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Ammonium recycling versus denitrification in Chesapeake Bay sediments

W. M. Kemp, P. Sampou, J. Caffrey, and M. Mayer
Horn Point Environmental Laboratories, University of Maryland, P.O. Box 775, Cambridge 21613

K. Henriksen
Department of Civil Engineering, University of Aalborg, Sohngaardsholmsvej 57, DK-9000 Aalborg, Denmark

W. R. Boynton
Chesapeake Biological Laboratory, University of Maryland, P.O. Box 38, Solomons 20688

Abstract

Contemporaneous measurements are reported for nitrification, denitrification, and net sediment–water fluxes of NH_4^+ and NO_3^- in the mesohaline region of Chesapeake Bay. Seasonal cycles over a 2-yr period were characterized by a midsummer maximum in NH_4^+ efflux to the overlying water and a May peak in NO_3^- 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 O_2 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 NO_3^- fluxes and net nitrification rates (nitrification minus NO_3^- reduction to NH_4^+) revealed that measurements of denitrification with the acetylene block method systematically underestimated actual rates. Rates of N_2 loss in denitrification were similar to NH_4^+ recycling fluxes to the overlying water in spring and fall, but in summer negligible denitrification contributed to enhanced NH_4^+ 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 NH_4^+ 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 NH_4^+. This NH_4^+ is regenerated by the decomposition and deamination of organic matter, with subsequent diffusion from sediments to the overlying water where it can be assimilated by phytoplankton. The relative influence of sediment N recycling on water-column processes tends to decrease with increasing depth (Harrison 1980) and is particularly pronounced during summer in temperate regions (Kemp and Boynton 1984).

In the presence of O_2, a portion of the NH_4^+ regenerated from benthic decomposition of organic matter is oxidized to NO_3^- (nitrification) before it can escape from the sediments. This NO_3^- may, in turn, be used as a terminal electron acceptor by denitrifying bacteria producing gaseous forms of nitrogen (N_2, N_2O) essentially unavailable to most coastal phytoplankton (Howarth et al. 1988). Thus, the coupled process of nitrification-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-

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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 thermistor, induction salinometer, and polarographic electrode. Bottom-water (1 m above sediment surface) samples were obtained with a high-volume,

submersible pump, and samples were filtered (GF/F, 0.8 μm) into vials and frozen immediately for subsequent analyses of NH_4^+, NO_2^-, and NO_3^- with standard methods on a Technicon autoanalyzer. Intact sediments were obtained at each station with a Bouma box corer, which collects rectangular cores (136 cm^2 area by ~30-cm depth) in clear acrylic liners that allow visual inspection of retrieved sediments. Cores with any signs of disruption of surface or sides were rejected.

Three of these core liners were used as incubation chambers to measure net fluxes of NH_4^+, NO_2^-, and NO_3^- between sediments and overlying water (Boynton et al. 1988). Water-column heights in these cores were adjusted to about 12 cm, and bottoms and tops of the core liners were then fitted to acrylic plates with foam gaskets to form air- and watertight seals. The water overlying the sediments in these cores was replaced with fresh, ambient bottom water. The tops of these chambers were fitted with sampling ports and an O_2 electrode with built-in stirrer (Orbisphere), which provided gentle mixing of the overlying water without resuspension of sediments (Boynton et al. 1988). An additional core liner containing only water served as a control. The four chambers (liners) were incubated at ambient temperature in a darkened water bath for 4–6 h. Samples (30 ml) were withdrawn from the overlying water (1.5–2 liters) at 30–60-min intervals over the incubation period, with sample volume replaced from a reservoir of ambient bottom water. Samples were filtered (GF/F) into vials, frozen, and stored for later nutrient analyses.

Rates of nitrification were measured with the N-serve inhibition method (Henriksen et al. 1981). Replicate (12–18), intact sediment cores (2.5-cm i.d., 25 cm long) were subsampled from the box core. Sediment depth in each was adjusted to a height of 4–6 cm, bottoms were secured with stoppers, and cores were placed in a large (8-liter) holding reservoir of ambient bottom water for transport to the laboratory. Overlying water in each core was replaced with filtered bottom water. We treated half of the cores with N-serve (nitrapyrin), the specific inhibitor of the first step in nitrification, by 4–5 line injections of N-serve solution (100 mg $liter^{-1}$) to sediment pore waters for each depth (10–15 μl) through side ports at 0.5-cm depth intervals along the cores and to the overlying water (1.5 ml) so as to produce final concentrations of 5 mg $liter^{-1}$. All cores, including the other half which served as controls, were incubated 2–4 d in the dark at ambient temperature. Overlying water, which was stirred continuously and aerated with bubblers, was sampled and replaced daily in each core (with N-serve added to treated cores), and samples were filtered and frozen for later NH_4^+ analysis. At the end of the incubation period, overlying water was removed and sampled again for NH_4^+, and sediments were sliced (0–1, 1–2, and 2–4-cm intervals) to sample pore waters for NH_4^+ (by KCl extraction and centrifugation).

