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(Nearly) A Decade of Directly Measured Sediment N₂ Fluxes

What Can Narragansett Bay Tell Us About
the Global Ocean Nitrogen Budget?

BY ROBINSON W. FULWEILER AND ELISE M. HEISS

*“...one is impressed with the enormous gaps in
our knowledge of the conditions of life in the sea.”*

—James Johnstone, 1908
Conditions of Life in the Sea

ABSTRACT. The tight coupling between nitrogen and carbon cycling has important implications for global climate. These two cycles are under growing anthropogenic pressures (e.g., warming temperatures, changes in nitrogen loading). In this article, we use Narragansett Bay as a model system to explore how large- and small-scale human forcings alter marine sediment nitrogen cycling. We measured net sediment N_2 fluxes at two stations in Narragansett Bay over a nine-year period (2005–2013), resulting in observed mean net denitrification rates of $85 \mu\text{mol m}^{-2} \text{h}^{-1}$ and $40 \mu\text{mol m}^{-2} \text{h}^{-1}$ at the highly impacted and the less impacted sites, respectively. However, mean net N-fixation was essentially the same at each site (-89 and $-88 \mu\text{mol m}^{-2} \text{h}^{-1}$). We found significant relationships between mean summer (June, July, August) water column chlorophyll and mean summer sediment N_2 fluxes. Using these relationships and the long-term chlorophyll record in Narragansett Bay, we predicted summer net sediment N_2 fluxes for the last 40 years. This approach suggests that the coastal ocean nitrogen cycle responds rapidly to changes in organic matter availability. If such trends hold true for the global ocean, the marine nitrogen cycle as a whole may also be undergoing significant changes.

INTRODUCTION

As marine phytoplankton bloom in surface waters, die, and descend to the deep ocean, they carry with them atmospheric carbon dioxide (CO_2). This oceanic “biological pump” drives Earth’s climate because it helps to determine the concentration of CO_2 in the atmosphere. If this biological pump were to disappear completely, it is estimated that atmospheric CO_2 concentrations would increase by more than 200 ppm (Gruber and Galloway, 2008). In marine waters, at least on short time scales, primary

production is generally considered to be nitrogen (N) limited. Thus, N availability helps regulate ocean primary productivity, atmospheric CO_2 levels, and ultimately global climate (Falkowski, 1997).

A major controlling factor of N limitation in marine systems is the balance of two microbially driven processes, nitrogen fixation and denitrification (Codispoti, 2007). N-fixation is the microbial conversion of inert dinitrogen (N_2) gas to biologically usable N. Conversely, denitrification converts nitrate (NO_3^-) into N_2 gas, thereby

removing it from the labile N pool for most organisms (Figure 1). Nitrogen loss via denitrification is critical for mitigating cultural eutrophication (such as fertilizer runoff and sewage discharge) and is responsible for removing up to 50% of biologically reactive N from coastal waters (Seitzinger et al., 2006). Canonical denitrification occurs through two pathways, direct and coupled denitrification. During direct denitrification, NO_3^- from the overlying water diffuses into anaerobic sediment where it is converted to N_2 . Alternatively, denitrification can be coupled to nitrification, the two-step oxidation of ammonium (NH_4^+) to NO_3^- (Figure 1). Coupled nitrification-denitrification is the dominant pathway of N removal in a variety of coastal and continental shelf environments (Fulweiler and Nixon, 2012, and references therein). Recently, another N_2 producing mechanism, anammox (anaerobic oxidation of ammonium by nitrite to N_2), was found to play an important role in some marine ecosystems. However, the role of anammox in coastal regions appears small and accounts for just 6% ($\pm 2\%$) of the total N_2 production in systems less than 16 m deep (Dalsgaard et al., 2005).



NARRAGANSETT BAY AS A MODEL SYSTEM

Human activities, including land use change, increased fertilizer application, and fossil fuel combustion, impact marine ecosystems at both local and regional/global scales. Teasing apart the effects of these different impacts is a challenging effort. Yet, it is a critical effort if we are to understand, protect, and restore marine ecosystems. Narragansett Bay provides an ideal natural laboratory to examine anthropogenic impacts across small and large scales.

Narragansett Bay is a temperate (41°N), 328 km², phytoplankton-based system with a mean depth of 8.6 m at Mean Low Water (MLW) and a mean water residence time of 26 days (Pilson, 1985). It runs along a north-south gradient with the city of Providence at the head and the Atlantic Ocean at

the mouth. Freshwater input is low (100 m³ s⁻¹), and salinity ranges from approximately 20 in Providence River Estuary surface waters to approximately 32 at the mouth (Figure 2). There is a strong gradient in anthropogenic nutrient loading and thus primary production rates and water column chlorophyll concentrations are highest in the Providence River Estuary and decrease down bay (Nixon et al., 2009).

