



High-resolution nitrogen gas profiles in sediment porewaters using a new membrane probe for membrane-inlet mass spectrometry

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Abstract

A probe inlet for membrane-inlet mass spectrometry (MIMS) was developed to measure dissolved nitrogen and argon gas in sediment porewaters. This technique represents a significant improvement in the measurement of dissolved gas ratios in sediment cores and in small volume samples (< 5 ml). The probe is stable, inexpensive and has relatively fast equilibration times (~ 4–5 min) for dissolved N₂/Ar ratio analyses. The membrane probe is mounted at the end of a stainless steel capillary (0.75 mm OD) connected directly to the inlet system of a quadrupole mass spectrometer. The membrane is ~ 1 mm × 0.5 mm resulting in profiles that have a depth resolution of < 2 mm. Nitrogen/argon ratios measured with the probe inlet have a precision of < 0.2%. Porewater N₂/Ar ratios measured in cores collected from Raritan Bay, NJ, indicated that N₂ was in equilibrium with the atmosphere in overlying waters and that nitrogen was up to 8% supersaturated by a depth of 1 cm. The increase in N₂ is consistent with nitrogen production from denitrification of ~ 2 mmol N₂ m⁻² day⁻¹. High-resolution nitrate profiles also provide evidence for denitrification, with nitrate being depleted at the same depth horizon where N₂ gas concentrations are increasing.

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1. Introduction

Membrane-inlet mass spectrometry (MIMS) systems have become a well-established method for the determination of dissolved gas concentrations in natural waters (Kana, 1990; Kana et al., 1994; Lloyd, 1993; Thomas and Lloyd, 1995). MIMS has been used to determine oxygen consumption and denitrification rates in incubation experiments (Kana et al., 1998; Laursen and Seitzinger, 2002) for stable-isotope tracer addition experiments (An et al., 2001; Jensen et al., 1996) and for measurements of methane and nitrous

oxide (Lloyd et al., 1985, 1996). The MIMS technique has made fast and precise gas ratio measurements routinely possible. The flow-through system originally designed for sample introduction to the MIMS system requires a minimum volume of ~ 5 ml of water (see Kana et al., 1994 for full details). This volume of water can become a limiting factor when dissolved gas measurements are made on small samples such as sediment porewaters or in closed chamber incubations. The additional requirement for discrete gas-tight samples makes measurement of gas samples from porewaters particularly difficult. Probe inlets for MIMS systems have been used to profile O₂ and methane in sediments at millimeter resolution (Lloyd et al., 1996). For N₂, lower-resolution profiles (0.5–1.0 cm) have

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been obtained with a probe-style inlet (Cartaxana and Lloyd, 1999; Thomas and Lloyd, 1995). In each of these probe studies, the response time, or dwell time, at each depth was approximately 15–20 min. In an effort to decrease the analysis time and improve the resolution of porewater dissolved N_2 profiles, we have constructed a probe inlet for a MIMS system that has significantly faster response times and millimeter-scale depth resolution. In addition, this probe is simple, relatively durable, and inexpensive to construct. In this paper, we detail the performance of the new probe-inlet in water and in sediments, as well as demonstrate its capabilities through the measurement of N_2/Ar gas profiles and subsequent denitrification rate calculations

for sediments collected from Raritan Bay, NJ. Raritan Bay is on the south side of the New York Harbor/Raritan Estuary system; it has sandy to muddy sediments with high organic carbon contents and thus represents a region with high denitrification rates. The naturally sandy sediments are also a good test of the durability of the probe.

2. Materials and methods

Our MIMS system is a quadrupole mass spectrometer dissolved gas analyzer (Balzers, Prisma™) with an electron multiplier detector (Kana et al.,