Nitrification rates were calculated as the sum of differences in NH_4^+ between treated and control cores for each depth interval; only the depth intervals for which differences were statistically significant were used in this summation. If no significant differences were found between treated and control cores at any depth, rates were considered 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_2O, 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_2O 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_2H_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_2O.

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 × *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 screens 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

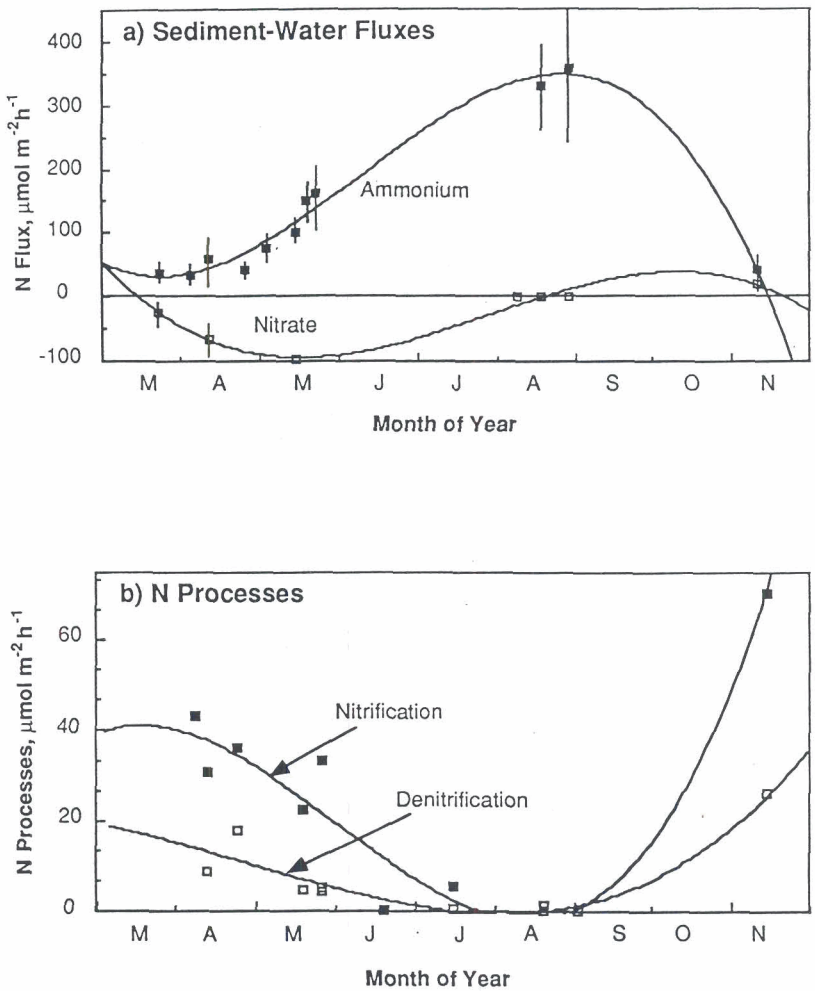

Fig. 1. Seasonal variations in (a) net fluxes of NH_4^+ and NO_3^- across the sediment–water interface and (b) net nitrification (N-serve inhibition) and denitrification (acetylene block) in sediments at Sta. 2 (mean depth, 9 m) in the mesohaline portion of Chesapeake Bay. Given are means (± SE) for net fluxes and mean rates for N transformation processes; data from 1986 and 1987 are combined here, and curves are drawn with third-order polynomial regression.

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 NO_3^- were generally directed out from sediments with highest rates in summer (Nixon 1981; Hopkinson 1987).

Rates of both net nitrification (nitrification minus 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).

		Nitrification*			Denitrification†	
			$[NH^+_4]$ (μmol $core^{-1}$)			
		Rate	Treated	Control	Rate	Coeff. (r^2)
Sta. 2						
1986	4 Apr	42.9	2.84±0.10	1.29±0.20	ND	ND
	20 Apr	36.0	3.79±0.26	3.12±0.10	17.8	0.94
	14 May	22.4	3.18±0.20	2.78±0.10	4.6	0.84
	22 May	ND†	ND	ND	5.1	0.85
	14 Jun	0	0.50±0.04*	0.83±0.27*	ND	ND
	26 Aug	0	1.65±0.12*	1.63±0.28*	(0.2)	(0.06)
1987	9 Apr	30.6	1.25±0.41	0.43±0.23	8.8	0.94
	22 May	33.0	1.76±0.27	1.12±0.18	4.1	0.81
	10 Jul	5.3	0.53±0.10*	0.40±0.03*	0.6	0.52
	13 Aug	0	1.96±0.37*	2.40±0.20*	(1.2)	(0.10)
	6 Nov	70.4	1.63±0.46	0.48±0.25	26.2	0.96
Sta. 3						
1986	4 Apr	51.6	5.22±0.19	3.39±0.06	ND	ND
	16 May	44.7	5.40±0.12	4.62±0.79	ND	ND
1987	22 May	ND	ND	ND	(0.2)	(0.10)
	6 Nov	ND	ND	ND	16.2	0.86

