Ammonium recycling versus denitrification in Chesapeake Bay sediments

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Abstract

Contemporaneous measurements are reported for nitrification, denitrification, and net sediment–water fluxes of NH₄⁺ and NO₃⁻ in the mesohaline region of Chesapeake Bay. Seasonal cycles over a 2-yr period were characterized by a midsummer maximum in NH₄⁺ efflux to the overlying water and a May peak in NO₃⁻ removal from water by sediments. Coherent temporal patterns for nitrification and denitrification were observed, with relatively high values in spring and fall and virtual elimination of both processes in summer. Indirect measurements indicate that nitrification was limited by the shallow O₂ penetration (<1 mm) here compared to reports for other marine sediments (2–6 mm). In addition, a strong positive correlation between the two processes suggested that denitrification was generally controlled by nitrification. Comparisons of NO₃⁻ fluxes and net nitrification rates (nitrification minus NO₃⁻ reduction to NH₄⁺) revealed that measurements of denitrification with the acetylene block method systematically underestimated actual rates. Rates of N loss in denitrification were similar to NH₄⁺ recycling fluxes to the overlying water in spring and fall, but in summer negligible denitrification contributed to enhanced NH₄⁺ recycling. These results suggest that inhibition of denitrification in eutrophic estuaries such as Chesapeake Bay may reinforce the effects of nutrient enrichment by allowing increased rates of NH₄⁺ recycling.

Nitrogen cycling in coastal marine sediments has been studied widely in the last decade both in terms of constituent biogeochemical processes and influence on primary production (Nixon 1981). In most coastal environments the vast majority of the recycled N released from sediments to water is in the form of NH₄⁺. This NH₄⁺ is regenerated by the decomposition and denitrification-denitrification represents a sink that shunts N away from recycling pathways (Jenkins and Kemp 1984). These coupled processes are quantitatively important in the N budgets of continental shelf sediments (Christensen et al. 1987) and of estuaries, where N losses via denitrification may account for half of the terrestrial inputs (Seitzinger 1988).

Seasonal cycles of either sediment nitrification or denitrification have been de-
scribed for a few marine systems, with two general patterns predominating. In one case, rates follow the annual temperature cycle, while the other pattern is characterized by a midsummer depression of these processes (Hansen et al. 1981; Seitzinger et al. 1984). Various evidence suggests that, in many coastal environments, seasonal trends of denitrification are determined largely by NO$_3^-$ availability (Koike and Sørensen 1988), which, itself, tends to be controlled by rates of nitrification (Henriksen and Kemp 1988). Thus, coherent temporal trends of nitrification and denitrification would be expected in most coastal sediments. Few contemporaneous measurements of the two processes are available, however, over an annual cycle.

Sediment nitrification rates are regulated generally by availabilities of O$_2$ or NH$_4^+$ (Henriksen and Kemp 1988). Because NH$_4^+$ regeneration rates and pore-water concentrations tend to increase with temperature (Nixon 1981), the pronounced summer nitrification maxima that have been reported for several sites might result from seasonal cycles of NH$_4^+$ availability. This mechanism would also explain reports of direct correlations between NH$_4^+$ regeneration and denitrification among sites (Kemp et al. 1982) and along an experimental eutrophication gradient (Kelly et al. 1985; Seitzinger and Nixon 1985). Ultimately, however, the depth of O$_2$ penetration defines the sediment zone in which nitrification can occur (Henriksen and Kemp 1988). The dimensions of this oxygenated zone are inversely related to sediment O$_2$ consumption rates (Jørgensen and Revsbech 1985) and are directly affected by burrowing and irrigation by benthic macrofauna (Henriksen et al. 1983). Thus, the observed summer depressions in nitrification (and, consequently, denitrification) may be explained by seasonal declines in O$_2$ penetration into sediments arising from increased temperature or organic inputs or from decreased macrofaunal activity.

In coastal marine systems, such as Chesapeake Bay, which experience summertime anoxia in bottom waters, a temporary loss of nitrification and denitrification would be expected. Jenkins and Kemp (1984), however, observed that nitrification and denitrification were virtually eliminated during summer in a large tributary of Chesapeake Bay, even for stations that did not undergo bottom-water O$_2$ depletion. In addition, denitrification capacity was also relatively reduced after fall turnover at deep, seasonally anoxic stations in this estuary (Twilley and Kemp 1986).

In the present paper, we describe contemporaneous measurements of nitrification, denitrification, and net fluxes of N across the sediment–water interface along a depth transect in the midsalinity region of Chesapeake Bay. We interpret these results to address the following: spatial and temporal variability of rates; factors regulating rates; and, relative balance among key sediment N transformations and particularly between NH$_4^+$ and N$_2$ fluxes across the sediment–water interface.

Methods
Two sampling stations were established along an east–west transect in the mesohaline region of Chesapeake Bay at 38°28.0’N (see Malone et al. 1986). During 1986 these stations were occupied approximately weekly from late March through early May and again in August; in 1987 stations were visited at 2–3-week intervals during the same spring and summer periods and on one occasion in November. The deeper of these two stations (Sta. 3, located in the center channel with a MLW depth of 20 m) experienced continual anoxia in its bottom waters from June to August, while at the other (Sta. 2, located on the western flank with a depth of 9 m) periodic hypoxic conditions (<2 mg O$_2$ liter$^{-1}$) occurred throughout summer (Malone et al. 1986; Boynton et al. 1988). In July 1987 three additional stations, which rarely experience hypoxic conditions, were also sampled (Sta. 0, 1a, and 1b at depths of 1.5, 4.3, and 6.4 m).