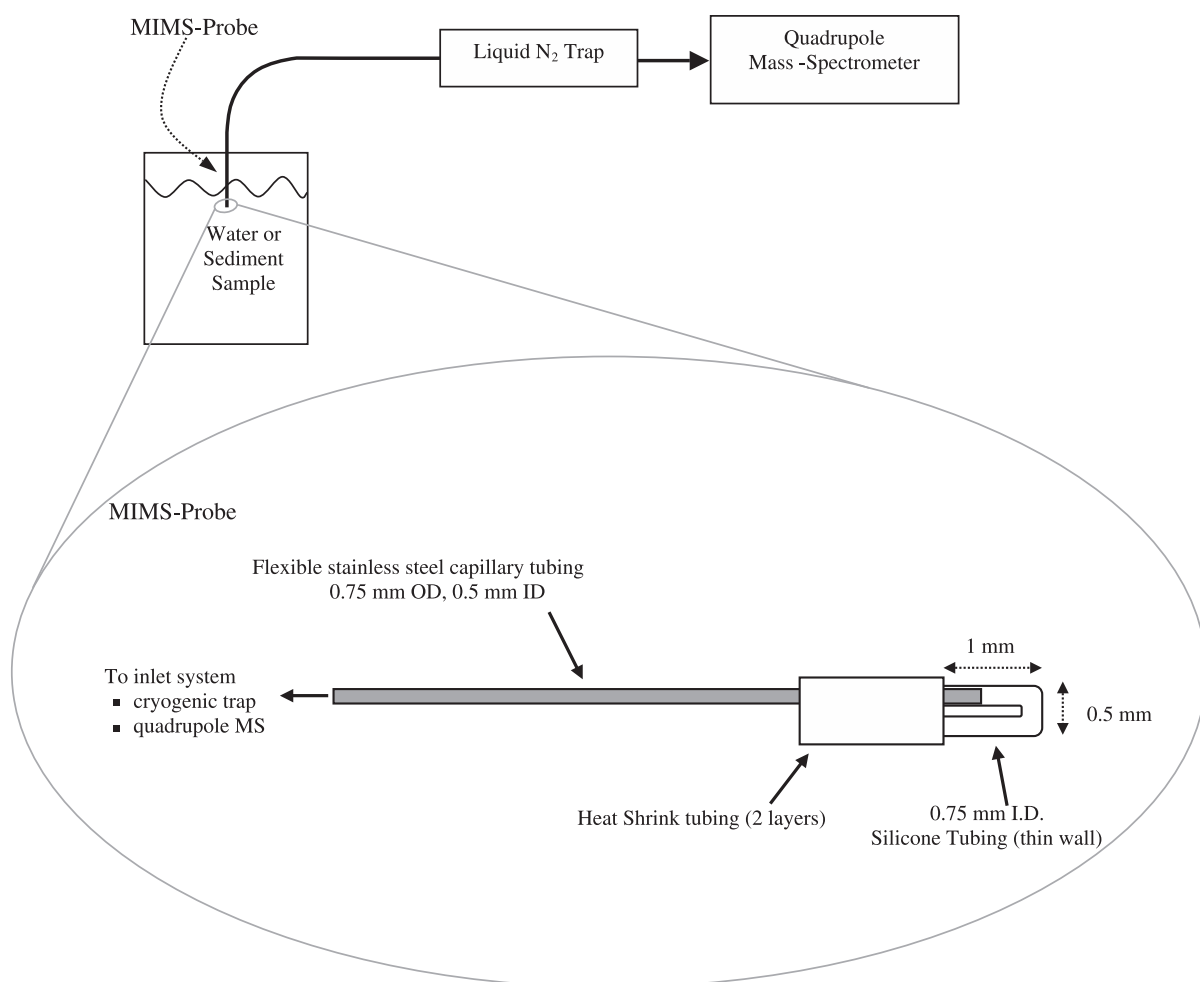


Fig. 1. Schematic diagram of MIMS system with probe inlet.

1994). The new gas inlet is configured as a probe at the tip of a flexible stainless-steel capillary. The capillary tubing is 0.75 mm OD and 0.5 mm ID. The diffusive membrane is silastic tubing (Dow Corning™) with an internal diameter of 0.7 mm. The silastic tubing is pressure fitted onto the stainless steel tubing, folded back to make a small loop and attached to the capillary with two layers of heat-shrink tubing (Fig. 1). The probe is approximately 1.0 mm long and 0.5 mm wide. The membrane probe allows the diffusion of gases into the vacuum system, whereupon they pass through a liquid nitrogen cryogenic trap before diffusing into the ionization chamber of the mass spectrometer (Fig. 1). The liquid nitrogen trap removes water vapor and CO₂ prior to the inlet. This set-up allows the probe to be placed directly into the water or sediment sample and does not require that water be pumped past the diffusive membrane as is the case for a flow-through inlet system.