Narragansett Bay is a well-defined system whose ecology has been studied since the early 1900s. There are time-series measurements of water temperature, water column nutrients, chlorophyll concentrations, phytoplankton species abundance, and benthic nutrient regeneration that span many decades.

As observed globally, sea surface temperature in Narragansett Bay is increasing. The most recent studies on

water temperature show an overall mean increase of 1.2°C in the four decades since the 1970s, with a 1.7°C increase in winter and a 1.0°C increase in summer (Nixon et al., 2009). This temperature increase has been linked to various ecological changes, including a decrease in mean annual water column chlorophyll concentrations (Li and Smayda, 1998) due to the loss of the winter-spring diatom bloom (Oviatt et al., 2002) and replacement of boreal demersal fish with demersal decapods (Oviatt, 2004). Significant changes have also been observed in the biogeochemical cycling at a station in mid-Narragansett Bay, including decreases in sediment oxygen demand, benthic nutrient fluxes, and denitrification rates (Fulweiler and Nixon, 2009; Fulweiler et al., 2010). In the summer of 2006, we observed a surprising shift from net denitrification

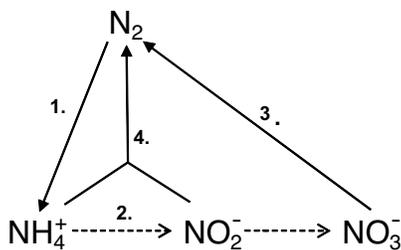


Figure 1. Diagram of N cycling processes discussed in this paper. (1) N fixation: transformation of dinitrogen (N₂) gas to ammonium (NH₄⁺). (2) Nitrification: the two-step oxidation of ammonium to nitrite (NO₂⁻) and then to nitrate (NO₃⁻), an aerobic process that can also occur in the water column. (3) Denitrification: the reduction of nitrate to N₂ gas, often fueled by nitrification. (4) Anammox: the anaerobic oxidation of ammonium by nitrite. *Figure modified from Gawarkiewicz et al. (2011)*

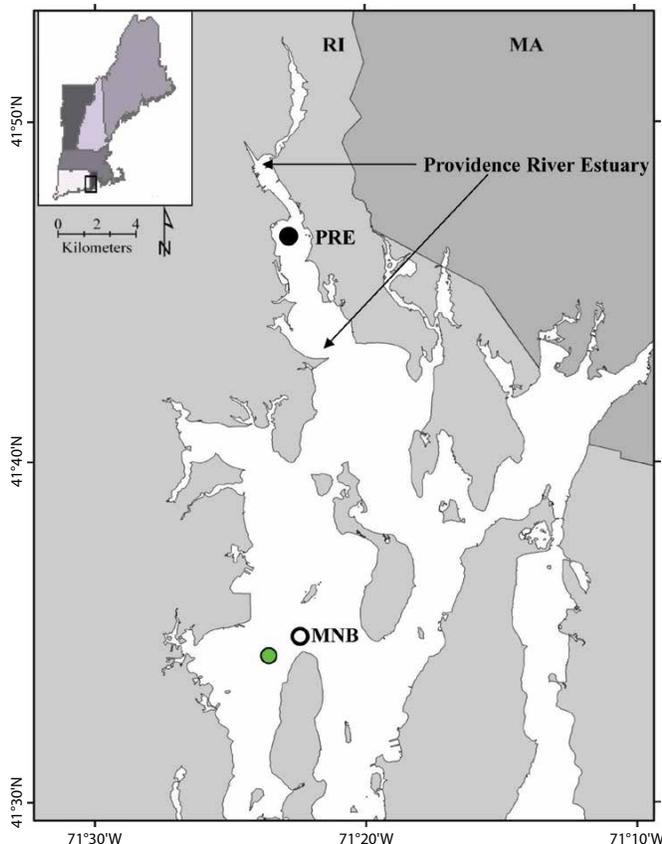


Figure 2. Sampling locations for net sediment N₂ fluxes across the sediment-water interface. Black circle = Providence River Estuary (PRE). Open circle = mid-Narragansett Bay (MNB). Green circle = long-term chlorophyll *a* sampling location.

to net N-fixation at multiple stations throughout the bay, including a historic site where the first direct N₂ measurements on intact, unamended, marine sediment cores were made over a seasonal cycle (Fulweiler et al., 2007). However, these same N cycling changes were not observed in the Providence River Estuary, the site most heavily altered by anthropogenic impacts. The marked difference in response between mid-Narragansett Bay, which exhibited signs of climate induced oligotrophication (i.e., decreased water column chlorophyll and subsequent decrease in carbon deposition to the benthos), and the Providence River Estuary, which exhibited no such change, highlighted the complex interplay between large-scale, climate-driven changes and local human impacts.