On each sampling date vertical water-column profiles of temperature, salinity, and dissolved O$_2$ concentration were obtained at 2-m intervals with a Hydrolab monitoring system with thermostor, induction salinometer, and polarographic electrode. Bottom-water (1 m above sediment surface) samples were obtained with a high-volume,
served to be zero. We refer to these measured rates as "net nitrification," to indicate that they represent the net sum of nitrification minus NO_3^- ammonification (NO_3^- reduction to NH_4^+, Koike and Sørensen 1988). This term is used because a portion of the NH_4^+ accumulated in the control cores will have been produced via NO_3^- reduction.

Denitrification rates were measured as nitrous oxide production in cores treated with acetylene to block reduction of N_2O to N_2 gas (Sørensen 1978). Replicate intact cores were collected in acrylic liners (as described above for nitrification). Sediments in cores were injected with C_2H_2-saturated seawater (100 µl total) along side ports (at 0.5-cm intervals), and overlying water was replaced with filtered, C_2H_2-amended bottom water to produce final aqueous concentrations of ~10%. Cores (with 10–15 ml of airspace) were sealed and incubated in darkness at ambient temperature, with their water columns stirred by small, suspended magnets. Duplicate cores were sacrificed at 0, 2, 4, and 6 h for analysis of N_2O. Cores were
shaken vigorously for 1–2 min to mix overlying and pore-water N$_2$O, and, after brief (2 min) equilibration, headspace gas was sampled (4 ml) and stored in evacuated vials for subsequent analysis (Christensen et al. 1989). N$_2$O concentrations were measured with a Hewlett-Packard gas chromatograph equipped with a 2-m Porapak Q column and $^{63}$Ni electron capture detector.

Potential rates of nitrification were estimated by the method of Henriksen et al. (1981), where aliquots (2–3 g) of wet sediment were weighed into replicate 125-ml Erlenmeyer flasks containing 50 ml of O$_2$-saturated, ambient water amended to 1.0 mM NH$_4^+$+. The flasks were incubated in darkness at 25°C on a rotary shaker table and sacrificed in duplicate at 0, 12, and 24 h, at which point water was sampled, filtered, and frozen for NO$_3^-$ analysis. Potential rates of denitrification (Christensen et al. 1989) were also measured with the same proportions of water and sediments as for nitrification above, but with deoxygenated water amended with C$_2$H$_2$ (10%) and NO$_3^-$ (0.5 mM). In this case incubations were conducted for 6 h, after which headspace gas was sampled (4 ml of gas) into vials for later analysis of N$_2$O.

Vertical profiles of NH$_4^+$ and NO$_3^-$ in sediment pore waters were measured with intact sediments subsampled from the box cores with acrylic core liners (7.5-cm o.d., 30 cm long). Sediment sections (~20 g) were extruded, sliced at 0.5–2-cm intervals, homogenized, and packed into 50-ml plastic centrifuge tubes. In most cases nutrients were extracted by adding 20 ml of 2 N KCl solution, shaking for 10 min followed by centrifugation at 10,000 $\times$ g for 5 min, with supernatant being decanted, filtered, and frozen. On selected occasions unamended pore waters were extracted by centrifugation.

Redox potential of sediment pore waters was estimated with a platinum wire electrode inserted into intact sediments (within 1–2 h of collection) through ports at 1-cm intervals along a core liner. The platinum electrode, which was coupled to a Beckman pH meter, was calibrated with a standard ZoBell’s solution.

Macrofaunal abundance was estimated by sieving three replicate box cores (135 cm$^2$) through 0.5-mm mesh cores on shipboard, staining with Rose Bengal, and preserving with 10% Formalin for subsequent sorting. Specimens in each sample were identified, counted, dried, and weighed (Kemp and Boynton 1981).

**Results and discussion**

**Spatial and temporal patterns**—During this study period, bottom-water temperatures at stations 2 (9 m) and 3 (20 m) varied from 6°C in early spring to 26°C in midsummer. Concentrations of O$_2$ during the same period ranged from 400 to 3 μM, with hypoxia (<60 μM) observed at station 2 on two occasions in July, and anoxic bottom water occurring periodically throughout summer at station 3. Nutrient concentrations in bottom waters at these stations also exhibited clear seasonality; NH$_4^+$ concentrations ranged from 1 μM in April to 30 μM in August, while NO$_3^-$ varied from 85 μM to <1 μM during the same interval, with peak fall concentrations of both N species approaching 25 μM. Bottom-water NO$_3^-$ concentrations declined continually between April and June at a mean rate of ~0.1–0.5 μM d$^{-1}$. These seasonal ranges are similar to those previously reported for this region of Chesapeake Bay (e.g. Boynton and Kemp 1985; Malone et al. 1986).

