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Net sediment N_2 fluxes in a southern New England estuary: variations in space and time

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Abstract Over the past three decades, Narragansett Bay has undergone various ecological changes, including significant decreases in water column chlorophyll *a* concentrations, benthic oxygen uptake, and benthic nutrient regeneration rates. To add to this portrait of change, we measured the net flux of N_2 across the sediment–water interface over an annual cycle using the N_2/Ar technique at seven sites in the bay for comparison with measurements made decades ago. Net denitrification rates ranged from about 10–90 μmol N_2–N m^{-2} h^{-1} over the year. Denitrification rates were not significantly different among sites and had no clear correlation with temperature. Net nitrogen fixation (−5 to −650 μmol N_2–N m^{-2} h^{-1}) was measured at three sites and only observed in summer (June–August). Neither denitrification nor nitrogen fixation exhibited a consistent relationship with sediment oxygen demand or with fluxes of nitrite, nitrate, ammonium, total dissolved inorganic nitrogen, or dissolved inorganic phosphate across all stations. In contrast to the mid-bay historical site where denitrification rates have declined, denitrification rates in the Providence River Estuary have not changed significantly over the past 30 years.

Keywords Sediment N_2 flux · Climate change · N_2/Ar technique · Denitrification · Nitrogen fixation · Narragansett Bay

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Introduction

> Integrated estimates of denitrification in coastal ecosystems are confounded by methodological difficulties, a lack of systematic understanding of the effects of the changing environmental conditions, and inadequate attention to spatial and temporal variability to provide both seasonal and annual rates. Cornwell et al. (1999).

The nitrogen (N) cycle is particularly complex and challenging to study due to the various forms of N in particulate, dissolved, and gaseous phases. An additional complication is that in the marine environment the supply of N is often limiting to primary production yet, when supplied in excess, it can lead to deleterious environmental conditions (Ryther and Dunstan 1971; Kemp et al. 2005). Whether N is the sole limiting nutrient (or if phosphorus also plays a role) in the marine environment and what the ultimate mechanism(s) responsible for N limitation in the marine environment is an area of continuing research and debate (Howarth et al. 1988a; Scott and

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McCarthy 2010; Howarth et al. 2011). Two opposing processes, denitrification and nitrogen fixation, are probably the main controlling mechanisms. Denitrification is the microbially mediated process that converts nitrate to dinitrogen (N_2) gas. Marine denitrification has received much attention in recent years because it can remediate, at least in part, cultural eutrophication (Seitzinger et al. 1984; Seitzinger 1987; Nowicki 1994; Cornwell et al. 1999). In contrast, N-fixation is the microbial conversion of N_2 gas to a bioavailable form of N. Until recently, the low rates of N fixation typically found in the marine environment were thought to account for the lack of biologically available (Howarth et al. 1988a, b; Galloway et al. 2003). However, several recent studies have found surprisingly high rates of marine N fixation using an assortment of techniques in a variety of environments (Capone 2001; Davis and McGillicuddy 2006; Gardner et al. 2006; Fulweiler et al. 2007).

As Cornwell et al. (1999), Groffman et al. (2006) and others have made clear, our understanding of denitrification across spatial and temporal scales and the mechanisms that control it are far from understood, at least in part because it is a difficult process to measure. Compared to the well-known Redfield stoichiometry of the open ocean, the low N:P ratios in coastal benthic nutrient fluxes (Nixon et al. 1976; Propp et al. 1980; Boynton and Kemp 1985) and the low N:P ratios in the water column first indicated that denitrification was an important N removal process. However, high background concentrations of N_2 in the water made direct flux estimates particularly challenging (Seitzinger et al. 1984; Cornwell et al. 1999; Groffman et al. 2006). Today, direct N_2 flux measurements are possible using high precision membrane inlet mass spectrometry (MIMS) and the N_2/Ar technique (Sisler and Zobell 1951; Kana et al. 1994, 1998). This approach is not without its problems (e.g., Eyre et al. 2002, 2004; Groffman et al. 2006), but it has the advantage of measuring direct net fluxes of N_2 compared with indirect estimates (e.g., stoichiometry or mass balance) and other direct estimates of N exchange (e.g., acetylene inhibition, ^{15}N tracers, etc.). Regardless of the method employed, various environmental factors have been shown to influence denitrification, including sediment organic matter, water column NO_3^- concentrations, bottom water oxygen concentrations, benthic microalgae and macrofauna, temperature, and salinity, (Sundback et al. 1991; Weston et al. 1996; Morlock et al. 1997; Cornwell et al. 1999; Cabrita and Brotas 2000).

The location of this study, Narragansett Bay, Rhode Island (USA), has had a pivotal role in the history of denitrification research. Nixon et al. (1976) were one of the first to observe that the dissolved inorganic nitrogen (DIN) flux stoichiometrically predicted from sediment oxygen uptake and DIP release was much higher than the measured DIN flux. The missing nitrogen was thought to have been lost as dissolved organic nitrogen (DON) or as N_2 gas (Nixon et al. 1976). Sediment DON fluxes were difficult to measure then and have been generally found to be low and into the sediments (Cowan and Boynton 1996; Burdige and Zheng 1998). An exception is a recent study in a subtropical estuary (Moreton Bay, Australia) which reported DON fluxes (16–64 μmol m^{-2} h^{-1}) comparable to observed DIN fluxes and generally higher than observed sediment N_2 fluxes (Ferguson and Eyre 2010). The first direct measurements of N_2 production (measured using gas chromatography) over an annual cycle on intact, unamended marine sediment cores were also made at three stations in Narragansett Bay (Seitzinger et al. 1980, 1984; Seitzinger and Nixon 1985). Combining these early studies with work by Nowicki (1994) and prorating denitrification rates for the fine grained sediment area in the bay, Nixon et al. (1995) estimated that 13–26% of the DIN entering Narragansett Bay from land and atmosphere was removed through sediment denitrification.