Motivated by these pronounced biogeochemical changes, we have been periodically sampling a site for net sediment N₂ fluxes in mid-Narragansett Bay for nearly a decade (Figure 2). Some years, we only sampled once and generally in the summer. However, during many years, we sampled more frequently, including over three seasonal cycles (2010–2012). Additionally, we intermittently sampled the more anthropogenically impacted Providence River Estuary between 2005 and 2013 (Figure 2). In this paper, we evaluate these sediment N₂ fluxes and explore relationships between the flux of N₂ and more easily

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measured parameters (e.g., sediment oxygen demand and water column chlorophyll). We then examine how the dynamic nature of sediment N₂ fluxes alters the N budget of this system, and we discuss larger implications for the ocean N budget.

“ IN THIS PERIOD OF OCEANIC CHANGE, INCLUDING INCREASED WATER TEMPERATURE, LOWER CONCENTRATIONS OF DISSOLVED OXYGEN, AND PERHAPS DECREASES IN PHYTOPLANKTON PRODUCTION, WE CAN BE ASSURED THE N CYCLE WILL RESPOND IN DYNAMIC AND PERHAPS UNPREDICTED WAYS. ”

(NEARLY) A DECADE OF SEDIMENT N₂ FLUXES IN NARRAGANSETT BAY

Over the past nine years, we sampled sediment N₂ fluxes at two stations: one in mid-Narragansett Bay and one in the highly nutrient enriched Providence River Estuary (Figure 2). At both sites, we measured N₂ fluxes in the dark at ambient field temperatures using intact sediment cores, filtered (0.2 micron) site water, and the N₂/Ar technique (Kana et al., 1994). The N₂/Ar technique is a measure of the net N₂ flux across the sediment-water interface (i.e., gross denitrification minus gross N-fixation below the sediment-water interface [SWI]). Thus, positive net N₂ fluxes indicate net denitrification and upward N₂ flux across the SWI released from the sediment to the water column, and negative net N₂ fluxes indicate net N-fixation

and downward N₂ flux across the SWI from the water column into the sediments. All fluxes were conducted under normoxic conditions and, in most cases, incubations were concluded before the overlying water became hypoxic (Fulweiler and Nixon, 2012).

We measured net sediment N₂ fluxes in the Providence River Estuary in 2005–2007 and then again in 2010–2013. Over these time periods, individual core net N₂ fluxes across the sediment-water interface ranged from –253 to 335 μmol m⁻² h⁻¹. Of the cores in the Providence River Estuary exhibiting negative N₂ fluxes, we observed a mean net N-fixation rate of –89 ± 31 μmol m⁻² h⁻¹ (n = 11), while in sediment cores exhibiting positive net N₂ fluxes we observed a mean net denitrification rate of 85 ± 23 μmol m⁻² h⁻¹ (n = 39). Accounting for all core measurements of both N-fixation and denitrification over the entire seven-year sampling period, Providence River Estuary exhibited an overall mean positive net N₂ flux of 46 ± 15 μmol m⁻² h⁻¹ (n = 50; Figure 3a). Thus, although high rates of N-fixation were observed on

several occasions in Providence River Estuary, this site is dominated by net denitrification. The most recent measurements were not statistically different ($p = 0.1147$) from those measured previously (Seitzinger et al., 1984).

Between 2005 and 2013, individual core net N_2 fluxes across the sediment-water interface in mid-Narragansett Bay ranged from -257 to $154 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 3b). The mid-Narragansett Bay mean net N-fixation rate was $-88 \pm 21 \mu\text{mol m}^{-2} \text{h}^{-1}$ ($n = 17$), and the mean net denitrification rate was $40 \pm 4 \mu\text{mol m}^{-2} \text{h}^{-1}$ ($n = 67$). Similar to Providence River Estuary, the overall nine-year mean net N_2 flux was positive ($14 \pm 8 \mu\text{mol m}^{-2} \text{h}^{-1}$, $n = 84$), indicating net fixed N removal. While we measured some net denitrification rates similar to those observed historically, our overall nine-year mean net denitrification rate was 80% lower than historic rates (Seitzinger et al., 1984; Nowicki, 1994).