Net fluxes of NH$_4^+$ and NO$_3^-$ exhibited distinctly different seasonal patterns at station 2 from late March to mid-November (Fig. 1a). Rates of NH$_4^+$ release from sediments were highest in summer, with a rapid increase occurring during vernal warming in May. NH$_4^+$ fluxes at station 3 (not shown) followed a comparable temporal sequence but with a wider range of rates from 46 μmol m$^{-2}$ h$^{-1}$ in April to 753 in August. These rates and seasonal trends are similar to those described for several other coastal sediments (Boynton et al. 1979; Nixon 1981; Hopkinson 1987). Net exchanges of NO$_3^-$ at stations 2 (Fig. 1a) and 3 (not shown) were directed into the sediments (negative rates) throughout spring, with highest rates in mid-May; rates were zero in summer and slightly positive (from sediments to water) in fall. Although NO$_3^-$ fluxes ($Y$) were inversely correlated with NO$_3^-$ concentrations ($X$) in
Sediment nitrogen cycling

**a) Sediment-Water Fluxes**

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Month of Year
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N Flux, µmol m⁻² h⁻¹
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Ammonium

Nitrate

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Month of Year
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The bottom water, the strength of the relation here \( Y = 6.3 - 1.7 X, r = 0.48 \) was much poorer than described previously for the Patuxent estuary (Boynton et al. 1979). This seasonal trend is markedly different from those reported for several other systems, where net fluxes of \( \text{NO}_3^- \) were generally directed out from sediments with highest rates in summer (Nixon 1981; Hopkinsinson 1987).

Rates of both net nitrification (nitrification minus \( \text{NO}_3^- \) ammonification, see methods) and denitrification at stations 2 (Fig. 1b) and 3 (Table 1) were relatively high in early spring and late fall and negligible in summer. Highest rates (70.4 and 26.2 µmol m⁻² h⁻¹, respectively) were measured in November, with values in April being 30–50% lower, and summer rates generally zero. The range of nitrification values measured here is similar to, but slightly lower than, that reported for other coastal areas (Henriksen and Kemp 1988). A summer depression of nitrification rates has also been observed for sites elsewhere in Chesapeake Bay (Jenkins and Kemp 1984) and in other
Table 1. Nitrification and denitrification rate (µmol m⁻² h⁻¹) measurements for sediments in the mesohaline region of Chesapeake Bay (n = 3 for each date; ND—experiments not conducted).

<table>
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<th>Sta. 2</th>
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<td></td>
<td></td>
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<tr>
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<td>3.12±0.10</td>
<td>17.8</td>
<td>0.94</td>
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<td>(0.10)</td>
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<td>70.4</td>
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<td>0.48±0.25</td>
<td>26.2</td>
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<td>[NH₄⁺]</td>
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<td>control</td>
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<tr>
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<td>4.62±0.79</td>
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<td>ND</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>22 May</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>(0.2)</td>
<td>(0.10)</td>
<td></td>
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<tr>
<td></td>
<td>6 Nov</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>16.2</td>
<td>0.86</td>
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*Replicate cores incubated for 36–72 h, half being injected with N-serve (to block nitrification) and half as controls. NH₄⁺ concentrations include that in pore water of 0–1 cm (or 0–2 cm) sediment depth and/or water overlying sediment surface; values noted by asterisk are for overlying water only. Nitrification rates given are those where NH₄⁺ concentrations were significantly (P < 0.05) different between control and treated cores; otherwise, rates are assumed to be zero. Given are means ± SE.

†Rates estimated as accumulation of N₂O over time for cores injected with C₂H₂ (to block N₂O reduction). Coefficient of explanation (r²) given for [N₂O] vs. time; values in parentheses are not statistically significant.

regions of the world (Hansen et al. 1981; Seitzinger et al. 1984; Seitzinger 1988). Although previous investigators have also reported summer reductions in denitrification (Seitzinger et al. 1984), overall rates at these Chesapeake Bay stations were substantially lower than most of those measured for other marine sediments (Koike and Sørensen 1988; Seitzinger 1988).

Vertical profiles of NH₄⁺ in pore waters at stations 2 and 3 in 1986 (Fig. 2) followed normal trends of increasing concentration with depth in sediments (Boynton and Kemp 1985). Patterns observed in 1987 (not shown) were essentially identical to these. As observed previously (Rosenfeld 1979), NH₄⁺ concentrations extracted with KCl (Y) were highly correlated with ambient pore water (X) in parallel cores (Y = −53.8 + 2.0 X, r = 0.92). At station 2 most of the increase in concentration with depth occurred in the upper 1 cm; this pattern also held for station 3 in August but not for April, May, and November. Concentration below 5-cm depth increased with temperature at both stations, which is consistent with the seasonal increase in NH₄⁺ fluxes to the overlying water (Fig. 1). Marked seasonal variations in pore-water NH₄⁺ pools have been reported for other estuaries (e.g. Watson et al. 1985), but few were as pronounced as those seen here. Vertical and seasonal distributions of redox potential were generally inverse of those for NH₄⁺, declining rapidly between the sediment surface and 2-cm depth and decreasing with increasing temperature (Fig. 2).