Nitrogen/argon ratios are calculated from the quadrupole instrument signal (essentially the N₂ and Ar pressures at the detector) and standardized using air-equilibrated water standards. The standards consisted of 2-liter reservoirs of artificial seawater at a range of salinities (salinity=0, 10, 21 and 31). The samples, standards, probe inlet and mass spectrometer were kept at a constant temperature (22 °C) in an environmental chamber to minimize instabilities due to temperature fluctuations. Standards were stirred slowly while the measurements were being made, and each determination generally took 1–2 min. A standard curve was established each day and was used to determine molar ratios of N₂ and Ar. Gas ratios for standards measured with the probe inlet were linearly related to the equilibrium solubility molar gas ratio over the entire range of salinities (Fig. 2). The reproducibility for the measured N₂/Ar ratios was ± 0.04 and the drift in the N₂/Ar ratio of the standard over the course of a day (~ 12 h) was $<0.3\%$. The precision with the probe inlet is comparable to that obtained with the flow-through inlet system (Kana et al., 1994; Laursen and Seitzinger, 2002). Equilibrated sediment cores made with artificial seawater standards ($S=0$ and 31) and clean sands (baked at ~ 500 °C for 4 h) were used to establish that the N₂/Ar ratios measured in an air-equilibrated core are the same as

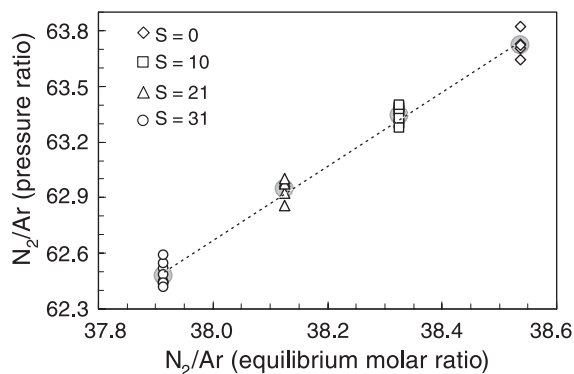


Fig. 2. N₂/Ar standard curve for dissolved gas standards measured with MIMS probe. Standards are plotted as the measured N₂/Ar ratio (pressure) vs. the equilibrium molar N₂/Ar ratio. The equilibrium ratio is calculated from the gas solubilities at a specified temperature (22 °C) and salinity. Multiple points for each standard are measured over the course of 12 h. The dashed line is a best fit to the averaged data (shaded circles) for each standard ($r^2=0.998$). The standard curve is used to convert the instrument signal (pressure, in mbar) to a molar ratio.

those determined in air-equilibrated overlying water and not due to changes in porosity.

3. Results and discussion

The signal strength for N₂ and Ar achieved in water using the MIMS probe was 10^{-8} to 10^{-6} mbar. This is comparable to the signals achieved using the standard flow-through inlet system (Table 1). In sediments, the signal strength was an order of magnitude lower for both N₂ and Ar, but it is still well above the absolute detection limit ($\sim 10^{-11}$ mbar) for the mass spectrometer. There is a decrease in response time with the MIMS probe as compared to the flow-through system because the area of the diffusive membrane is smaller. In sediments, the absolute gas signal from the mass spectrometer decreases by about a factor of 3 over the first few minutes in the sediments due to a diffusive loss of gas around the probe tip (Fig. 3). The N₂ and Ar signals decrease concomitantly and the signal stabilizes after about 7 min. The N₂/Ar ratio stabilizes within 4–5 min. The effective response time in sediments is therefore on the order of ~ 5 min. This represents a significant improvement in response time, compared to the 20-min response time reported previously (Cartaxana and Lloyd, 1999; Lloyd et al.,

Table 1

Signal strength for N₂ and Ar using the MIMS probe in water and in sediments compared to the signal strength using the standard flow-through method

	MIMS probe		Standard MIMS
	In water	In sediment	In water
Signal strength (mbar)			
N ₂	$\sim 1 \times 10^{-6}$	$\sim 3 \times 10^{-7}$	$\sim 1 \times 10^{-6}$
Ar	$\sim 2 \times 10^{-8}$	$\sim 3 \times 10^{-9}$	$\sim 2 \times 10^{-8}$
Time to stabilize	~ 1 min	~ 5 min	< 1 min

1996). This improvement in response time increases the spatial resolution that can be achieved by minimizing the diffusion range surrounding the probe (Thomas and Lloyd, 1995). While the signal strength obtained with the probe is lower than obtained using the flow-through mode, the advantages gained with respect to smaller sample volumes and the ability to profile sediments potentially outweigh any loss in sensitivity.