There are at least two critical observations from these data. First, denitrification rates are significantly higher ($p < 0.0001$) in the Providence River

Estuary than in mid-Narragansett Bay. In fact, mean and maximum net denitrification rates in Providence River Estuary are double those found in mid-Narragansett Bay. This is consistent with the fact that Providence River Estuary is both more nutrient-rich and more productive than mid-Narragansett Bay, and nitrogen and organic matter availability are known to be key factors regulating sediment denitrification rates (Cornwell et al., 1999; Fulweiler et al., 2008). Second, and more surprising, net N-fixation rates are not significantly different at these two sites.

These data highlight that net N-fixation can, and routinely does, occur at measurable rates in marine sediments. In fact, net N-fixation accounted for 22% and 20% of the total net N_2 measurements made in the Providence River Estuary and mid-Narragansett Bay, respectively, over the past nine years. Further, because our N_2 fluxes are net measurements, we cannot know for certain that N-fixation was not occurring within the sediments during the net positive fluxes. Instead, we only know

that N-fixation was not the dominant N_2 controlling process. This is particularly important because the expression of both *nifH* (a gene encoding for N-fixation) and *nirS* (a gene encoding for denitrification) was recently observed simultaneously in space and time in sediments from mid-Narragansett Bay (Fulweiler et al., 2013). This expression of gene encoding for both N_2 -cycling processes was found even though net N_2 flux rates were positive, indicating that N-fixation and denitrification were co-occurring. Recently, Brown (2013) also reported both *nifH* and *nirS* expression in Providence River Estuary and mid-Narragansett Bay sediments as well as on the New England continental shelf. Such findings are not limited to Narragansett Bay. In Waquoit Bay (just east of our study sites), *nifH* expression was observed simultaneously with net N_2 production or denitrification (recent work of author Fulweiler). Together, these data suggest that denitrification and N-fixation regularly co-occur in marine sediments and that the balance between these two processes may be much more dynamic than previously thought.

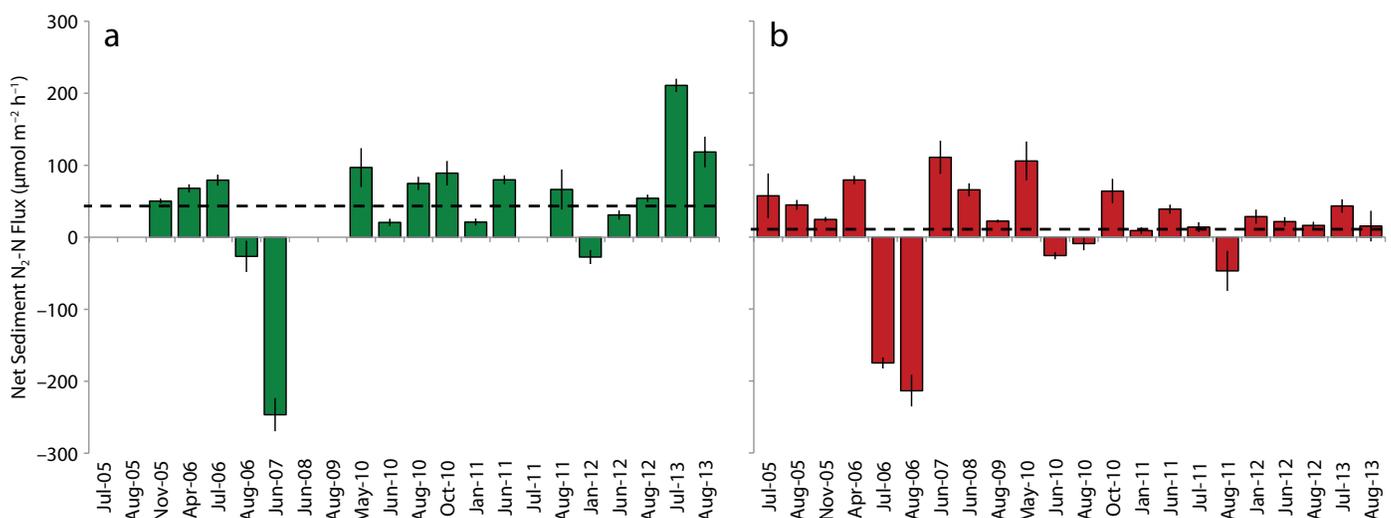


Figure 3. Monthly net sediment N_2 -N flux (\pm standard error) across the sediment-water interface over a nine-year record for (a) the Providence River Estuary, and (b) the historic mid-Narragansett Bay site. Overall nine-year mean N_2 -N flux is highlighted in each (dashed line).