Since those first denitrification measurements were made over 30 years ago, Narragansett Bay has undergone some dramatic ecological changes (Sullivan et al. 2001; Nixon et al. 2004, 2009; Oviatt 2004; Li et al. 2009). Most notably, mean annual water column chlorophyll *a* concentrations in the mid-bay have declined by about 60% and mid-bay benthic nutrient regeneration rates are substantially depressed compared with measurements in the 1970s and 1980s (Fulweiler and Nixon 2009). As part of a larger study (Fulweiler et al. 2007; Fulweiler and Nixon 2009), we returned to two of the sites measured by Seitzinger et al. (1984) and added five additional sites in upper Narragansett Bay and the Providence River Estuary to measure net N_2 fluxes across the sediment water interface with the N_2/Ar technique.

Our purpose was to see if the changing ecology of the bay might also have impacted the major N removal process in the system. We previously reported the shift from net sediment denitrification to net sediment N fixation at some sites in Narragansett Bay (Fulweiler et al. 2007). Our purpose here is to report how net sediment N_2 fluxes vary spatially and temporally in Upper Narragansett Bay and the Providence River Estuary and, when appropriate, we include the mid-bay historical site data for comparison. We then relate sediment N_2 fluxes to benthic metabolism. The sites were chosen to take advantage of the north south gradient in nutrient concentrations and sediment organic matter found in the bay. We anticipated that denitrification rates would be higher in the more eutrophic portion of the upper bay and would decrease seaward.

Methods

Site description

Narragansett Bay and the sites for this study have been described in detail elsewhere (Nixon et al. 1995; Fulweiler et al. 2007; Fulweiler and Nixon 2009). Briefly, Narragansett Bay is a 328 km^2 phytoplankton-based temperate ecosystem (latitude 41°N) with a mean depth of 8.6 m and a mean flushing rate of 26 days (Pilson 1985; Nixon 1995). Unlike many estuaries, freshwater input is low (100 m^3 s^{-1}), resulting in a generally well-mixed system with occasional vertical stratification (Nixon et al. 2005). Salinity is fairly uniform and only exhibits a slight down-bay gradient from around 26 psu at the mouth of the Providence River Estuary to around 32 psu at the mouth of Narragansett Bay. Mean annual bottom water concentrations (μM) of DIN and DIP are highest in the eutrophic Providence River Estuary (12.2 ± 8.4; 2.4 ± 11.6, respectively) and Upper Bay (8.8 ± 8.5; 1.6 ± 1.0) and decrease toward the mouth of the estuary (lower bay: 6.4 ± 6.9; 1.0 ± 0.4; (Kremer and Nixon 1978). The annual cycles of all of the major nutrients in near- surface and near- bottom water at a mid bay site are available at http://www.gso.uri.edu/phytoplankton/.

Silt and medium/coarse sand sediments characterized the majority of our sites (Table 1). From here forward we define Narragansett Bay proper as the main section of the estuary below Conimicut Point and excluding Mount Hope Bay and the Sakonnet Passage; Providence River Estuary is the northern most stem of the bay above Conimicut Point, and Greenwich Bay is the western arm (Fig. 1).

Sediment collection and incubation

We collected sediment samples for net N_2 flux analysis at seven stations in Narragansett Bay between June 2005 and September 2006. Each station was sampled at least four times during this period and incubated in the dark at in situ temperatures ranging from 6 to 23°C, approximately the annual temperature range. Intact triplicate cores (10 cm inner diameter and 30.5 cm long) were taken at each site using either a 4.5 m long pull corer or SCUBA divers. In either case, the overlying water and delicate flocculent surface layer were retained during core collection. We took care to maintain sediment structure whenever cores were collected or moved. We transported the capped cores in ambient water-filled coolers to an environmental chamber at the Graduate School of Oceanography. The sediment cores were placed in a water bath in the dark and air was gently bubbled through the surface water overnight or until the incubation began (8–16 h). Before each incubation we carefully replaced the water overlying each core with filtered (1 μM) lower Narragansett Bay (~32 psu) water collected concomitantly with the sediment cores and maintained in the same environmental chamber. Thus, the replacement water was at the same temperature and conditions as the sediment cores. The cores were then sealed with a gas tight lid (no headspace) and gently stirred at approximately 40 rpm using magnetic stir bars attached to the core lids. Replicate water samples for N_2/Ar analysis were collected at five points over the course of an incubation and preserved in exetainers with 20 μl of saturated $HgCl_2$ solution. The exetainers were then stored under water at incubation temperature until analysis. Typically analysis was completed with 4–6 weeks of sample collection. Initial and final water samples were collected for Winkler analysis of dissolved oxygen (Carrit and Carpenter 1966). An additional core container with filtered water and no sediments was incubated as a "control". If necessary, corrections were made for any changes that occurred in the

Table 1 Some characteristics of the seven stations where sediments were collected for net N_2 measurements from June 2005 to September 2006