The behavior of the quadrupole ionization system with respect to N₂/Ar stability and NO production at low O₂ concentrations was evaluated because the sediment cores have fairly shallow O₂ penetration depths (on the order of 10 mm). The formation of NO can occur through the reaction of charged O and N ions and can cause an apparent increase in the N₂/Ar signal at low O₂ concentrations (i.e., when there is

less O₂ present, less NO is formed, and the N₂ signal appears larger; Eyre et al., 2002). The production of O²⁻ ion and NO is thought to be somewhat system dependent and a function of the characteristics of the particular ionization system (T. Kana, personal communication). The MIMS system using the Prisma™ quadrupole does not tend to form NO in the ionization chamber. We tested our MIMS system N₂/Ar signal stability using standards with a range of O₂ concentrations. Sodium dithionite was added at a range of concentrations to remove O₂ from our standards, and the O₂ concentrations were determined using standard Winkler-style O₂ titrations (Carpenter, 1964). There does not appear to be a significant trend in the N₂/Ar ratio or the NO concentration (data not shown) over a range of O₂ levels (0–100% saturation with respect to the atmosphere; Fig. 4).

Nitrogen/argon profiles in sediment cores comprised of clean sands with air-equilibrated artificial seawater show little variation in the gas ratios with depth (Fig. 5), indicating that changes in the N₂/Ar profile with depth in field sediments are not simply a function of changing porosity. The clean-sand cores had no active denitrification as they were organic carbon-free and there was no nitrate in the water. The combustion of the sands should also have killed any bacteria present. The measured N₂/Ar ratios indicate generally that the gas ratios measured in the

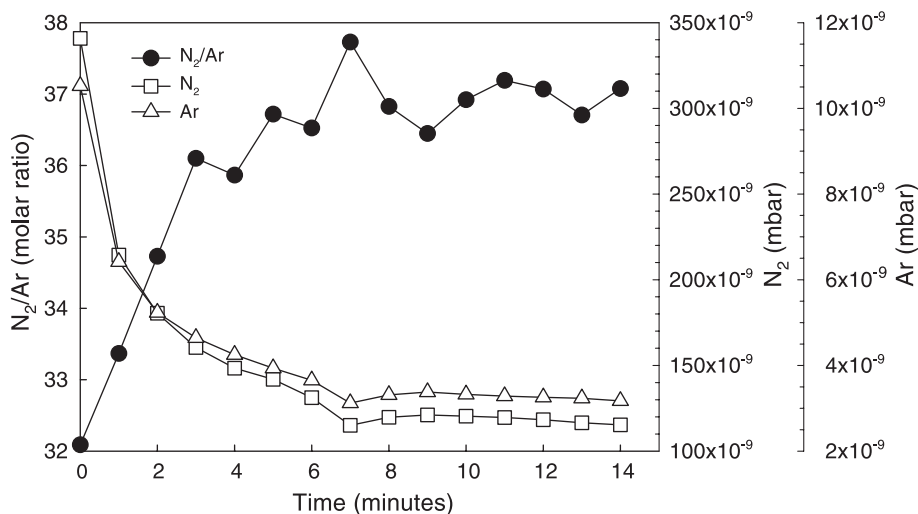


Fig. 3. Time for N₂/Ar molar ratio to stabilize in sediments using the MIMS probe. The absolute N₂ and Ar signals (pressure in mbar) are plotted on the secondary axis to show the concomitant change in the signal with time for both gases.