* Replicate cores incubated for 36–72 h, half being injected with N-serve (to block nitrification) and half as controls. NH_4^+ 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 NH_4^+ 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 N_2O over time for cores injected with C_2H_2 (to block N_2O reduction). *Coefficient of explanation* (r^2) given for $[N_2O]$ 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 NH_4^+ 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), NH_4^+ 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 NH_4^+ fluxes to the overlying water (Fig. 1). Marked seasonal variations in pore-water NH_4^+ 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 NH_4^+, declining rapidly between the sediment surface and 2-cm depth and decreasing with increasing temperature (Fig. 2).

Pore-water NO_3^- 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

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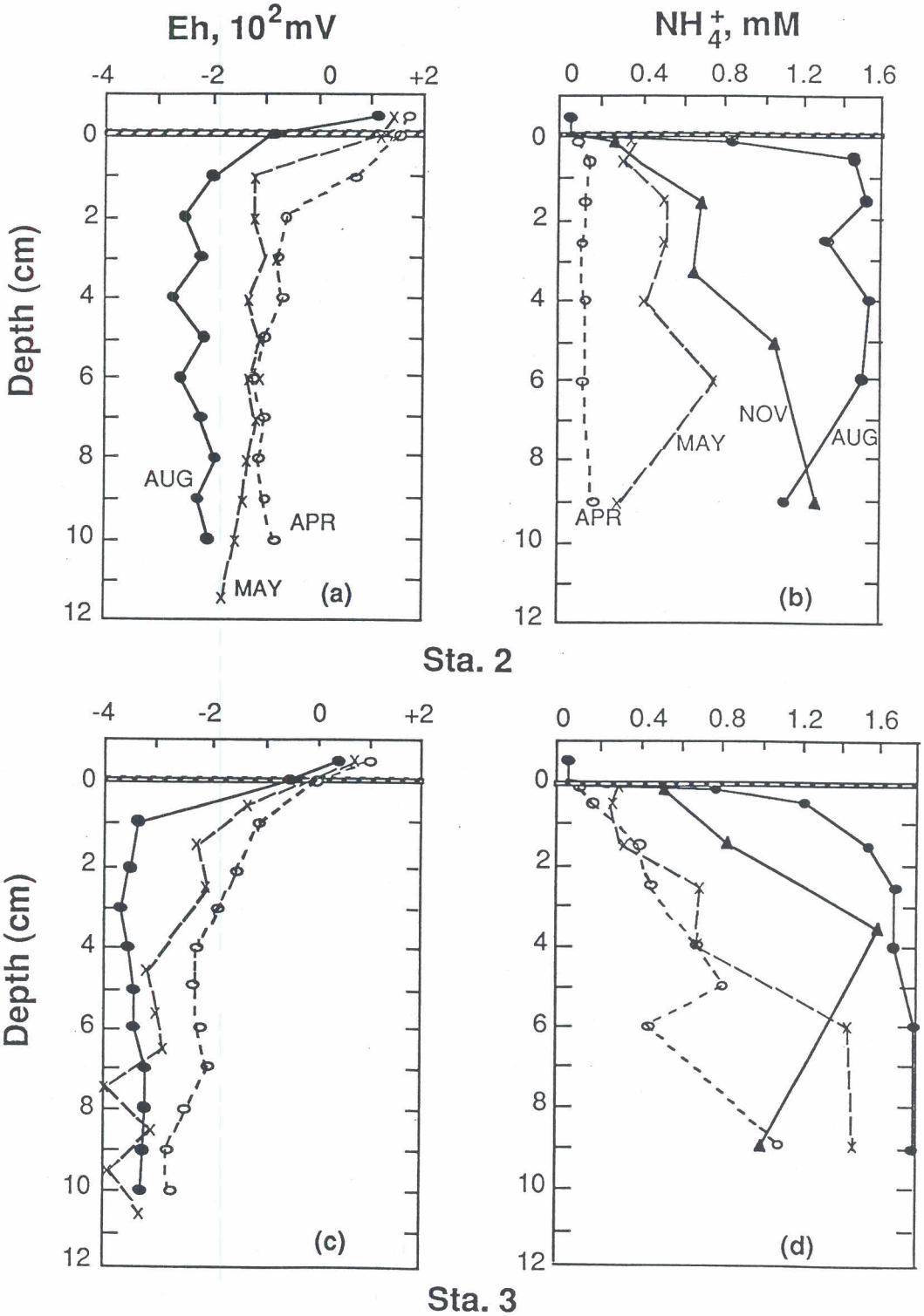
Fig. 2. Vertical profiles of redox condition (a, c) and pore-water NH_4^+ concentration (b, d) for sediments at stations 2 and 3 in April, May, and August 1986. Note that in 1987 similar patterns for NH_4^+ were observed, but parallel redox data are not available.