Site	Grain size 0–2 cm[a]	Chl *a* 0–1 cm μg g^{-1}[b]	C:N 0–1 cm[c]	1% light level, m[d]	Mean water depth, m
Field's point	78% Silt/coarse silt	3.3 (±2)	16.6 (±5.1)	6	3
Conimicut point	nm	9.6 (±0.1)	11.4	7.2	3
Barrington	87% Medium/fine sand	4.7 (±2.1)	6.1 (±0.1)	nm	3
Greenwich Bay—Inner	77% Medium/coarse sand	9.9 (±1.6)	9.2 (±0.6)	6.7	3
Greenwich Bay—Middle	63% Medium/coarse sand	5.1 (±4.8)	6.7 (±0.7)	nm	4
Greenwich Bay—Outer	80% Medium/coarse sand	5.6 (±3)	7.2 (±3.6)	nm	3
Jamestown	75% Silt/coarse silt	2.4 (±0.9)	10.3 (±0.3)	9	8

[a] Grain Size analysis performed by Rex Tien from Narragansett, RI EPA Lab using a Malvern2000 grain size analyzer. www.malvern.com/ms2000. Fulweiler et al. (2007)

[b] Sediment chlorophyll a concentrations measued in 7/2006 for Conimicut Point, Barrington and Jamestown; for all stations it was measured in 10/2006

[c] Sediment C:N analyzed by the University of Georgia Stable Isotope Laboratory. All values from summer sediment collection except for Field's Point (10/2006)

[d] Light level calculated from Oviatt et al. (2002); *nm* not measured

control core, but generally these changes were negligible. Oxygen concentrations declined by at least 2 mg l^{-1}, but incubations were stopped before oxygen dropped below 2 mg l^{-1}. Incubations lasted between 4 and 31 h.

After the N_2/Ar incubation, sediment cores were incubated for the dissolved inorganic nutrient fluxes. A complete description of these incubations has been published elsewhere (Fulweiler et al. 2010). Briefly, the overlying water was carefully removed and replaced with filtered (1 μM) lower Narragansett Bay water. The cores were then sealed with the gas-tight lid used in the N2/Ar incubations. Over the course of an incubation we collected water samples for DIN (ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-)) and DIP (PO_4^{3-}). We collected water samples at three time points (initial, mid, and final) using acid washed 60-ml polypropylene syringes and glass fiber filters (Whatman GF/F 0.70 μm). The filtrate was captured and stored in acid-washed polyethylene bottles and stored at −15°C until analysis on a Lachat Instrument QuikChem 8000 flow injection analyzer using standard techniques (Grasshoff 1976). Nutrient incubations lasted between 5 and 34 h depending on the season and were stopped after O_2 concentrations had dropped by at least 2 mg l^{-1} (Fulweiler et al. 2010).

Sample and data analysis

Dissolved gas samples were analyzed with a quadrupole membrane inlet mass spectrometer that requires a small sample size (<10 ml), and no sample preparation. The instrument allows rapid throughput (~20–30 samples h^{-1}) and provides a precision of ±0.03% (Sisler and Zobell 1951; Kana et al. 1994, 1998). For the N_2/Ar method, the change in N_2 concentration was determined from the change in the measured N_2/Ar multiplied by the predicted water Ar concentration at air saturation (Colt 1984). N_2 change for each of the triplicate cores was determined from a five-point linear regression. Rates were then prorated for the volume of water overlying the core and the sediment area of the core. The N_2/Ar technique is actually a measure of net N_2 flux (gross denitrification—gross N fixation). From here forward, positive N_2 fluxes are considered to be a net denitrification rate, while negative N_2 fluxes indicate net N fixation.

We tested for differences among sites and relationships with temperature with two-way ANOVA and analysis of co-variance using the statistical program SAS. If differences existed, we used a least significant difference (LSD) post hoc test to determine which stations were different from each other. We used an alpha level of 0.05 for all statistical tests unless noted.

Results and discussion

Spatial and temporal variability

Denitrification rates ranged from about 10–90 μmol N_2–N m^{-2} h^{-1} (Table 2), with the highest mean rate observed at the inner Greenwich Bay site (Fig. 1 site 4). Rates were not significantly different among stations, confirming the surprising finding of Seitzinger et al. (1984) who also reported similar denitrification rates throughout the bay despite the more organic rich sediments in the Providence River Estuary versus Narragansett Bay proper [>4% and 2–3% C LOI, respectively; (Murray et al. 2007)] (Table 3). Low rates of N-fixation were measured at the outer Greenwich Bay site in August of 2005 and high rates of N fixation at four other sites in the summer of 2006, ranging from −5 to −650 μmol N_2–N m^{-2} h^{-1} (Fig. 2; Table 2). N fixation rates were also not significantly different among sites except for Barrington ($p < 0.01$). The lack of any clear spatial pattern in net sediment N_2 fluxes in this system is