ORGANIC MATTER AS A CONTROL OF NET N₂ FLUXES

Environmental controls on denitrification and N-fixation have been studied extensively (Cornwell et al., 1999). In some cases, strong relationships between in situ environmental conditions and N₂ fluxes have been used to expand the limited number of direct core measurements in order to inform larger spatial- and temporal-scale modeling efforts (Seitzinger and Giblin, 1996; Fennel et al., 2006).

One relationship often used is between sediment oxygen demand (SOD) and denitrification (Seitzinger and Giblin, 1996). SOD is theoretically an ideal proxy for estimating denitrification as it is straightforward to measure, and a robust data set is available for a variety of systems. Despite the strong correlations others have found between SOD and denitrification rates, we do not observe such a relationship in Narragansett Bay. While the individual net N₂ fluxes were significantly correlated ($p = 0.0006$) to SOD, the predictive power of this relationship was dismal ($R^2 = 0.09$) (Figure 4). If we instead evaluate the annual net N₂ flux and SOD means for the data set as a whole, the predictive power of this relationship improves slightly ($R^2 = 0.31$, $p = 0.0306$, data not shown). We also examined the relationship between SOD and net denitrification (i.e., positive N₂ fluxes only) and net N-fixation (i.e., negative N₂ fluxes only) separately, but again found no predictive relationship. We propose that the lack of relationship between SOD and N₂ fluxes in Narragansett Bay is explained by the fact that we are quantifying a *net* flux of N₂. That is, using the N₂/Ar technique, we cannot determine the absolute rate of denitrification or N-fixation at any given

time, but instead only the net product of these two processes across the sediment-water interface. Thus, while we may have denitrification increasing with SOD, the overall net efflux is dampened because of active N-fixation.

Denitrification rates have also been modeled using relationships between denitrification and the flux of organic matter to the benthos (Middelburg et al., 1996; Fennel et al., 2009) or between N₂ fluxes and primary production (Seitzinger and Giblin, 1996). A connection between denitrification and organic matter has been observed in many marine ecosystems (Eyre et al., 2013, and references therein). In Narragansett Bay, experimental manipulations in which organic matter was added to large shallow mesocosms demonstrated that both net denitrification and net N-fixation were strongly correlated with organic matter flux (Fulweiler et al., 2007, 2008). One complicating issue with this method

is that measuring rates of primary production can be challenging in terms of both methodology and expense. Additionally, quantifying or predicting how much organic matter from surface water production reaches the benthos is not straightforward.

A much more common in situ or satellite measurement is water column chlorophyll *a*, which can be used as a proxy for primary production. For Narragansett Bay, we have chlorophyll *a* measurements that span more than four decades (Figure 5). The long-term trend in water column chlorophyll *a* concentrations, while recently punctuated with some increased phytoplankton blooms reminiscent of the historic winter-spring blooms, is still decreasing (Figure 5). We compared this chlorophyll record to N₂ flux measurements made on mid-Narragansett Bay sediments, including those from previous studies measured with a gas chromatograph technique