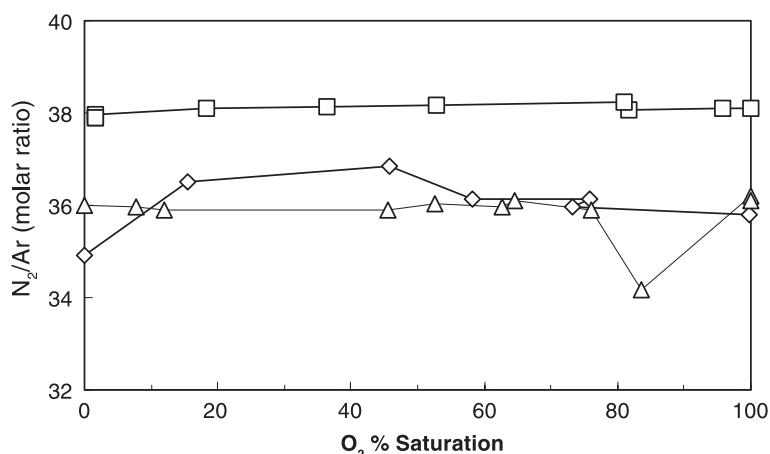


Fig. 4. N_2/Ar ratios for standards at different O_2 saturations (% saturation relative to air). Different symbols represent standards at different temperatures and salinities (Δ : $T=0$ °C, $S=35$; \diamond : $T=15$ °C, $S=24$; \square : $T=22$ °C, $S=0$).

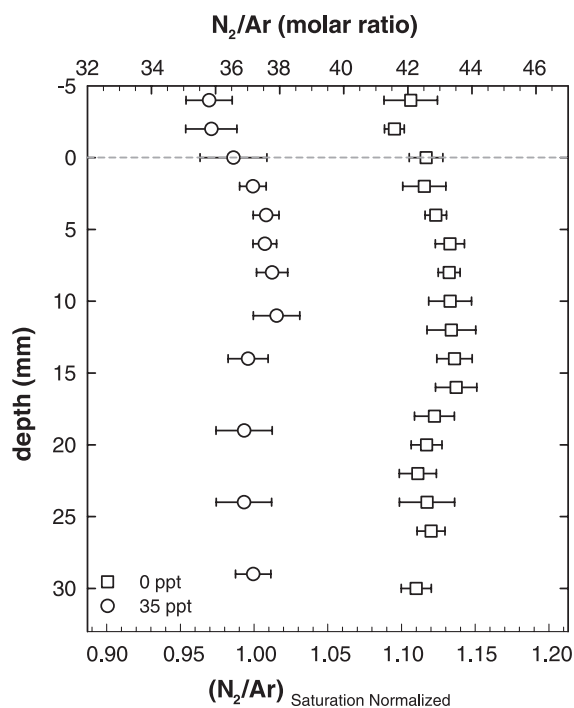


Fig. 5. N_2/Ar profiles in sediments comprised of air-equilibrated seawater and clean sands measured with the MIMS probe. The gas ratio is presented as the molar ratio of N_2/Ar ; the second scale is the saturation-normalized N_2/Ar ratio (the molar N_2/Ar ratio divided by the N_2/Ar ratio at equilibrium for a given temperature and salinity). The profiles show little change in the ratio with depth below the sediment–water interface (dashed line) indicating that the gas ratio is not changing as a function of porosity.

clean-sand cores do not change dramatically from those measured in the overlying water, although the profile in the core with $S=35$ does show a small inflection from the overlying water value to the value near the interface. The changes in the N_2/Ar ratio within both cores are small relative to changes in the N_2/Ar ratio in the Raritan Bay sediments. The bottom scale in Fig. 5 indicates that the normalized N_2/Ar ratio in the clean-sand cores (see the discussion below) has a range of only 0.03 units, or less than 20% of the change in the N_2/Ar ratio in the Raritan Bay sediment cores (due to denitrification).

Sediment cores with intact overlying water were collected for N_2/Ar profiling from a depth of approximately 8 m from Raritan Bay, NJ, during the summer. The Raritan Bay sediments had organic carbon contents of ~ 3 wt.% and are composed predominantly of muddy sands (Komada and Reimers, 2001). These sediments have high carbon oxidation rates and thus should have easily measurable denitrification rates. The sandy sediments are also a good demonstration of the robust nature of the probe. Water column oxygen concentrations in the bottom waters of the bay were near saturation equilibrium at the time of sampling. The subcores, with their overlying water, were equilibrated with the atmosphere at the in situ temperature (22 °C) for 24 h prior to N_2/Ar profiling in order to mimic the conditions at which they were collected. The MIMS probe was attached to a micromanipulator, lowered through the overlying water, and into the

sediments at 2 mm intervals. The probe was held at each depth until the signal for the N_2/Ar ratio stabilized (~ 3 – 5 min). A profile of 22 discrete depths was obtained in approximately 1 h. Nitrogen/argon ratios in standards (both air-equilibrated water and air-equilibrated sand cores) as well as in the overlying water of the sediment core were determined before and after each profile to evaluate drift in the signal over time.