Eh, 10^2mV
NH_4^+, mM
Depth (cm)
AUG
APR
MAY
NOV
(a)
(b)
Sta. 2
(c)
(d)
Sta. 3

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 ($Y = 64.9 - 2.46\ X$, $r = 0.93$), this correlation undoubtedly results from the inverse covariance of temperature and oxygen.

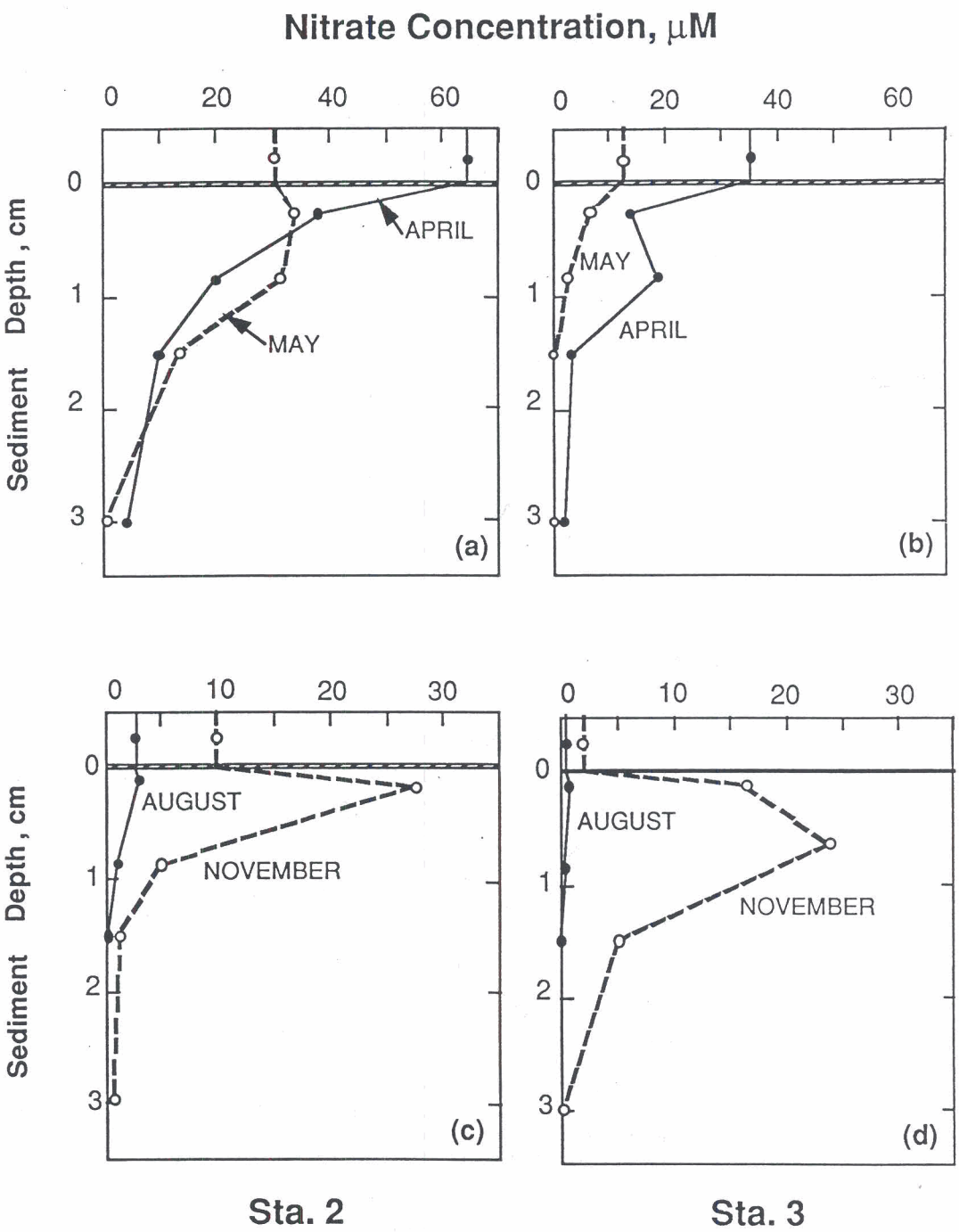


Fig. 3. Vertical profiles of NO_3^- concentration in pore waters at stations 2 and 3 in April and May (a, b) and August and November (c, d) 1987. Note change of scale between upper and lower panels.