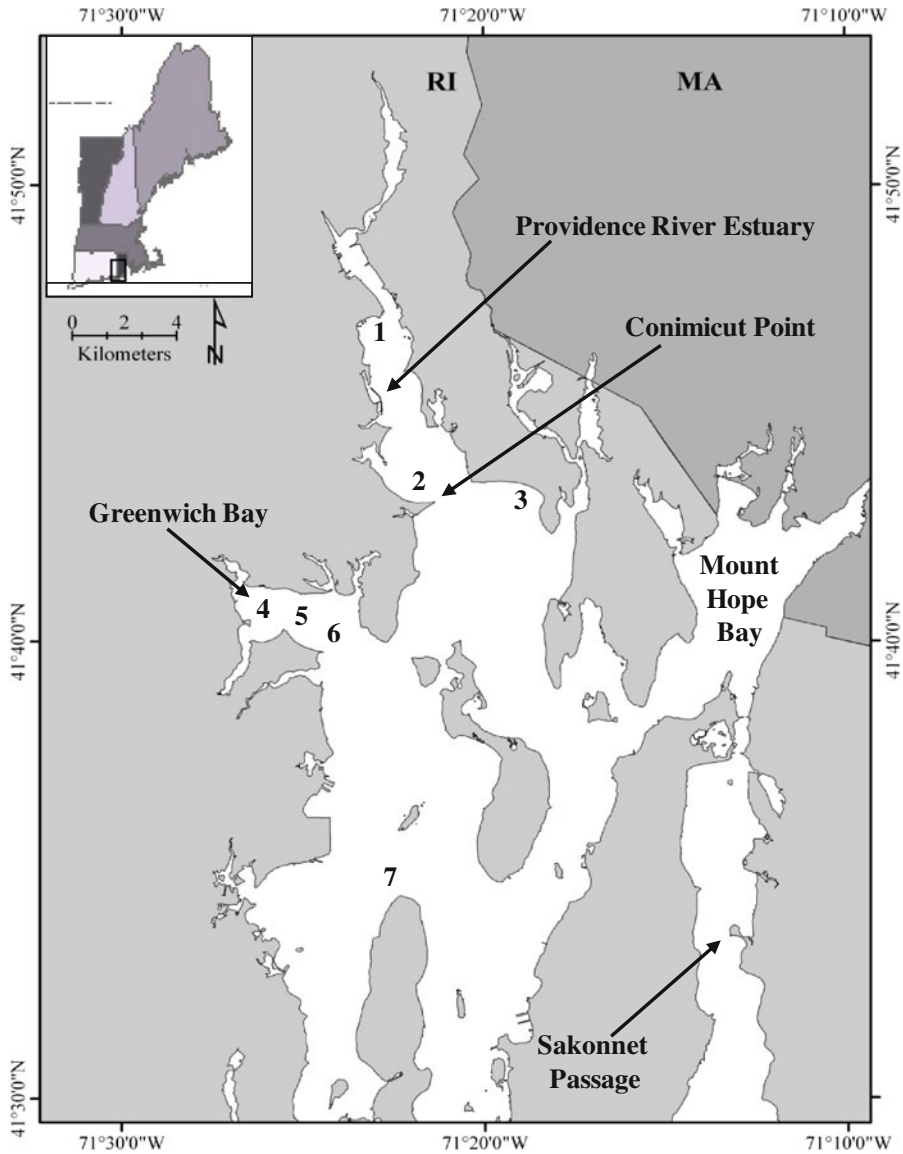

Fig. 1 Sampling locations for net N_2–N fluxes across the sediment–water interface in Narragansett Bay, Rhode Island. *1* Field's Point, *2* Conimicut Point, *3* Barrington, *4* Greenwich Bay—Inner, *5* Greenwich Bay—Middle, *6* Greenwich Bay—Outer, *7* Jamestown

consistent with the lack of significant spatial gradients in benthic metabolism in Narragansett Bay proper as measured by oxygen uptake or dissolved inorganic nutrient regeneration (Hale 1975, Nixon et al. 1976).

While significant differences ($p < 0.05$) were found among sites at each temperature, no clear pattern emerged (Fig. 2; Table 4). Temperature only had a significant effect on the most anthropogenically impacted sites in the upper bay (Fig. 1 sites 1–3) and inner Greenwich Bay (Fig. 1 site 4; Table 5). No clear correlation of sediment denitrification with temperature in this system was also reported by Seitzinger et al. (Seitzinger et al. 1984).

Various studies in other systems have shown a strong seasonal pattern in denitrification, where higher temperatures increased denitrification (Jorgensen 1989; Cabrita and Brotas 2000). In addition, a variety of studies have observed a strong sediment N_2 flux response to changes in organic matter deposition and/or content (Seitzinger and Giblin 1996; Caffrey et al. 1998; Cornwell et al. 1999; Fulweiler et al. 2008). Increases in sediment denitrification have also been found in mid Narragansett Bay sediments in mesocosm nutrient addition experiments (Seitzinger and Nixon 1985; Nowicki and Oviatt 1990). Thus, the lack of a significant difference in N_2 fluxes

Table 2 Net N_2–N fluxes at the sediment water interface from seven stations in Narragansett Bay (±SD)

Site (# on map, Fig. 1)	Date	Temperature °C	N_2–N μmol m^{-2} h^{-1}
Field's point (#1)	4/17/2006	6	67.9 (±25.3)
	11/20/2005	13	50.3 (±10.4)
	7/8/2006	18	−26.6 (±3.6)
	8/31/2006	22	−246.4 (±9.8)
Conimicut point (#2)	4/17/2006	6	17.5 (±8.3)
	11/20/2005	13	21.8 (±20.8)
	7/8/2006	18	−30.3 (±5.2)
	8/22/2005	23	62.6 (±24)
Barrington (#3)	4/17/2006	6	38.3 (±32.3)
	11/20/2005	13	8.2 (±3)
	7/17/2006	18	−136.6 (±19.4)
	8/31/2006	22	−652.0 (±200.5)
Greenwich Bay—Inner (#4)	4/7/2006	6	59.1 (±5.8)
	11/14/2005	14	11.9 (±2.9)
	6/23/2005	18	93.3 (±25.6)
	7/28/2005	22	29.5 (±20.6)
	9/21/2005	23	33.3 (±11.6)
Greenwich Bay—Middle (#5)	4/7/2006	6	48.6 (±25.4)
	11/14/2005	14	13.2 (±10.9)
	6/23/2005	18	38.0 (±59.7)
	8/11/2005	23	65.2 (±53.2)
Greenwich Bay—Outer (#6)	4/7/2006	6	29.1 (±30.6)
	11/5/05	14.2	19.7 (±11.2)
	6/29/2005	18	38.6 (±36.9)
	8/18/2005	23	−4.8 (±29.2)
Jamestown (#7)	4/30/2006	6	79.3 (±9.8)
	11/5/05	14	24.5 (±5.7)
	7/1/2005	18	57.3 (±53.7)
	7/17/2006	18	−174.9 (±13.2)
	8/12/2006	22	−213.5 (±37.8)
	8/26/2005	23	44.6 (±12)