Pore-water NO₃⁻ concentrations were negligible below 2-cm depth, and vertical distributions fell into one of three patterns in the upper sediments at these stations (Fig. 3). In spring, and particularly in April at
Sediment nitrogen cycling

**Sta. 2**

**Eh, 10^2 mV**

**NH₄⁺, mM**

**Sta. 3**

Depth (cm)

Depth (cm)

AUG

APR

MAY

AUG

APR

MAY

NOV
station 2 and May at station 3, relatively high concentrations in the overlying water exhibited exponential decrease with depth. This pattern is similar to the NO$_3^-$ distributions described by Billen (1977) for muddy North Sea sediments. NO$_3^-$ was virtually absent from pore and overlying waters at both stations in August. In fall samples at both stations, subsurface NO$_3^-$ maxima were evident, with surficial pore-water concentrations greatly exceeding those in the water column. These NO$_3^-$ distributions, which have been observed for many other marine sediments (e.g. Hopkinson 1987), result from nitrifying activity being concentrated in the NH$_4^+$-rich region near the bottom of the oxygenated zone of sediments (Henriksen and Kemp 1988). Decreasing NO$_3^-$ concentrations above and below this maximum result from vertical diffusion and microbial reduction.

Nitrification potential, which provides an index of nitrifying bacterial densities in natural sediments (Henriksen and Kemp 1988), exhibited consistent vertical distributions, with highest values in surface sediment and relatively low variance at each station depth (Fig. 4). At station 2 in spring and fall, nitrification potentials were 3-4 times higher in surficial (0-0.5 cm) compared to deeper (2-4 cm) sediments. Values in summer, while still significant, were greatly reduced relative to those in the other two seasons (Fig. 4a). Surficial potentials in spring at station 3 were comparable to those at station 2, while values in the 2-4 cm stratum were zero at the deeper station (Fig. 4a). Although summer rates were negligible at station 3, there was some recovery in surface sediments by November. Similar depth profiles of nitrification potential have been observed for other marine sites (Henriksen and Kemp 1988). The presence of nitrifying bacteria at depths into anaerobic sediments well below the zone into which O$_2$ can penetrate is attributable to macrofaunal irrigation of sediments, as well as to vertical mixing of sediments by physical resuspension and bioturbation (Henriksen et al. 1981).

Vertical patterns of nitrification potential in summer varied markedly along a shore-normal transect, with water-column depths (MLW) ranging from 1.5 to 20 m (Fig. 4b). At the three intermediate depths (4.5-9 m), where sediments graded from muddy sands to sandy muds, potential rates and profiles were comparable. Values at both the deepest and shallowest sites were, however, negligible. At the shallow end this result is probably attributable to the low organic content (and associated low NH$_4^+$ concentrations) of the sandy sediments, while anoxic conditions at the deep end (Sta. 3) account for the absence of nitrifiers.

In contrast to these patterns for nitrification, vertical distributions of denitrification potential (0-4 cm) were generally constant with depth, where rates ranged from 3 to 6 nmol N g$^{-1}$ h$^{-1}$ (data not shown). Overall, there was little evidence of site-to-site or seasonal variations in denitrification potentials in surface sediments. Previous studies of denitrification potentials have reported distinct vertical profiles and widely varying geographic distributions of rates (Kaspar 1982; Twilley and Kemp 1986).

Values measured in the present study for fall at station 3 are consistent with those reported earlier, which were among the lowest observed in a survey of 10 stations in Chesapeake Bay and its tributary estuaries (Twilley and Kemp 1986).

Factors regulating N cycling—The flux of NH$_4^+$ from sediments to overlying water at stations 2 and 3 exhibited strong positive responses to increasing temperature from early spring through midsummer. As reported previously by Nixon (1981) and others, these relations are described well by exponential equations ($r = 0.96$ and 0.90, respectively, for Sta. 2 and 3). It appears that the slopes of the curves for these sites (and especially Sta. 3) are substantially steeper than reported for other estuaries (Nixon 1981; Hopkinson 1987). The relatively high rates of NH$_4^+$ recycling at high temperatures may be attributable in part to the decline in nitrification and denitrification (and associated N$_2$ loss) during summer at these mesohaline Chesapeake Bay sites. Although nitrification ($Y$) followed an inverse function of temperature ($X$) at station 2 ($Y = 64.9 - 2.46X$, $r = 0.93$), this correlation undoubtedly results from the inverse covariance of temperature and oxygen.
Fig. 3. Vertical profiles of NO$_3^-$ concentration in pore waters at stations 2 and 3 in April and May (a, b) and August and November (c, d) 1987. Note change of scale between upper and lower panels.
a) Temporal Pattern (Sta. 2 and 3)

Nitrification Potential, nmol g\(^{-1}\)h\(^{-1}\)

![Graphs showing temporal pattern of nitrification potential for April, August, and November.]

b) Spatial Pattern (July)

Nitrification Potential, nmol g\(^{-1}\)h\(^{-1}\)

![Graphs showing spatial pattern along 38°28.0’N running westward from the main Chesapeake Bay channel (Sta. 3) to the shoal area (Sta. 0).]

Fig. 4. Vertical profiles of nitrification potential. a. Temporal pattern for April, August, and November. b. Spatial pattern along 38°28.0’N running westward from the main Chesapeake Bay channel (Sta. 3) to the shoal area (Sta. 0). Note that variances in these rates were relatively low, with standard errors ranging from 5 to 10% of means.