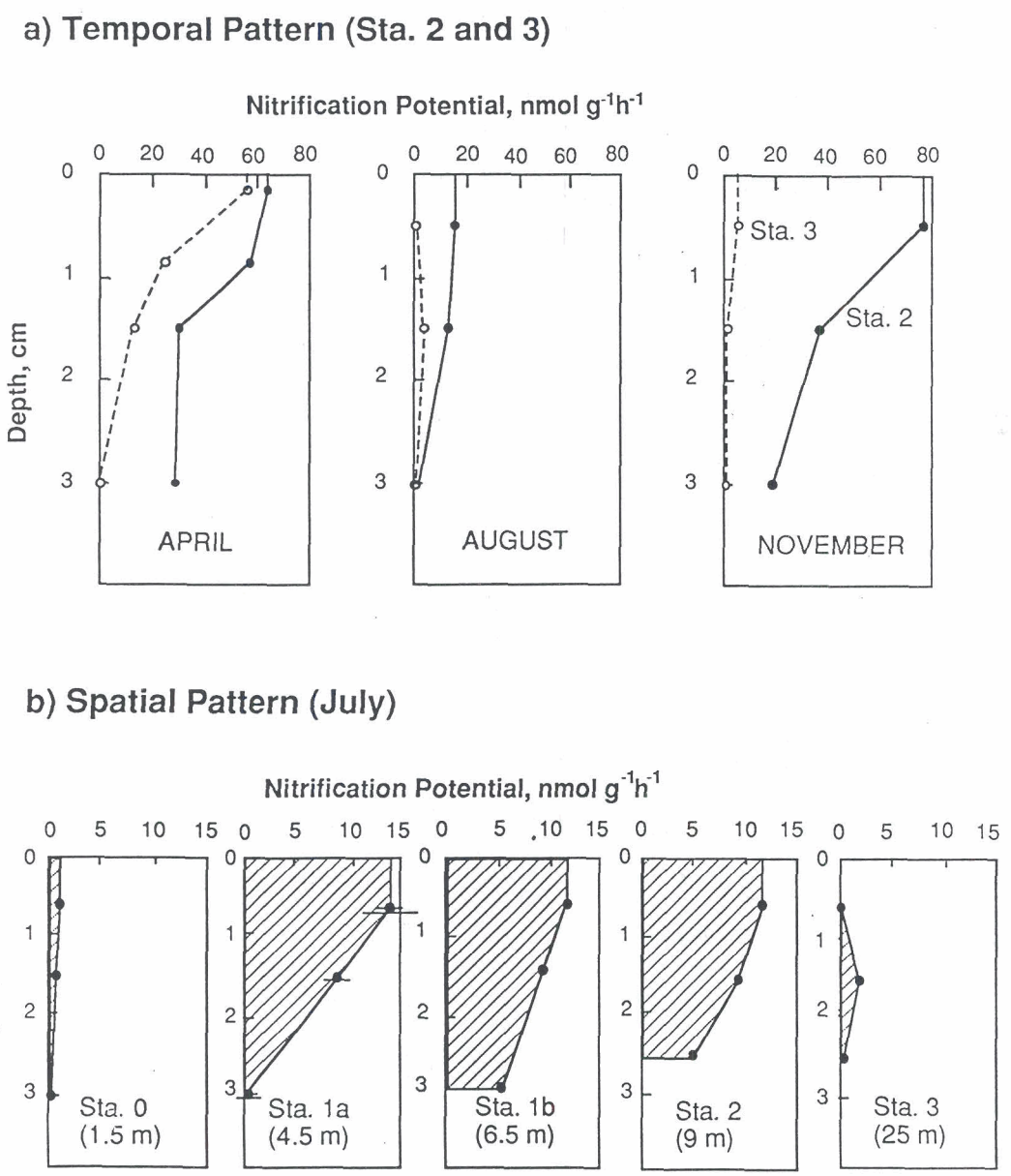


Fig. 4. Vertical profiles of nitrification potential. a. Temporal pattern for April, August, and November. b. Spatial pattern along 38°28.0'N running westward from the main Chesapeake Bay channel (Sta. 3) to the shoal area (Sta. 0). Note that variances in these rates were relatively low, with standard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