Nitrogen/argon profiles from Raritan Bay sediments (Fig. 6) are presented as the saturation normalized N_2/Ar ratio, $(N_2/Ar)_{\text{sat}}$, where $(N_2/Ar)_{\text{sat}} = (N_2/Ar)_{\text{molar ratio}} / (N_2/Ar)_{\text{saturation equilibrium ratio}}$ (Emerson et al., 1991).

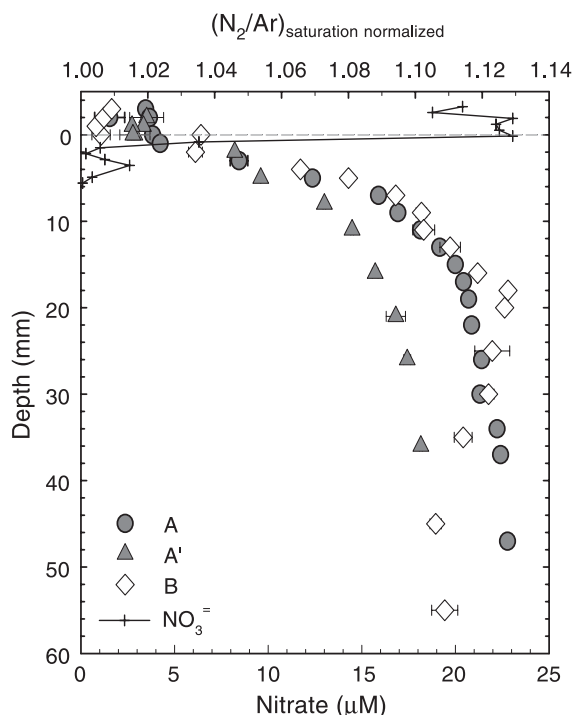


Fig. 6. N_2/Ar and NO_3^- profiles for Raritan Bay sediments. The saturation normalized N_2/Ar ratio is the molar ratio divided by the ratio at equilibrium for a given temperature and salinity; it emphasizes the degree of oversaturation in the gas ratio. The profiles labeled A and A' are from ~ 4 cm apart in same subcore; B is a profile from a second core taken at the same location. The dashed line represents the sediment–water interface. Note the increase in N_2 and the decrease in NO_3^- occur at roughly similar depths in the sediment. Error bars are the standard deviation for three determinations at each depth; they are generally smaller than the symbols. Overlying water values measured at the end of the profile overlay those measured at the beginning of the profile. Nitrate is determined colorimetrically from porewater collected by whole core squeezing.

$(Ar)_{\text{molar ratio}} / (N_2/Ar)_{\text{saturation equilibrium ratio}}$ (Emerson et al., 1991). This parameterization emphasizes the relative excursion from solubility equilibrium with the atmosphere. The equilibrium solubilities are determined for the in situ temperature and salinity (Weiss, 1970). Using this normalization, equilibrium values are equal to 1.0; supersaturated and undersaturated values are greater than 1.0 and less than 1.0, respectively. The N_2/Ar ratios increased smoothly from near equilibrium values (~ 1.01) in the overlying water to supersaturated values of 1.08–1.13 at depth in the sediment cores. The values of the measured N_2/Ar ratio at the beginning and end of each profile were the same within the error of the measurements (the measured N_2/Ar ratio varied by $< 0.2\%$) indicating that there was no significant drift in the ratio over the course of the profile. The increasing N_2/Ar ratios correspond to increasing N_2 concentrations as there is no mechanism for the downcore loss of Ar in these sediments. The obvious source of N_2 in these sediments is denitrification. These sediments have relatively high organic carbon contents (~ 3 wt.%) and the rapid decrease in porewater nitrate (see the discussion below) is further confirmation that these are strongly denitrifying sediments. The probe can also be used to investigate spatial heterogeneity in a sediment core. Nitrogen/argon profiles from two locations within the same subcore (Fig. 6, profiles A and A') and from two different cores taken at the same location (Fig. 6, profiles A and B) indicated that the sediments were spatially heterogeneous on relatively short length scales (~ 4 cm).