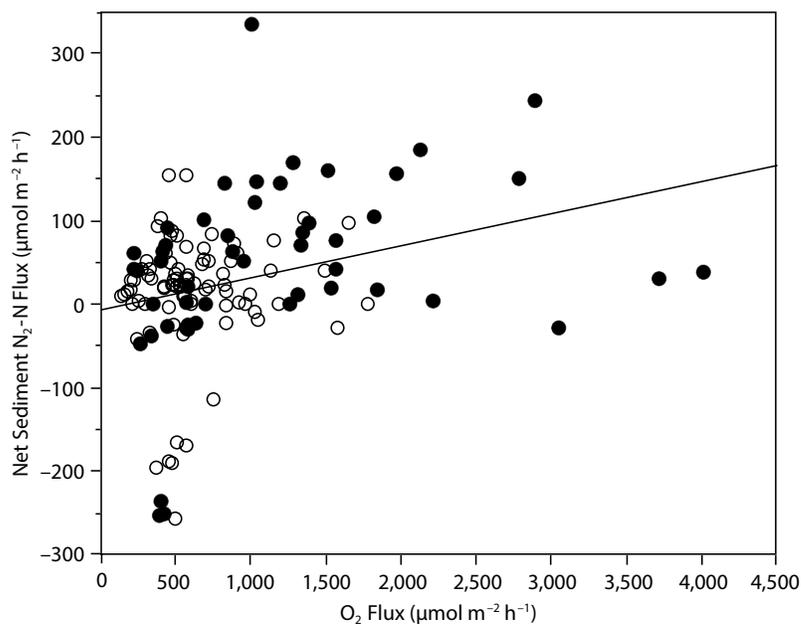


Figure 4. Individual net sediment N₂ fluxes as a function of sediment oxygen demand for the Providence River Estuary (closed circles) and mid-Narragansett Bay (open circles). N₂ was significantly correlated (0.0006) to sediment oxygen demand but the overall predictive power of the relationship was weak ($N_2-N \text{ flux} = 0.038(O_2 \text{ flux}) - 5.58$; $R^2 = 0.09$, $n = 134$).

in core incubations (Seitzinger et al., 1984; Nowicki, 1994) and from the large marine ecosystem (MERL) studies in the 1980s (Seitzinger and Nixon, 1985). We found a significant relationship ($p < 0.0001$) between mean summer (June, July, August) surface water column chlorophyll *a* and mean summer sediment N_2 flux (Figure 6). We also examined the relationship between mean summer water column chlorophyll *a* and mean summer sediment N_2 fluxes measured using only the N_2/Ar technique over the last nine years. In this case, we found a moderately significant relationship ($p = 0.0505$; Figure 6). Finally, we examined the relationship between only our mean summer net denitrification (i.e., positive N_2 fluxes) and mean summer water column chlorophyll for the

past nine years, and again found a significant relationship ($p = 0.0037$) (Table 1).

The finding that water column chlorophyll is a better predictor of sediment denitrification than N-fixation is intriguing. It suggests that denitrification is more directly controlled by the flux of fresh organic matter deposition to the seafloor, while N-fixation may rely on previously deposited organic matter and could also be driven by other environmental factors. Regardless, we can use these linear regressions to constrain threshold chlorophyll concentrations between 1.8 and 2.8 mg m^{-3} where the sediments switch from denitrification dominated to N-fixation dominated (Table 1).

We can also use these relationships to estimate long-term sediment N_2 fluxes in

Narragansett Bay where we do not have direct sediment N_2 flux measurements (Table 1). Summer chlorophyll concentrations are available from 1968 through 2004 with only a few missing years (Ted Smayda, University of Rhode Island, *pers. comm.*, November 4, 2013). We used these mean summer chlorophyll concentrations and all of the simple regression models between chlorophyll and sediment N_2 fluxes (Table 1) to constrain historic N_2 fluxes in mid-Narragansett Bay over this period. Combining these predicted values with directly measured rates gives us a continuous picture of what sediment N_2 fluxes in Narragansett Bay may have looked like over the last 45 years (Figure 7). These simple models do not accurately predict the high values of N-fixation we observed in the summer of 2006 and clearly are only estimates of what N_2 fluxes may have been over the last four decades. However, they are useful in that they highlight the dynamic nature of N_2 fluxes in this system and how the N_2 fluxes may have changed over time.

One long-standing question has focused on whether the high N-fixation rates observed in 2006 were representative of a new ecosystem state in Narragansett Bay or were a return to what the bay was like before anthropogenic impacts. We can use the estimated pre-European settlement chlorophyll *a* concentration (1.4 mg m^{-3}) determined by Nixon (1997) to help answer this question. In this case, we predict that in 1524, when Verrazzano sailed into Narragansett Bay, the sediment N_2 flux was between -8 and $-100 \mu\text{mol m}^{-2} \text{ h}^{-1}$ (Figure 7). Conceptually, low net denitrification or high net N-fixation in Narragansett Bay sediments at this time is consistent with the overall idea that organic matter helps regulate the balance