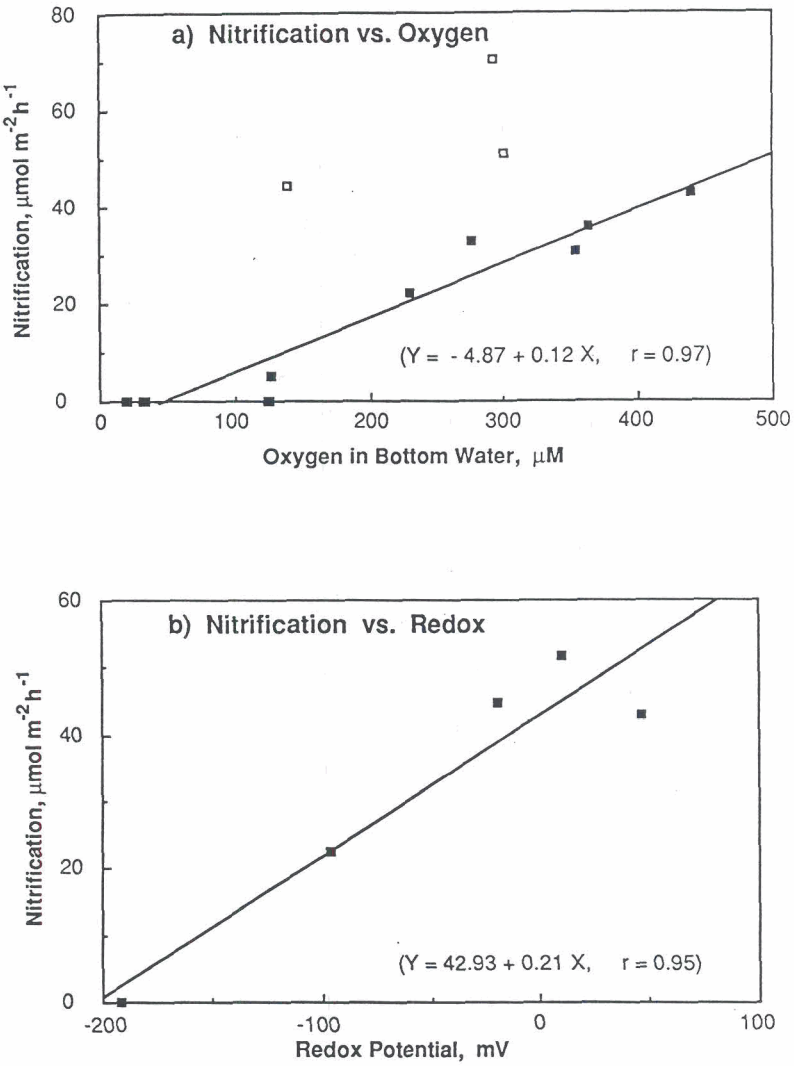


Fig. 5. Relation between sediment net nitrification rate and dissolved oxygen in overlying water column at station 2 in spring and summer (■) and in November (□). Regression line is for spring and summer data at station 2. b. Relation between sediment net nitrification rate and redox potential in surficial (0–1 cm) pore waters at station 2 in spring and summer.

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

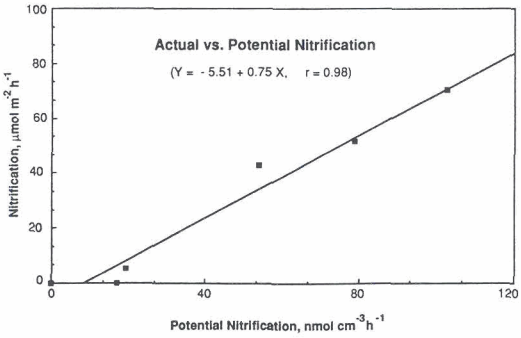


Fig. 6. Relation between actual (N-serve inhibition for intact cores) and potential [NO_3^- production from NH_4^+-amended slurries of surficial (0–1 cm) sediments] nitrification for station 2.

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 O_2 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 O_2 penetrates the sediments. Therefore, the slope of the equation in Fig. 6 (0.75 mm) represents a crude estimate of the mean depth of O_2 penetration into the sediments. This value, which corresponds closely to direct measurements with polarographic O_2 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 O_2 in the overlying water (Fig. 5a) may indicate an effect of reduced O_2 diffusion into the sediments. In addition, the relatively high rates of O_2 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 O_2 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. H_2S 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 NO_3^- (Koike and Sørensen 1988). Such inferences have been based either on the stimulation of rates by NO_3^- additions (Jenkins and Kemp 1984) or on the fact that pore-water NO_3^- concentrations were below presumed kinetic saturation values (Kaspar 1982). In addition, denitrification rates have been directly correlated with NO_3^- 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 NO_3^- 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

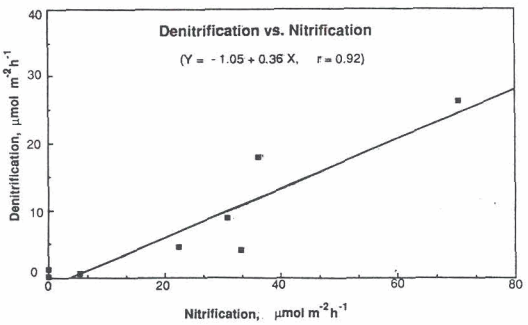


Fig. 7. Relation between nitrification (N-serve inhibition) and denitrification (acetylene block) rates for sediments at station 2.

of the former process on NO_3^- 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 abun-