Positive N_2–N indicates net denitrification and negative N_2–N indicates net N Fixation

Table 3 Spatial correlation of mean N_2–N fluxes at seven stations in Narragansett Bay

Site	Grouping
Site 1: Field's point	C
Site 2: Conimicut point	ABC
Site 3: Barrington	D
Site 4: Greenwich Bay—inner	A
Site 5: Greenwich Bay—middle	AB
Site 6: Greenwich Bay—outer	ABC
Site 7: Jamestown	BC

Means with the same letter are not significantly different

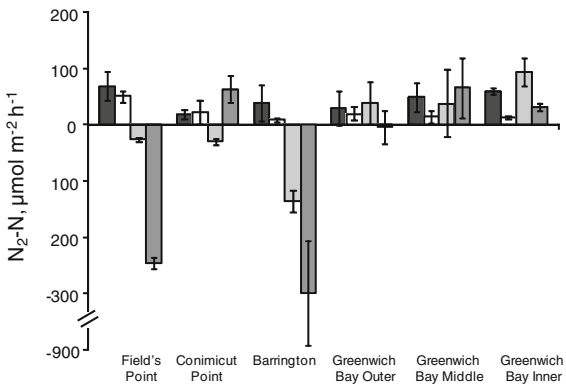

Fig. 2 Spatial distribution of mean net N_2–N fluxes for stations 1–6. N_2–N fluxes are averaged by temperature: 6°C (*dark bar*), 14°C (*open bar*), 17°C (*light grey bar*), 22°C (*dark grey bar*). Temperatures are 1°C

between the Providence River Estuary with higher water column nutrient concentrations, primary production, and sediment organic matter and the mid bay site is puzzling. The Providence River Estuary also exhibited the highest rates of sediment oxygen demand (SOD) (Fulweiler et al. 2010). We only observed N fixation in these sediments during summer at ambient water temperatures of 17 and 22°C. This is consistent with other studies in a variety of environments which have observed a strong correlation between rates of N fixation and ambient temperature (Chapin et al. 1991; Marcarelli and Wurtsbaugh 2006; Boyd et al. 2010).

Sediment net N_2 flux and benthic metabolism

Various studies have reported a strong positive relationship between SOD and denitrification rates (Seitzinger and Giblin 1996; Laursen and Seitzinger 2002; Piehler and Smyth 2011). However, we found no significant relationship between net sediment N_2 fluxes and SOD for any of the stations except Barrington (Table 6). Sediment net N_2 fluxes varied strongly as a function of sediment nitrite flux at Field's Point and Barrington ($R^2 = 0.77$, 0.62, respectively). Sediment net N_2 fluxes were not a function of sediment nitrate flux at any of the stations except Conimicut Point (Fig. 1 site 2; Table 6). At Conimicut Point, sediment nitrate uptake was positively correlated ($R^2 = 0.65$) with net N_2 production (i.e., denitrification). This correlation between sediment nitrate uptake and net N_2 production is indicative of direct denitrification.

Sediment net N_2 fluxes varied significantly as a function of ammonium for each of the sites (Fig. 3, Table 6) except Inner Greenwich Bay (Fig. 1 site 4). Only in some cases were high ammonium fluxes out of the sediment accompanied by high N fixation rates (Site 1: $R^2 = 0.82$) and low denitrification rates by high ammonium uptake rates (Site 6: $R^2 = 0.50$). Net sediment N_2 flux did not vary consistently with sediment DIN flux, but at Sites 1 and 3, increasing DIN efflux corresponded with high rates of N fixation ($R^2 = 0.80$, 0.51, respectively). Finally, net sediment N_2 flux did not vary as a function of DIP flux at any of the stations except in the upper Providence River (Fig. 1 site 1), where an increase in DIP flux out of the sediment was accompanied by an increase in N fixation (Table 6).

Nitrate for denitrification can come directly from the water column and diffuse into the sediments (direct denitrification) or it can be produced by the microbial oxidation of ammonium during nitrification (coupled nitrification–denitrification) (Jenkins and Kemp 1984; Seitzinger 1988; Risgaard-Petersen 2003). In many coastal marine systems coupled nitrification–denitrification dominates and can account for 60–100% of the total denitrification (Laursen and Seitzinger 2002). Denitrification was positively correlated with nitrate uptake only at Conimicut Point (Fig. 1 site 2) suggesting that this estuary is dominated by coupled nitrification–denitrification. This is consistent with earlier work in Narragansett Bay that observed that the mean net flux of $NO_3^- + NO_2^-$ was out of, rather than into, the sediments and therefore concluded direct denitrification was not important (Seitzinger et al. 1984). In addition, low summer water column nitrate concentrations make direct denitrification particularly

Table 4 Spatial variability of the net sediment N_2 fluxes as a function of temperature at seven stations in Narragansett Bay, RI