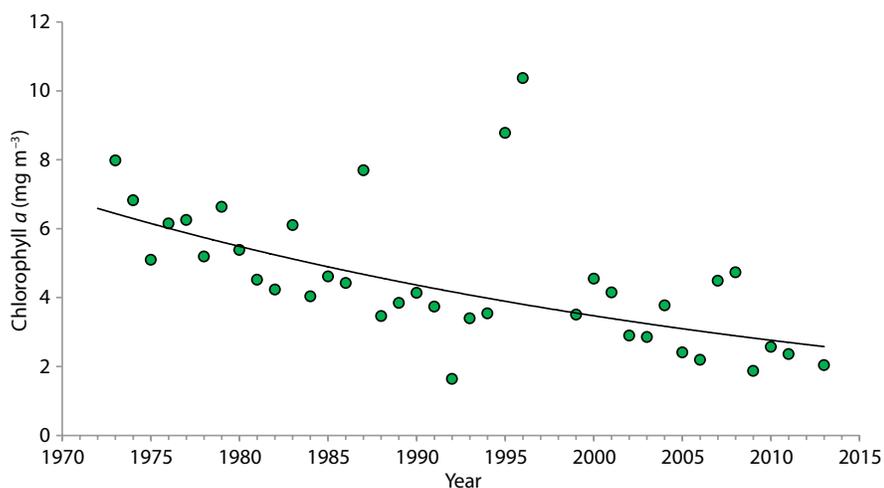


Figure 5. Mean annual water column chlorophyll *a* concentrations over the past four decades at the long-term monitoring station in the middle of Narragansett Bay's west passage, expanded from Nixon et al. (2009) ($\text{Chl } a = 3.0 \times 10^{20} e^{-0.023(\text{Year})}$; $R^2 = .40$). The mean annual chlorophyll decline is significant ($p < .0001$). Annual data from Li and Smayda (1998) through 1990. Historical data (1991–1997) from Ted Smayda (University of Rhode Island) based on personal communication from Scott Nixon. All data from 1999 to present are from the University of Rhode Island Graduate School of Oceanography (GSO) plankton monitoring program (<http://www.gso.uri.edu/phytoplankton>); the year 2012 is not included as there were only two months of chlorophyll data available. Note that in May 2007, the GSO monitoring program changed to an immediate extraction method. The new and traditional extraction techniques were compared over a one-year period (July 2007 to July 2008; Graff and Rynearson, 2011). We used this year-long study to correct data from May 2007 to the present so that we could compare the long-term trend in chlorophyll. (All new data were multiplied by the slope of the linear regression of the traditional method as a function of the new method, $y = 0.4323x - 1.2094$; $R^2 = 0.88$).

between denitrification and N-fixation.

During the pre-European settlement era, dissolved inorganic nutrient loading and primary production would have been much lower. With fewer phytoplankton, the water column may have been clearer so that more light may have reached the benthos, allowing the growth of sea grass beds (Nixon, 1997). Sea grass beds are known to harbor N-fixing communities that can provide a significant source of nitrogen to the surrounding environment (McGlathery et al., 1998). Therefore, the overall N-fixation rate may have been much higher than we predict here. If chlorophyll concentrations continue to decline in mid-Narragansett Bay, and we suspect they will (see below), then it is likely that N-fixation will become a more prominent feature in these sediments and in time may contribute a sizeable portion of N to the system N budget.

NARRAGANSETT BAY NITROGEN BUDGET

Narragansett Bay has been an intensively nitrogen-fertilized estuary since the late 1800s (Nixon et al., 2008). Its nitrogen budget has remained essentially constant since the 1970s, but that has changed very recently (Nixon et al., 2009). Poor water quality and low-oxygen conditions in the Providence River Estuary have led to major nutrient mitigation efforts. When fully active, the mandated sewage treatment will lower the amount of reactive N entering Narragansett Bay between May and October by about 40% (Nixon et al., 2008). These reductions began in 2004 for 11 of the 29 sewage treatment facilities that discharge directly into the bay or its major tributaries. Thus far, a 30% reduction in the annual inorganic nitrogen and a 17% decrease in total annual nitrogen

load have been achieved (Krumholz, 2012, and references therein). However, these nitrogen reductions have not yet led to decreases in average or maximum chlorophyll concentrations (Krumholz, 2012) or primary production rates (Smith, 2011).

In 1995, Nixon et al. published a complete nutrient budget for Narragansett Bay. At that time, sediment denitrification could remove 85–170 million moles of N per year (Seitzinger et al., 1984; Nowicki, 1991, 1994) when prorated for the fine-grained depositional area or