Between net nitrification rates and bottom-water \(O_2\) concentration, we find a strong positive correlation for spring and summer data at station 2 (Fig. 5a). Although it can be safely assumed that nitrification at station 3 was zero under anoxia, summertime rates were measured only twice at this site. At comparable \(O_2\) levels, net nitrification was generally higher at station 3 compared to station 2. Rates at station 2 in the fall were also substantially greater than would be expected from its summer correlation, suggesting that factors other than bottom-water \(O_2\) concentration contributed to the
relatively lower nitrification in spring and summer. The correlation of oxygen and nitrifying activity for station 2 during this period (Fig. 5a) is characterized by a positive x-intercept of 41 μM, and rates were negligible at bottom-water O$_2$ concentrations <125 μM. This result is surprising because nitrifying bacteria are generally considered microaerophilic (Henriksen and Kemp 1988). Evidently, sediment O$_2$ consumption rates were high enough in summer to completely preclude O$_2$ diffusion into sediments under hypoxic conditions.

The mean depth of O$_2$ penetration into sediments can be estimated from the strong positive correlation found between potential and actual rates of net nitrification at station 2, where potential rates were measured in the 0–1-cm stratum (Fig. 6). The existence of relations such as that in Fig. 6 suggests that the abundance of nitrifying bacteria in surficial sediments is closely tied
to availability of suitable growth conditions and that mortality leads to reduced populations under unfavorable situations. Henriksen et al. (1981) measured nitrification potentials in surficial sediments and applied corrections for temperature and vertical depth of O2 penetration to develop a set of predicted ambient nitrification rates which corresponded closely to measured values.

If oxygen was the principal factor limiting nitrification rates per square meter (Henriksen and Kemp 1988), then the depth over which "nitrification potentials" were realized would be the mean depth to which O2 penetrates the sediments. Therefore, the slope of the equation in Fig. 6 (0.75 mm) represents a crude estimate of the mean depth of O2 penetration into the sediments. This value, which corresponds closely to direct measurements with polarographic O2 microelectrodes (J. Caffrey unpubl. data) in late spring, is substantially lower than those depths (2–6 mm) reported for Danish coastal sediments in summer and fall (Henriksen et al. 1981). The decrease in nitrification observed at station 2 with declining O2 in the overlying water (Fig. 5a) may indicate an effect of reduced O2 diffusion into the sediments. In addition, the relatively high rates of O2 consumption in these Chesapeake Bay sediments, compared to those in Danish coastal regions (Henriksen and Kemp 1988), contribute to a relatively small surficial layer in which nitrification can occur. Thus, the dramatic reduction in nitrification rates during summer may be largely attributable to a thinning of the surficial oxidized zone of sediments.

Redox potential in sediments, which provides an index of heterotrophic metabolic activity, was positively correlated (at 0–1-cm depth) with nitrification rates for the five dates when both were measured at station 2 (Fig. 5b). Rates were zero at redox levels of −200 mV. Jenkins and Kemp (1984) previously reported negligible rates of coupled nitrification-denitrification at similar sediment redox levels for two Chesapeake Bay sites in August, even though O2 concentrations were >94 μM in overlying water. Although Billen (1976) found no nitrification in river water when redox fell below +200 mV, significant rates were observed for sediments at station 2 when redox values were between −100 and 0 mV (Fig. 5b). In coastal marine sediments Eh is controlled largely by sulfide concentration (Fenchel 1969), so that the loss of nitrification at low redox values may also be related to high sulfide levels. H2S concentrations at stations 2 and 3 ranged from 0.01 to 1.0 mM in sediment (0–2 cm) pore waters (P. Sampou et al. unpubl.), levels high enough to significantly reduce the activity of nitrifying bacteria (Henriksen and Kemp 1988).

Indirect evidence has led several previous investigators to conclude that denitrification in marine sediments was limited by availability of NO3− (Koike and Sørensen 1988). Such inferences have been based either on the stimulation of rates by NO3− additions (Jenkins and Kemp 1984) or on the fact that pore-water NO3− concentrations were below presumed kinetic saturation values (Kaspar 1982). In addition, denitrification rates have been directly correlated with NO3− concentrations in the overlying water for several coastal regions (Smith et al. 1985; Twilley and Kemp unpubl.). In the present study we found only weak correlations between denitrification rates (Y, μmol m−2 h−1) and NO3− levels (X, μM) either in pore water (Y = 4.68 + 0.33 X, r = 0.42) or overlying water (Y = 7.87 + 0.15 X, r = 0.19). We did, however, observe a statistically significant relation between denitrification and nitrification rates (Fig. 7), illustrating directly the dependence
Sediment nitrogen cycling

40

Denitrification

Fig. 7. Relation between nitrification (N-serve inhibition) and denitrification (acetylene block) rates for sediments at station 2.

of the former process on NO₃⁻ produced by the latter.

Strong seasonal patterns in macrofaunal community structure were evident for stations 2 and 3 during this study (Table 2). Maxima for macrofaunal abundance and biomass occurred in spring at both stations; benthic populations in summer were eliminated at the deeper station and underwent a 60% reduction at station 2. Benthic macrofauna continued to decline into fall at station 2, while recovering to some extent at station 3. Spionid polychaetes (primarily Streblospio benedicti, Scolecolepides viridis, and Paraprionospio pinnata) dominated macrofauna at both stations and were largely responsible for the fall recovery at station 3. The larger polychaete, Nereis succinea, was also important in spring. Small molluscs (Macoma balthica, Macoma mitchelli, and Mulinia lateralis) were also relatively abundant, especially at station 2. These annual trends in abundance and community composition are similar to previous reports for this region, where peak abundance is typically observed in June followed by a precipitous decline even at stations in shallow (3 m) water depths (Kemp and Boynton 1981; Holland 1985).