Site	Temperature °C			
	6	14	17	22
Site 1: Field's point	AB	A	ABC	B
Site 2: Conimicut point	C	B	ABC	A
Site 3: Barrington	BC	B	C	C
Site 4: Greenwich Bay—inner	AB	B	A	A
Site 5: Greenwich Bay—middle	ABC	B	AB	A
Site 6: Greenwich Bay—outer	BC	B	AB	A
Site 7: Jamestown	A	B	BC	A

Means with the same letter are not significantly different

At 6, 14 and 17°C $p < 0.05$; at 22°C $p < 0.001$

Table 5 The effect of temperature on the net N_2 flux at seven stations in Narragansett Bay, RI

Site	Temperature °C			
	6	14	17	22
Site 1: Field's point**	A	A	B	C
Site 2: Conimicut point**	B	B	C	A
Site 3: Barrington***	A	A	A	B
Site 4: Greenwich Bay—inner**	B	C	A	C
Site 5: Greenwich Bay—middle	ns	ns	ns	ns
Site 6: Greenwich Bay—outer	ns	ns	ns	ns
Site 7: Jamestown	ns	ns	ns	ns

Means with the same letter are not significantly different

** $p < 0.001$; *** $p < 0.0001$; *ns* not significant

Table 6 Results of regression analysis of N_2–N as a function of other benthic flux constituents

Site	O_2^-	NO_2^-	NO_3^-	NH_4^+	DIN	DIP
Site 1: Field's point	ns	***	ns	***	***	**
Site 2: Conimicut point	ns	ns	**	*	*	ns
Site 3: Barrington	**	**	ns	*	**	ns
Site 4: Greenwich Bay—inner	ns	ns	ns	ns	ns	ns
Site 5: Greenwich Bay—middle	ns	ns	ns	*	*	ns
Site 6: Greenwich Bay—outer	ns	ns	ns	**	**	ns

ns not significant

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

unlikely for sediments in the mid and lower bay (Fulweiler and Nixon 2009). In fact, experimental additions of 50 μM nitrate water to sediment cores from the mid-bay did not change the net sediment N_2 flux (Fulweiler et al. 2008).

Net N_2 flux historical trends in Narragansett Bay

Denitrification was measured in 1978 and 1979 at two sites in Narragansett Bay with what was then a novel direct N_2 method (Seitzinger et al. 1984). Briefly, this

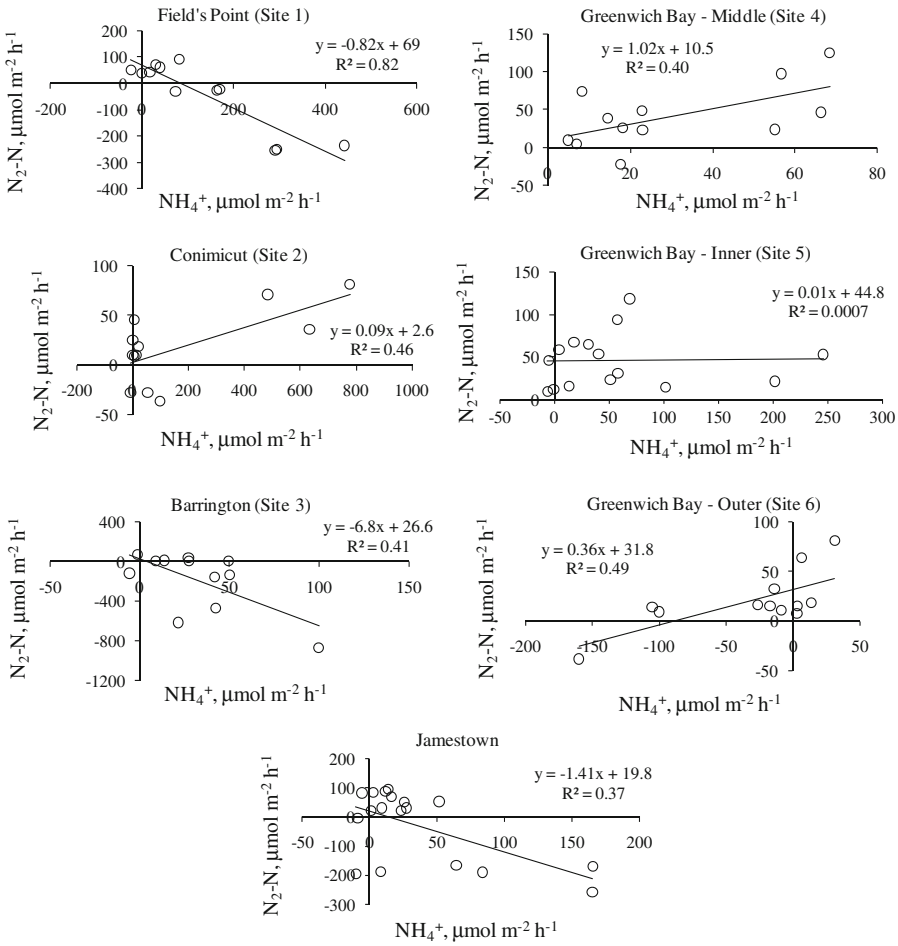

Fig. 3 Sediment net N_2–N fluxes as a function of sediment ammonium fluxes for seven sites in Narragansett Bay. Significant correlations are observed for all of the sites except Greenwich Bay Inner (Site 5)

