshore coastal waters are natural highly productive environments which in recent years have been subject to increased anthropogenic inputs of nitrogen arising from such diverse sources as fertilizer run-off, sewage discharges and aquaculture [230–233]. The net effect of these elevated nitrogen inputs is to stimulate primary production [234,235]. These effects have been most severe in areas such as shallow embayments or where tidal flushing is limited [236–238]. In general, increased nitrogen loadings (hypernutrification) accompanied by excessive phytoplankton growth (eutrophication) result in a sharp decline in the rooted phanerogam communities due to decreased water transparency and build up of epiphytes [239–243]. Aquatic systems with extensive phytoplankton blooms frequently progress to systems dominated by opportunistic, free floating macroalgae belonging to the orders Ulvales or Cladophorales (chlorophyta) and cyanobacterial blooms [236,243]. This excessive primary production in turn leads to high rates of production in the rest of the biological food web in these ecosystems [235,244]. The increased pool of autochthonous particulate matter produced results in intense microbial activity when it is deposited at the sediment surface [235,245]. As a result of these high decomposition rates oxygen demand in the sediment is high and may lead to a temporary disappearance of dissolved oxygen in the overlying water column with the concomitant release of toxic sulfide [236–238]. This phenomenon known as dystrophic crisis causes mass mortality of the benthic macrofauna and fish stocks in enclosed lagoons such as those found in the southern Mediterranean [235,237,238,242].

Increased nutrient loadings to shallow marine environments and the accompanying stimulation of primary production have as might be expected a profound effect on benthic metabolism and nitrogen mineralisation processes. Since the progressive decline in seagrass meadows and their replacement by phytoplankton and opportunistic macroalgae such as
Ulva not only increases the total quantity of organic matter produced in these ecosystems but also its composition [96,236,246]. Fast growing macroalgae such as Ulva assimilate and store nitrogen in excess of their growth requirements. This ‘luxury’ uptake coupled with a rapid growth rate enables this macroalga to outcompete other primary producers [247–249]. A consequence of the elevated nutrient content of macroalgae such as Ulva is that their decomposition is more rapid due to their high N:C ratios [96,97]. As a result, the replacement of seagrass meadows by macroalgae changes not only the timing and rate of detritus production but also the decomposition rate. A less obvious effect of the change in the primary producer community is the oxygenation of the surficial sediments. Rooted phanerogams provide gas transport throughout the surficial sediment and hence contribute to its oxygenation. In contrast, floating macroalgae do not and because of their morphology can promote physical stratification of the overlying water column [250]. The large thalli of Ulva act as a physical barrier separating the water column into two layers, the upper one well oxygenated or even super-saturated and the lower one anoxic and highly reduced [242]. Pelagic macroalgae such as Ulva can achieve biomass values >1 kg dry wt m\(^{-3}\) during the active growth phase in spring and early summer [251]. In shallow coastal lagoons decomposition commences in mid-summer (July–August) when the growth of Ulva has ceased [242,251]. This results in a rapid release of organic matter to the sediment and overlying water and concomitant onset of anoxia. In the absence of oxygen, organic carbon oxidation is coupled to sulfate reduction. The removal of oxygen and as a result of the abiotic oxidation of sulfide in the sediment whilst optimum for denitrification is inhibitory to nitrification and hence nitrogen removal via coupled nitrification denitrification is also inhibited. Under these conditions nitrogen can only be lost to the atmosphere through denitrification using water column nitrate. In the shallow Sacca di Goro Lagoon, northern Italy, high rates of denitrification (~1 g N m\(^{-2}\) day\(^{-1}\)) have been reported to occur during the annual dystrophic period and represent a significant loss of nitrogen from this ecosystem [252]. Using benthic chambers incubated in the dark Viaroli and co-workers [238,252] showed that ~14% of the original Ulva nitrogen was released as total dissolved nitrogen (DON+DIN) over a 3 day incubation period but only 6% of this was ammonium whilst in the light the values were 8% and 1% respectively. These data not only indicate that mineralisation of Ulva nitrogen is relatively slow but that the major decomposition products were DON rather than DIN. Subsequent experiments have confirmed that nitrogen release from decomposing Ulva was slow and after 60 days did not exceed 50% of the initial N-content [253]. These data indicate that there is temporal uncoupling between the growth and decomposition phases in macroalga such as Ulva.