In general, the summer decline in macrofaunal densities coincided with the decreases in nitrification and denitrification in this period (Tables 1 and 2). In fact, we found a significant correlation between net nitrification (Y) and total macrofaunal abundance at station 2. This correlation was not present at station 3, where nitrification and denitrification rates were similar. The data suggest that the seasonal changes in macrofaunal abundance are influenced by changes in the nitrogen cycle, particularly the rate of denitrification.

Table 2. Benthic macrofaunal abundances (No. × 10⁳ m⁻²) and biomasses (g dw m⁻²) at Sta. 2 and 3 for selected sampling dates (means ± 1 SE).

<table>
<thead>
<tr>
<th>Organisms</th>
<th>Sta. 2 Abundance</th>
<th>Sta. 2 Biomass</th>
<th>Sta. 3 Abundance</th>
<th>Sta. 3 Biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>April</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spionidae</td>
<td>1.75 ± 0.73</td>
<td>0.85</td>
<td>4.53 ± 1.53</td>
<td>1.63</td>
</tr>
<tr>
<td>Nereidae</td>
<td>0.17 ± 0.15</td>
<td>3.99</td>
<td>0.44 ± 0.21</td>
<td>1.56</td>
</tr>
<tr>
<td>Other annelids</td>
<td>0.09 ± 0.04</td>
<td>0.17</td>
<td>0.44 ± 0.15</td>
<td>0.32</td>
</tr>
<tr>
<td>Molluscs</td>
<td>1.61 ± 0.36</td>
<td>1.22</td>
<td>0.20 ± 0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>Amphipods</td>
<td>0</td>
<td>0</td>
<td>0.70 ± 0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>3.65 ± 0.80</td>
<td>6.23</td>
<td>5.69 ± 1.39</td>
<td>3.60</td>
</tr>
<tr>
<td>May</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spionidae</td>
<td>2.73 ± 1.24</td>
<td>1.00</td>
<td>3.99 ± 3.19</td>
<td>1.12</td>
</tr>
<tr>
<td>Nereidae</td>
<td>0.27 ± 0.22</td>
<td>4.36</td>
<td>0.24 ± 0.08</td>
<td>1.68</td>
</tr>
<tr>
<td>Other annelids</td>
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<td>0.17</td>
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<tr>
<td>Molluscs</td>
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<td>0.05 ± 0.08</td>
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<tr>
<td>Amphipods</td>
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<td>0.05</td>
<td>0.15 ± 0.15</td>
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</tr>
<tr>
<td>Total</td>
<td>3.87 ± 1.44</td>
<td>6.31</td>
<td>4.55 ± 3.21</td>
<td>3.04</td>
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</tr>
<tr>
<td>Spionidae</td>
<td>1.44 ± 0.47</td>
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<tr>
<td>Nereidae</td>
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<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Other annelids</td>
<td>0.12 ± 0.04</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Molluscs</td>
<td>0.09 ± 0.08</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Amphipods</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>1.68 ± 0.46</td>
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<td>0</td>
<td>0</td>
</tr>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.01</td>
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<td>0</td>
<td>0.01</td>
<td>0</td>
</tr>
<tr>
<td>Molluscs</td>
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<td>0.12</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>Amphipods</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Total</td>
<td>0.76</td>
<td>0.77</td>
<td>0.43</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Unpublished data provided by F. Holland and A. Shaughnessy.
dance ($Y$) for station 2 ($Y = 11.3 \times X - 7.0$, $r = 0.87$). Previous studies have demonstrated the tendency for enhanced activities of nitrifying and denitrifying bacteria to occur in association with macrofaunal irrigation of burrows (Henriksen et al. 1983; Kristensen et al. 1985). It is unclear to what extent these summer declines in nitrification and denitrification might be attributable to reductions in macrofaunal populations. It is likely, however, that the same factors—depletion of bottom water $O_2$ and accumulation of sulfide—may have contributed to both mortality of macrofauna and reduction of nitrification.

The seasonal contributions of macrofaunal populations to sediment budgets can be estimated using these biomass data in conjunction with literature reports of tissue composition and excretion rates. The mean net rate of incorporation of $N$ into macrofaunal tissue from November to April was calculated to be almost 0.5 mmol N m$^{-2}$ d$^{-1}$ at station 2, based on the observed increase in animal biomass (Table 2) and assuming a mean body tissue $N$ content at 10% of dry weight (Jørgensen 1979). If we used typical rates of $N$ excretion from marine polychaetes and bivalves [30–80 µmol (g dw)$^{-1}$ d$^{-1}$, Blackburn and Henriksen 1983], direct NH$_4^+$ production from macrofaunal metabolism would have ranged from 0.5 mmol m$^{-2}$ d$^{-1}$ in April to 0.2 in August at station 2, representing 33 and 10%, respectively, of the rates of NH$_4^+$ efflux from sediments to overlying water.