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

		Sta. 2		Sta. 3	
	Organisms	Abundance	Biomass	Abundance	Biomass
Apr	Spionidae	1.75±0.73	0.85	4.53±1.53	1.63
	Nereidae	0.17±0.15	3.99	0.44±0.21	1.56
	Other annelids	0.09±0.04	0.17	0.44±0.15	0.32
	Molluscs	1.61±0.36	1.22	0.20±0.04	0.07
	Amphipods	0	0	0.70±0.12	0.02
	Total	3.65±0.80	6.23	5.69±1.39	3.60
May	Spionidae	2.73±1.24	1.00	3.99±3.19	1.12
	Nereidae	0.27±0.22	4.36	0.24±0.08	1.68
	Other annelids	0.29±0.19	0.27	0.12±0.15	0.17
	Molluscs	0.56±0.33	0.63	0.05±0.08	0.05
	Amphipods	0.02±0.04	0.05	0.15±0.15	0.02
	Total	3.87±1.44	6.31	4.55±3.21	3.04
Aug	Spionidae	1.44±0.47	1.56	0	0
	Nereidae	0.30±0.60	0.02	0	0
	Other annelids	0.12±0.04	0.02	0	0
	Molluscs	0.09±0.08	0.02	0	0
	Amphipods	0	0	0	0
	Total	1.68±0.46	1.62	0	0
Nov*	Spionidae	0.43	0.51	0.33	0
	Nereidae	0.05	0.14	0.01	0
	Other annelids	0.16	0	0.01	0
	Molluscs	0.12	0.12	0.05	0
	Amphipods	0	0	0.03	0.03
	Total	0.76	0.77	0.43	0.03

* Unpublished data provided by F. Holland and A. Shaughnessy.

dance (X) for station 2 ($Y = 11.3\ X - 7.0$, $r = 0.87$). 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 porewater 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_2H_2 blockage (Table 1) seriously underestimated actual rates here. The slope of the equation for Fig. 7 indicates that denitrification (C_2H_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_2S can alleviate the blocking effect of C_2H_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_2H_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_2O can also lead to underestimates of actual denitrification with the C_2H_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). Christensen et al. (1989) have recently demonstrated that even at higher NO_3^- levels, conventional C_2H_2 block methods may underestimate N_2O produced, because of N_2O diffusion into regions of the sediment where NO_3^- is absent. Because the rate of N_2O diffusion would be a direct function of

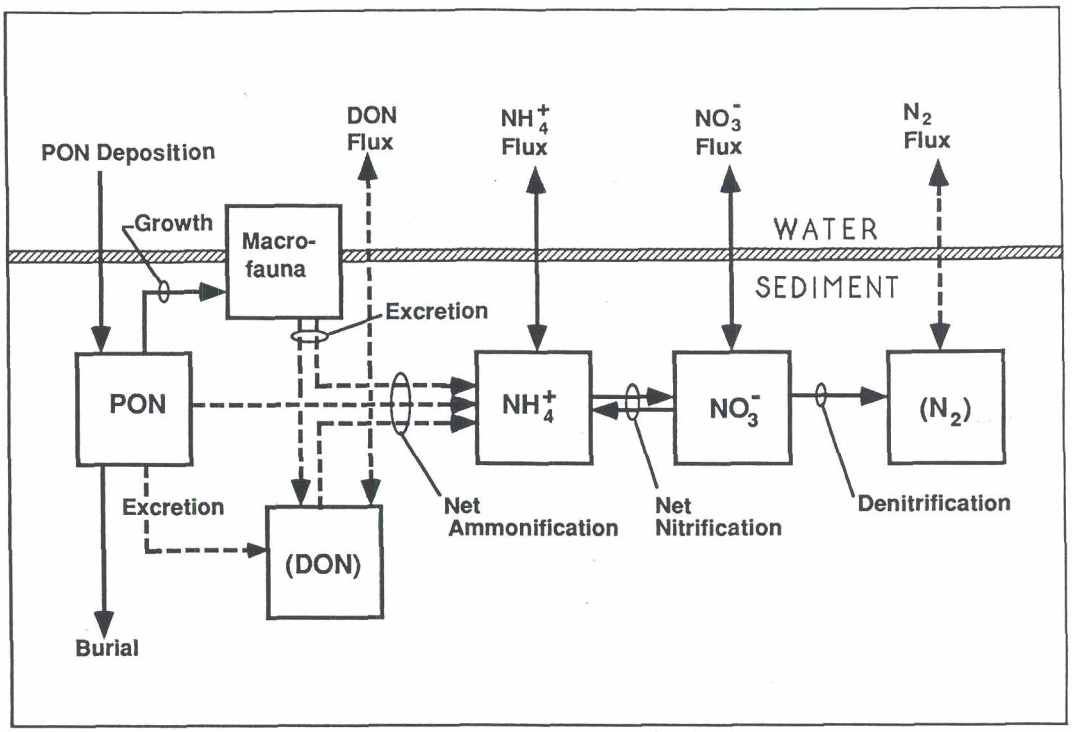


Fig. 8. Conceptual diagram depicting N pools, transformations, and fluxes across the sediment–water interface considered in this study. Processes and fluxes for which direct measurements are available are shown as solid lines, whereas broken lines are used for those rates estimated by subtraction. Pools not measured are indicated in parentheses. Table 3 summarizes rates.