method involved the gas tight incubation of sediment cores at ambient temperature. The overlying water was repeatedly replaced until all background N_2 from porewater was removed and N_2 production could be measured overtime, from head space samples collected for measuring N_2 concentrations on a gas chromatograph (Seitzinger et al. 1984). The historical denitrification measurements from Site 2 (Conimicut Point) and those from this study are not statistically different (Fig. 4). SOD and sediment fluxes of ammonium, nitrate, and nitrite at this site and in the upper Providence River Estuary have not changed significantly since earlier measurements in 1975 and 1976 by Elderfield et al. (1981) or in 1983 and 1984 by Nixon et al. (1990a, b) (Fulweiler et al. 2010). This is contrary to our findings from a historic site in mid Narragansett Bay (Fig. 1 site 7), where the mean annual denitrification rate significantly declined ($p < 0.01$) from 74 µmol N_2–N m^{-2} h^{-1} in 1979 to 40 µmol N_2–N m^{-2} h^{-1} in 2005 and the spring of 2006; oxygen uptake and nutrient regeneration rates had also declined markedly in 2005 compared with the 1970s (Fulweiler and Nixon 2009). This suggests that the ecological changes affecting the mid-bay site [e.g., declining chlorophyll and productivity, shifting phenology of blooms; (Fulweiler and Nixon 2009; Nixon and Fulweiler 2009)] may not be altering the more anthropogenically impacted Upper Bay and Providence River Estuary.

Nitrogen fixation

At this time, we do not know what organisms were responsible for the sediment nitrogen fixation in the bay. It is unlikely that the N fixation was driven by cyanobacteria because the sediment cores were maintained in darkness and all of our incubations were conducted in the dark. Sediments from several sites

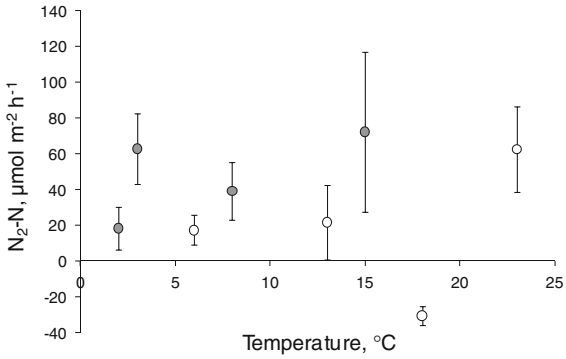

Fig. 4 N_2–N fluxes (mean ± SD) as a function of temperature measured in 1979 by Seitzinger (1984) (*shaded circle*) and those of this study (*open circle*) for Conimicut Point

(Fig. 1 sites 1, 3, 5, and 7) were also analyzed for the presence or absence of the cyanobacteria pigment, Zeaxanthin (Pinckney et al. 2001; Paerl et al. 2003). Only Site 1 at the head of the Providence River Estuary tested positive (K. Rossignol, University of North Carolina, Chapel Hill, pers. commun.). While chlorophyll *a* was present in the sediment at each station, we don't know if this was epibenthic chlorophyll or settled chlorophyll from the water column (Table 1). The lack of cyanobacteria pigment at the other sites implies that they are likely not the main contributor to N fixation in Narragansett Bay. If we discount Site 1, then the observed sediment N fixation was probably primarily carried out by heterotrophic bacteria. We also measured nitrogen fixation in surface sediment (0–2 cm) at three sites (Fig. 1 sites 1, 3, and 7) with the acetylene reduction assay (ARA). Measured in this way, nitrogen fixation rates followed a similar pattern to that observed using the N_2/Ar technique, with the highest rates at Site 3. The addition of molybdate, a specific inhibitor of sulphate-reducing bacteria, inhibited acetylene reduction by about 60% for Site 1 (Fulweiler et al. 2007). This suggests that the bacteria responsible for N fixation are probably sulfate reducers and that at Site 1 fixation may be due to both autotrophic and heterotrophic nitrogen fixers.

The question remains as to why bacteria in sediments presumably rich in nitrogen would need fix their own nitrogen. After all, nitrogen fixation is an energetically expensive process consuming approximately 16 mol ATP per mol of N_2 fixed (Postgate et al. 1987). Traditionally, organisms that fix N tend to have lower growth rates than those who use ammonium (Postgate 1982; Yoch and Whiting 1986). In addition, it is widely assumed that ammonium concentrations control rates of N fixation through regulation of the enzyme nitrogenase. Unfortunately, we did not measure porewater ammonium concentrations in this study. However, we did measure ammonium fluxes and at the outer Greenwich Bay site and mid-Narragansett Bay site (Fig. 1 site 6 and 7, respectively) we found significant decreases ammonium flux from the sediments over the last 30 years (Fulweiler et al. 2010). This suggests that lower ammonium concentrations would also be found in the sediments, thus increasing the potential for N fixation. In addition, it is well known that O_2 quickly and permanently inactivates nitrogenase, the enzyme responsible for N fixation (Paerl and Carlton 1988; Tibbles et al. 1994; Coyer et al. 1996). Estuarine sediments, such as these, maybe provide hypoxic or anoxic conditions that preserve the nitrogenase enzyme thus making N fixation possible.