**Seasonal balance of $N$—A conceptual model of $N$ pools, transformations, and sediment–water fluxes** (Fig. 8) for the coastal sediments examined in this study provides a framework for quantitative comparisons among key rates in the $N$-cycling network. In this simplified system we consider six sediment $N$ pools, four of which have been described here with direct measurements. Of the five $N$ fluxes between sediments and overlying water, three have been measured directly in this or related studies (solid lines, Fig. 8). Similarly, data are also available to directly calculate three of six aggregated $N$ transformations. First-order approximations are developed for most (but not all) of the remaining unmeasured rates by considering observed changes in sediment $N$ pools or assuming steady state conditions, where appropriate (Table 3).

Although methodological uncertainties complicate interpretations, the fact that estimates of all of the major internal $N$ transformations were based on contemporaneous measurements on the same sediments renders them generally comparable (Table 3). In addition, measurements of net nitrification form an integral part of the estimates of the other two processes, where net ammonification is taken as NH$_4^+$ efflux plus net nitrification and changes in the pore-water NH$_4^+$ pool, while denitrification (by "NO$_3^-$-balance") is taken as net nitrification minus NO$_3^-$ efflux.

There is reason to believe that the direct measurements of denitrification using C$_2$H$_2$ blockage (Table 1) seriously underestimated actual rates here. The slope of the equation for Fig. 7 indicates that denitrification (C$_2$H$_2$ block) accounted for only 36% of the total NO$_3^-$ generated by net nitrification. In addition, the substantial rates of NO$_3^-$ diffusion from overlying water into the sediments measured during spring (Fig. 1) further increase the unaccounted portion of total NO$_3^-$ loss. H$_2$S can alleviate the blocking effect of C$_2$H$_2$ (Tam and Knowles 1979), which leads to an underestimate of actual rates. High summertime sulfide concentrations (1 mM) in surficial (0–1 cm) pore waters at our study sites may have made the C$_2$H$_2$ block ineffective during our summer measurements. Sulfide was not, however, present in surficial pore waters during spring and fall.

Under low concentrations of NO$_3^-$ (<1.0 µM), significant bacterial consumption of N$_2$O can also lead to underestimates of actual denitrification with the C$_2$H$_2$ block method (Koike and Sørensen 1988). At our study sites, NO$_3^-$ levels in surficial (0–1 cm) pore waters varied from zero in summer to >20 µM in spring and fall (Fig. 3). Kristensen et al. (1989) have recently demonstrated that even at higher NO$_3^-$ levels, conventional C$_2$H$_2$ block methods may underestimate N$_2$O produced, because of N$_2$O diffusion into regions of the sediment where NO$_3^-$ is absent. Because the rate of N$_2$O diffusion would be a direct function of
denitrification rate, this source of error would probably lead to a systematic underestimate of denitrification with the C\textsubscript{2}H\textsubscript{2} block method. The significant correlation between nitrification and denitrification measurements observed in this study (Fig. 3) further suggests a systematic error. Thus, we conclude that our measurements of denitrification with the C\textsubscript{2}H\textsubscript{2} block method probably represent consistent underestimates of actual rates.

We have also calculated denitrification rates by an alternative method, assuming a steady state balance in pools of pore-water NO\textsubscript{3}\textsuperscript{-}. It can be seen from pore-water NO\textsubscript{3}\textsuperscript{-} profiles (Fig. 3) that seasonal rates of change in these sediment NO\textsubscript{3}\textsuperscript{-} pools were relatively small compared to rates of net nitrification or NO\textsubscript{3}\textsuperscript{-} flux across the sediment surface (Fig. 1). For example, maximal pore-water NO\textsubscript{3}\textsuperscript{-} pools occurring in April and November in the upper 3 cm of sediments were 0.3–0.4 mmol m\textsuperscript{-2}. If we assume that the near-zero NO\textsubscript{3}\textsuperscript{-} concentrations measured in August prevailed for the entire period from June through September, then mean rates of net NO\textsubscript{3}\textsuperscript{-} loss and gain associated with this reduction (from April to June) and subsequent accumulation (from September to November) in pore-water pools would be <0.005 mmol m\textsuperscript{-2} d\textsuperscript{-1}. Thus, because the N-serve inhibition rates (Table 1) represent net nitrification (including NO\textsubscript{3}\textsuperscript{-} reduction to NH\textsubscript{4}\textsuperscript{+}), denitrification can be estimated as the algebraic sum of the N-serve rate plus ambient NO\textsubscript{3}\textsuperscript{-} flux across the sediment–water interface. Denitrification rates calculated by this "NO\textsubscript{3}\textsuperscript{-} balance" were 2–7 times higher than those measured by C\textsubscript{2}H\textsubscript{2} blockage in spring and fall (Table 3). Previous reports indicate that the relative proportion of total NO\textsubscript{3}\textsuperscript{-} reduction that goes to NH\textsubscript{4}\textsuperscript{+} (vs. N\textsubscript{2} or N\textsubscript{2}O) ranges from 20 to 60% for marine sediments (Enoksson and Samuelsson 1987; Koike and S\Orensen 1988). This implies that actual nitrification
rates were considerably greater than the net rates estimated by N-serve inhibition.

Although all of the fluxes and changes in N pools summarized in Table 3 are based on observations in the same region of the estuary, these rates were estimated from a wide range of measurement methods in which rates were averaged over various time scales. Thus, all of these rates are not strictly comparable. Specifically, burial represents a mean rate over a decade or more, while rates for PON deposition and changes in N pool sizes are averaged over weeks, and N effluxes are measured over hours. The objective of this table is not to obtain closure for a sediment N budget, but rather to provide a framework for examining the relative magnitudes of these processes.