In hyper-eutrophic coastal lagoons such as Sacca di Goro, northern Italy, and the Étang du Prévoist, France, Ulva plays a central role in controlling the nitrogen cycle: in the active growth phase Ulva outcompetes the phytoplankton for available nitrogen by virtue of its high affinity uptake systems for nitrate and ammonium whilst during the decomposition phase nitrogen regeneration is slow resulting in a low efflux of dissolved inorganic nitrogen to the overlying water column [247,248]. The degree of nitrogen limitation is further increased by the stimulation of denitrification of water column nitrate during the dystrophic crisis period. Whilst it appears paradoxical that nitrogen could be the growth limiting nutrient in these systems which annually receive substantial nitrogen inputs from anthropogenic sources the bulk of it is sequestered in Ulva biomass and therefore unavailable. The slow release of dissolved inorganic nitrogen to the overlying water suggests a prolonged retention of nitrogen in the sediment over the winter months which is then released during the following spring when macroalgal growth is again initiated. In these systems reduction of macroalgal growth can only be achieved by improving water exchange or by reducing the nitrogen input in the inflow streams and rivers.

In more hydrodynamic marine environments such as estuaries which receive considerable nitrogen inputs from fertiliser run-off and sewage discharges from the adjacent land areas denitrification may account for between 20 and 50% of the annual nitrogen input into these systems. Denitrification has been proposed as a ‘natural control’ of coastal eutrophication [170,216,211]. However, nutrient mass balance data are only available for a limited number of es-
tuaries [173,254]. As a consequence it is difficult to assess the role of denitrification in mitigating the effects of increased anthropogenic nitrogen loads into coastal marine environments. Nowicki and co-workers [173] carried out an extensive 3 year study of denitrification in Boston Harbour and Massachusetts Bay using the N₂ flux method. They recorded highest denitrification rates in summer in Boston Harbour \((6 \times 10^4 \text{ mg N m}^{-2} \text{ day}^{-1})\) and in spring and autumn in Massachusetts Bay \((6 \times 10^12 \text{ mg N m}^{-2} \text{ day}^{-1})\) coincident with phytoplankton maxima. Denitrification rates correlated with temperature, organic carbon content and benthic macrofaunal activity. Whilst recorded sediment denitrification rates were high relative to other US east coast estuaries, the annual integrated denitrification loss for Boston Harbour was only 8% of the annual total nitrogen load. One explanation for the low removal of nitrogen by denitrification is the relatively short water residence time, 2–10 days in the harbour. Recent studies have postulated that the magnitude of nitrogen loss through denitrification in estuaries is a function of the water residence time [163,181]. Data presented in Fig. 3 show that in systems with short residence time viz Norsminde Fjord, Boston Harbour and Ochlockonee Bay little denitrification occurs and the bulk of the nitrogen load is exported offshore whereas in estuaries, lagoons and bays with low flushing rates significant removal of nitrogen occurs. Currently little is known about the coupling between estuaries and the adjoining continental shelf areas and the relative role of denitrification in the economy of these systems. Few direct measurements of denitrification for shelf sediments are available and more comprehensive studies are required to assess the magnitude of denitrification as a permanent sink for nitrogen inputs in these systems before the significance of this process can be fully appreciated [255].

8. Concluding remarks

The past decade has seen very major advances in our understanding of the physico-chemical and biotic factors regulating nitrogen cycling in shallow coastal marine sediments. Much of this is due to significant improvements in experimental methodologies resulting in greatly improved spatial and temporal resolution of the individual processes that make up the benthic nitrogen cycle. In particular, the development of microelectrodes for measuring O₂, nitrate, nitrous oxide, sulfide and light irradiance in sediments with a spatial resolution of \(<0.1 \text{ mm}\) represents an important technological advance. The application of microsensors has led to new insights into the spatial distribution of the different processes involved in nitrogen mineralisation and how they are regulated by oxygen, light, sulfide and carbon availability. A further significant advance has been the development of sophisticated computer models to simulate the complex interactions which occur during nitrogen cycling in marine sediments. Such an experimental approach enables the analysis of interactions at a resolution that would be unobtainable by other methods. Mathematical models can also play an invaluable role in designing field experiments by identifying the key parameters and processes worthy of more detailed investigation. The recent trend to integrated research programmes studying nitrogen cycling in whole ecosystems involving multi-disciplinary research teams has been scientifically extremely productive and has identified the important role played by the infauna and macrophyte roots in benthic nitrogen cycling. These new insights into how organic matter is mineralised in shallow coastal sediments provide a firm foundation on which to develop effective management programmes for these environmentally sensitive ecosystems. They also pro-
vide the basis for remediation programmes to rehabilitate seagrass communities in lagoons currently dominated by pelagic macroalgae and/or cyanobacterial blooms.

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