Greenwich Bay and Narragansett Bay nitrogen budgets

Before this study, denitrification had not been measured in Greenwich Bay, an embayment in the northwest corner of Narragansett Bay (Fig. 1). Various nitrogen input inventories for Greenwich Bay have been developed (DiMilla et al. 2011). Granger et al. (2000) and the Rhode Island Coastal Resources Management Council (CRMC) Special Area Management Plan (SAMP) independently estimated a range of N inputs of about 10–18 million moles per year. And a recent isotopic study by DiMilla et al. (2011) reported that Narragansett Bay proper contributes approximately 54% of the DIN input to Greenwich Bay. Recent mapping has shown a variety of sediment types in Greenwich Bay, ranging from sand in the eastern Bay to fine-grained silt and silty sand in the western portion (Oakley and Boothyroyd 2006). The surface sediments (0–6 cm) from our Greenwich Bay sites were predominantly (>70%) medium sand (Table 1). Because mean site denitrification rates were not significantly different from each other we applied the average denitrification rate to the entire Greenwich Bay. On an annual basis, the mean denitrification rate for all of Greenwich Bay, about 4×10^6 mol year, could remove 20–40% of the total nitrogen input. This is similar to

denitrification removal rates found in other estuaries (Seitzinger 1988) and roughly equal to the combined amount of N entering Greenwich Bay directly from the local wastewater treatment plant and from groundwater (DiMilla et al. 2011).

Determining N removal by denitrification for Narragansett Bay proper is not as straightforward as it was for Greenwich Bay. Nixon et al. (1995) previously reported an annual input of 650 million moles of N to the Bay. If we apply the mean denitrification rates of Seitzinger et al. (1984) and Nowicki (1994) to the area of fine-grained sediment in the bay as a whole (217 km^2 or ~70% of Narragansett Bay), then denitrification removed approximately 13–18% of the total N input. However, Nixon et al. (2008) recently revised the annual input to 576 million moles N to Narragansett Bay. The 11% decrease is due to the handling of unmeasured and un-gauged rivers, seeps, or surface flows. If we apply the denitrification rates of Seitzinger et al. (1984) and Nowicki (1994), again restricted to the area of fine-grained sediment, to the revised total N input (576×10^6 mol N year), then denitrification previously removed 15–20% of the total N input.

The net denitrification we measured in 2005 and 2006, when applied to the area of fine grained sediment, could remove about 76 million moles annually, or about 13% of the total annual N input. The situation changed markedly in 2006, when N fixation was found in the summer months. Averaging the summer 2006 net N fixation rates from all Narragansett Bay proper sites and applying them to the area of fine grained sediment, we estimate total N fixation in June, July, and August of about 100×10^6 mol of N. This is almost twice as much as summer N inputs from direct sewage discharge and atmospheric deposition combined (Nixon et al. 2008). Sediment N fixation increased total annual N inputs by almost 16% (Table 7). If we apply the net denitrification rate of 2005/06 (76×10^6 mol year) to the remaining 9 months of the year, denitrification could remove about 57×10^6 mol of N. Thus, over the complete annual cycle, at least in 2006, the sediments added ~40×10^6 mol of N to the bay in contrast to the past, when they were a net sink removing about 80×10^6 mol year. Recent and upcoming N reductions from wastewater treatment plants may further markedly increase the importance of sediment N dynamics in the bay (Nixon et al. 2008).

Table 7 Nitrogen inputs to Narragansett Bay, units are millions (10^6) mol N per year

Direct atmospheric deposition[a]	30
Rivers[b]	322
Unmeasured surface drainage[c]	16
Urban runoff[c]	37
Direct sewage discharge[d]	171
Nitrogen fixation[e]	99
Total Inputs	675

Table modified from Nixon et al. (2008) for 2003–2004

[a] DIN and DON

[b] Includes DIN and DON for all measured rivers and the Taunton River

[c] Includes DIN and DON

[d] Includes DIN and DON

[e] Mean summer 2006 nitrogen fixation rates measured in Narragansett Bay proper

Conclusion

Despite strong down bay gradients in water column inorganic nutrients, chlorophyll *a*, and primary production that characterize Narragansett Bay as a whole [e.g. (Oviatt et al. 2002)], we did not observe a down bay gradient in net sediment N_2 fluxes. In addition, there was no clear relationship between net N_2 fluxes and temperature, SOD, or benthic nutrient fluxes. In some ways, this is surprising as various studies have reported strong connections between these environmental factors and N_2 fluxes [e.g., (Piehler and Smyth 2011)]. At the same time, we know that metabolic processes in the sediment can be patchy [coefficients of variation of triplicate benthic inorganic nutrient flux measurements in Narragansett Bay range from 40 to 140%; (Nixon et al. 1980)], and there are probably an equal number of studies reporting no significant relationships between N_2 and common environmental parameters. It is possible that our sample size of triplicate cores was not enough to overcome the inherent variability in the system and if we increase the number of cores we may be able to observe spatial and temporal variations. For example, Bartoli et al. (2003) reported that four replicate cores were sufficient for good accuracy for measuring SOD and nitrate fluxes but that over ten replicates were needed for accurate ammonium fluxes. In addition, because the N_2/Ar technique provides a net measurement of N_2 flux by the entire microbial community within the

sediment, it is possible that significant relationships between environmental parameters and either denitrification or N fixation may be masked in the overall net N_2 flux.

The natural addition of nitrogen through sediment N fixation in Narragansett Bay leads to an interesting dilemma for scientists and managers alike. Narragansett Bay is in the process of undergoing a substantial reduction in sewage derived nitrogen as the major wastewater treatment plants move toward tertiary treatment from May to October. However, the ecology of at least the central portions of the bay where there are multi decadal records is already responding in surprising ways to climate mediated changes (Nixon et al. 2009). Narragansett Bay is good example of the complex response of ecosystems to human forces both at local (i.e., nutrient loading) and regional/global (i.e., warming water temperatures) scales. These findings highlight that as we move forward with nutrient mitigation in coastal systems we must keep in mind the dynamic nature of ecosystems—as Duarte et al. (2009) have argued, we should not be surprised by their non-linear response to change.

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