Although dissolved organic N (DON) compounds and their associated pools, fluxes, and transformations may be important in these sediment systems (e.g. Burdige and Martens 1988), currently no data are available to allow inclusion in this analysis. Data are available for particulate organic N (PON) and associated rates of deposition, burial, and changes in surficial (0–1 cm) sediment pools from a companion research project conducted contemporaneously at the same study sites (Boynton et al. 1988). Here PON deposition was measured via 4–7-d deployments of sediment traps positioned at the top of the pycnocline; a cylindrical trap design was used (ht: diam of 10) to maximize collection efficiency (Gardner 1980). Although such sediment trap systems have been criticized for potential biases due to hydrodynamic variabilities (e.g. Butman et al. 1986), they have been widely used as coastal marine research tools (Smetacek 1984), and rates measured here compare well with other independent estimates of particulate organic deposition (Malone et al. 1986; Boynton et al. 1988). PON burial and changes in pool size are calculated from biweekly observations on profiles of sediment PON (Boynton et al. 1988) combined with extensive analyses of sediment accretion with 210Pb dating (Nixon 1987). Overall, mean rates of N burial (Table 3) con-
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constituted a relatively small fraction (15–25%) of PON deposition to sediments in this region, consistent with previous calculations for the entire Chesapeake Bay (Nixon 1987). During all three seasons summarized in Table 3, the major pathway of N input to the sediments was via PON deposition, while N losses were distributed more equitably over several processes. In August, however, NH$_4^+$ efflux from sediments to overlying water actually exceeded PON inputs, leading to a net deficit in the sum of N fluxes listed in the table. The predominant species of N efflux from sediments was in the form of N$_2$ in spring and fall and NH$_4^+$ in summer. In this sediment system, changes in N pools (PON, NH$_4^+$, and macrofauna), although never dominant, always constituted substantial rates in the overall N cycle. In fact, during April when each of these sediment N pools was decreasing, the sum of the three terms composed more than a third of PON input. It is evident, then, that the common practice of ignoring changes in storage when constructing sediment N budgets (e.g. Billen 1977) may be misleading. There are numerous processes not included in this analysis which might have had significant impact on monthly N budgets at this station. They include dissolved organic N fluxes and pool-size changes, horizontal transport of PON, and grazing by demersal nekton. Mismatch in time scales over which these rates were averaged and the propagation of uncertainties associated with the sum of these rates (Table 3) precludes, however, any speculation on the potential magnitude of missing terms in the budget.

Conclusions and implications

In spring and fall when measurable rates occurred in these sediments, nitrification was clearly a pivotal component of the N cycle, with net rates approximating those for ammonification (Table 3). Similarly, losses of N$_2$ gas via denitrification, although negligible in August, were of the same order as rates of NH$_4^+$ recycling in April and November. The ratios of N$_2$ to NH$_4^+$ fluxes across the sediment–water interface estimated for spring and fall at this site therefore approach 1.0, consistent with the annual pattern reported for other coastal marine sediments (Seitzinger 1988). What is unique about this Chesapeake Bay site is the absence of denitrification in summer and the concomitantly high rates of NH$_4^+$ recycling that result.

Mesocosm experiments at the MERL facility in Narragansett Bay have demonstrated that, in eutrophic marine systems, sediment denitrification is capable of removing a substantial portion of the excess N loading (Seitzinger and Nixon 1985). Denitrification rates increased with higher N loading to the experimental systems, but the ratio of N$_2$ to NH$_4^+$ fluxes to overlying water decreased with increased nutrient inputs (Kelley et al. 1985), indicating a declining role of denitrification relative to other N-cycling processes.

Conditions for denitrification in the mesohaline region of Chesapeake Bay are evidently more severe than those at the upper end of the simulated eutrophication gradient at MERL. This difference is probably attributable to the vertically mixed water column of the MERL compared to the stratified conditions in Chesapeake Bay. Estimated annual mean denitrification rates at this Chesapeake Bay site (0.8 mmol N m$^{-2}$ d$^{-1}$) were low relative to those reported for other coastal regions and were less than half those in the Narragansett Bay sediments that served as MERL “controls.” Recent evidence suggests that biological and chemical processes in this portion of Chesapeake Bay have undergone significant changes as a result of eutrophication, with decreased concentrations of O$_2$ and increased concentrations of sulfide in bottom waters and sediment pore waters (Officer et al. 1984).

These results suggest an ironic sequence of interactions. It is clear that coupled nitrification-denitrification can lead to removal of a substantial portion of the N inputs to coastal marine systems (Smith et al. 1985; Seitzinger 1988), thereby representing a natural mechanism for partial buffering against the global trend of coastal eutrophication. For some estuaries such as Chesapeake Bay, the increased production and consumption of organic matter associated with eutrophication may, however, lead to marked reduction in rates of nitrifi-
fication and denitrification. Hence, this natural process which might help to keep eutrophication in check is itself inhibited in such organic-rich environments. In this case the NH$_4^+$ produced in organic decomposition is no longer transformed to N$_2$ but is recycled back to the overlying water to support further primary production. This sequence constitutes a positive-feedback loop that allows eutrophication to catalyze itself once initiated.

References

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