These N_2/Ar gas profiles have a very high degree of vertical resolution (1 mm) and thus can be used to estimate N_2 fluxes in sediments. An N_2 flux was estimated from the gas profiles using Fick's first law ($N_2 \text{ flux} = -D_s(\delta N_2/\delta z)$). The concentration gradient at the interface was determined using the measured N_2/Ar profile. We assumed a sedimentary diffusion coefficient (D_s) for N_2 of $5.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Lehrman, 1979). We used an equilibrium overlying water N_2 concentration of $\sim 430 \mu\text{M}$ and a constant equilibrium Ar concentration of $11.4 \mu\text{M}$ ($T=22^\circ\text{C}$, and $S=27.5$; Weiss, 1970) to calculate N_2 concentration changes. The maximum N_2/Ar ratios correspond to a supersaturation of 8–13%, or an increase of 34–55 μM N_2 . The concentration gradients from these profiles yield N_2 flux estimates that range from 1.9 to 3.7

$\text{mmol N}_2 \text{ m}^{-2} \text{ day}^{-1}$. To our knowledge, there have been no published denitrification rate measurements for Raritan Bay; however, this is a typical (if somewhat polluted) coastal/estuarine environment, and these values are comparable to N_2 fluxes measured in other estuarine sediments, using benthic chambers ($1.2\text{--}6 \text{ mmol m}^{-2} \text{ day}^{-1}$; Seitzinger, 1988). Further supporting evidence that the magnitude of the calculated N_2 flux is reasonable can be found in the porewater NO_3^- profiles. High-resolution porewater NO_3^- profiles (Fig. 6) were obtained using a whole core squeezer and standard colorimetric methods (Bender et al., 1987; Strickland and Parsons, 1972). The NO_3^- flux calculated from the profile is $\sim 1 \text{ mmol NO}_3^- \text{ m}^{-2} \text{ day}^{-1}$. The nitrate is rapidly removed by $\sim 6 \text{ mm}$ depth in the core; assuming all the NO_3^- is lost to denitrification, this NO_3^- flux can support an N_2 flux of $0.5 \text{ mmol N}_2 \text{ m}^{-2} \text{ day}^{-1}$. The N_2/Ar profiles are steepest (maximum gradient) at approximately the same depth in the core where NO_3^- is completely removed from the porewaters ($\sim 6\text{--}10 \text{ mm}$). This further suggests that the production of N_2 in the cores is a result of denitrification.

The N_2 flux calculated above is a measure of the total denitrification rate; it includes not only denitrification of NO_3^- supplied from the overlying water but also of NO_3^- supplied from the nitrification of ammonia in the upper portion of the sediment column. Coupled nitrification–denitrification has been shown to account for more than 50% of the N_2 production in coastal and near-shore sediments that have oxygenated overlying water (Devol and Christensen, 1993; Hartnett and Devol, 2003). The removal of $24 \mu\text{M}$ of NO_3^- in the sediments via denitrification can account for $\sim 12 \mu\text{M}$ of N_2 . This assumes that all of the $24 \mu\text{M}$ NO_3^- supplied from the overlying water is denitrified (i.e., two NO_3^- are required to form each N_2 molecule). Assuming the increase in N_2 saturation of 8–13% above the equilibrium value of $430 \mu\text{M}$ requires the addition of $\sim 34\text{--}55 \mu\text{M}$ N_2 suggests that an additional $22\text{--}43 \mu\text{M}$ of N_2 must be supplied via coupled nitrification–denitrification in the sediments.

4. Conclusions

The MIMS probe has been shown to be a fast, precise method for determining N_2/Ar ratios that can

be used in sediment porewaters as well as in small-volume water samples. The probe is sturdy enough for use in sediment cores and small enough to be used to assess spatial heterogeneity with a small subcore. We have demonstrated that the N_2/Ar profiles determined with this method can be used to estimate the N_2 flux from sediment cores. The measured N_2/Ar ratios from Raritan Bay cores correspond to an N_2 flux of 1.9 to $3.7 \text{ mmol N}_2 \text{ m}^{-2} \text{ day}^{-1}$, well within the range for estuarine sediments exhibiting coupled nitrification–denitrification. This probe inlet for the membrane-inlet mass spectrometer will allow the further development of novel experimental techniques that require high-precision gas ratio measurements on small samples (for instance, small volume incubation experiments) that have not been heretofore possible.

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