denitrification rate, this source of error would probably lead to a systematic underestimate of denitrification with the C_2H_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_2H_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_3^-. It can be seen from pore-water NO_3^- profiles (Fig. 3) that seasonal rates of change in these sediment NO_3^- pools were relatively small compared to rates of net nitrification or NO_3^- flux across the sediment surface (Fig. 1). For example, maximal pore-water NO_3^- pools occurring in April and November in the upper 3 cm of sediments were 0.3–0.4 mmol m^{-2}. If we assume that the near-zero NO_3^- concentrations measured in August prevailed for the entire period from June through September, then mean rates of net NO_3^- 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^{-2} d^{-1}. Thus, because the N-serve inhibition rates (Table 1) represent net nitrification (including NO_3^- reduction to NH_4^+), denitrification can be estimated as the algebraic sum of the N-serve rate plus ambient NO_3^- flux across the sediment–water interface. Denitrification rates calculated by this "NO_3^- balance" were 2–7 times higher than those measured by C_2H_2 blockage in spring and fall (Table 3). Previous reports indicate that the relative proportion of total NO_3^- reduction that goes to NH_4^+ (vs. N_2 or N_2O) ranges from 20 to 60% for marine sediments (Enoksson and Samuelsson 1987; Koike and Sørensen 1988). This implies that actual nitrification

Table 3. Summary of major N transformation processes and N fluxes across the sediment–water interface for April, August, and November at Sta. 2 (9-m depth) in the mesohaline region of Chesapeake Bay [$\bar{x} \pm$ SE (n)]. Sign convention is relative to the sediment–water interface, where effluxes from sediments and increases in sediment N pools are negative. Net fluxes of NH_4^+ and NO_3^- as well as net nitrification (nitrification minus NO_3^- reduction to NH_4^+) and denitrification estimates by C_2H_2 blockage are from Fig. 1.

N fluxes and transformation processes	N rates (mmol N m^{-2} d^{-1}) Apr	Aug	Nov
Internal N processes			
Net ammonification*	2.4±0.4 (3)	9.0±0.2 (3)	1.2±1.2 (3)
Net nitrification	0.9±0.1 (3)	0.0±0.0 (3)	1.7±0.5 (3)
Denitrification			
$-C_2H_2$ block	0.3±0.1 (3)	0.1±0.0 (3)	0.6±0.1 (3)
$-NO_3^-$ balance*	2.0±0.4 (3)	0.0±0.0 (3)	1.2±0.2 (3)
Inputs, outputs, Δ storage			
PON deposition†	+11.1±0.4 (3)	+7.7±0.8 (3)	+6.7±2.0 (3)
Long-term burial†	−1.8±0.4 (10)	−1.8±0.4 (10)	−1.8±0.4 (10)
Δ PON pools†	−2.9 (1)	+1.8 (1)	−1.4 (1)
Δ NH_4^+ pools‡	−0.4 (1)	−0.8 (1)	+0.3 (1)
Δ macrofaunal N‡	−0.5±0.1 (3)	+0.3±0.1 (3)	+0.1±0.0 (3)
NH_4^+ efflux	−1.1±0.2 (3)	−8.2±0.2 (3)	+0.2±0.2 (3)
NO_3^- efflux	+1.1±0.2 (3)	0.0±0.0 (3)	−0.5±0.1 (3)
N_2 efflux*	−2.0±0.4 (3)	0.0±0.0 (3)	−1.2±0.2 (3)
Net difference§	+3.5±1.5	−1.0±1.7	+2.6±3.1

* Net ammonification calculated as sum of NH_4^+ efflux plus net nitrification plus Δ NH_4^+ pools; denitrification estimated by NO_3^- balance (net nitrification minus NO_3^- efflux) assuming no significant Δ NO_3^- pools. N_2 efflux based on NO_3^- balance assuming steady state.

† PON dynamics from data of Boynton et al. (1988). Deposition estimated from replicate sediment trap collections corrected for resuspension (Taguchi 1982). Sediment PON pools taken in upper 1 cm, with concentrations ranging from 0.30 to 0.39% dw, and bulk density varying from 0.55 to 0.67 g dw cm^{-3}. PON burial estimated from 10 measures of ^{210}Pb profiles (Nixon 1987) near study site.

‡ Changes in pore-water (KCl extractable) NH_4^+ pools in upper 10 cm of sediment (Fig. 2); changes in macrofaunal tissue N based on changes in total biomass (Table 2) and assuming 0.1 g N (g dw)$^{-1}$ (Jørgensen 1979).

§ Mean ± propagated error(s) for eight input, output, and Δ storage rates, assuming independence of errors.

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 ^{210}Pb dating (Nixon 1987). Overall, mean rates of N burial (Table 3) con-

stituted 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 (Kelly 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 nitri-

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.

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