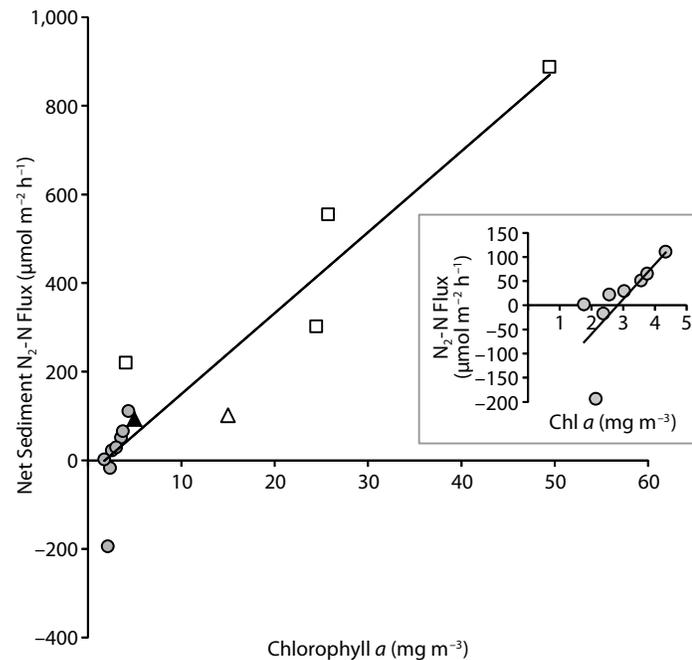


Figure 6. Mean summer (June, July, August) net sediment N_2 -N flux as a function of summer surface water column chlorophyll *a* for sediments from mid-Narragansett Bay over the last 40 years. Shaded circles = 2005–2013. Closed triangle = 1979 (Seitzinger et al., 1984). Open triangle = 1985 (Nowicki, 1994). Open squares = MERL 1981 (Seitzinger, 1982). Unpublished summer chlorophyll *a* data from 1968 to 1996 is from Ted Smayda (University of Rhode Island). This relationship is significant ($p < 0.0001$). The inset shows the relationship between mean summer water column chlorophyll and net N_2 fluxes from 2005 to 2013 only ($p = 0.0505$). See Table 1 and the text for more details.

Table 1. Equations used to predict mean summer sediment N_2 fluxes using the relationships between mean summer water column surface chlorophyll and directly measured sediment N_2 fluxes.

Description	Equation	R ²	p-value	n
¹ All N_2 Flux Data	$y = 18.3 \times chl - 33.4$	0.87	< 0.0001	14
² Net N_2 Fluxes	$y = 72.3 \times chl - 204.5$	0.49	0.0505	8
³ Net Denitrification Fluxes	$y = 39.7 \times chl - 79.5$	0.90	0.0037	6

¹ This equation includes all historic and recent N_2 flux measurements including those from the MERL experiments.

² This equation only uses N_2 fluxes from 2005–2013 measured with the N_2 /Ar technique.

³ This equation only uses net positive N_2 fluxes (i.e., net denitrification) from 2005–2013 measured with the N_2 /Ar technique.

total bay area, respectively (Nixon et al., 1995). At this rate, sediment denitrification removed between 10 and 25% of the total N load. Since 1995, various iterations of the N inputs have been described with some changes in how N loading from urban runoff and ungauged areas of the watershed have been estimated (Nixon et al., 2008; Krumholz, 2012). The most recent N budget, including the treatment plant reductions described above, estimate a current total N load to Narragansett Bay of 488 million moles of N per year (Krumholz, 2012). If we apply the Seitzinger and Nowicki rates to the newly defined N load, then denitrification could remove between 17% and 35% of the total N load.

There are numerous ways to apply the most recent 2005–2013 net sediment N_2 fluxes to current N budget for Narragansett Bay. Perhaps the most straightforward is to simply use the average net sediment N_2 flux. Because most of the anthropogenic N entering Narragansett Bay is first discharged

into the Providence River Estuary and because net sediment N_2 fluxes are statistically different ($p = 0.0383$) between the Providence River Estuary and mid-Narragansett Bay, we calculate separate N_2 removal rates for each area. If we prorate the Providence River Estuary 2005–2013 mean net sediment N_2 flux ($46 \mu\text{mol m}^{-2} \text{h}^{-1}$) to the Providence River Estuary area (21.3 km^2), we find 2% of the total N load is removed annually, leaving much of the human-derived N to flush into the rest of Narragansett Bay. Similarly, if we apply the mean 2005–2013 net sediment N_2 flux ($14 \mu\text{mol m}^{-2} \text{h}^{-1}$) from mid-Narragansett Bay to the fine-grained depositional or total area (in each case with the area of the Providence River Estuary removed), we find that sediment denitrification can remove an additional 5% to 8% of the N load per year. This represents a 30% to 70% decrease from historical levels in N removal via denitrification. Additionally, the sediments can be a source of N. If we carry out the

same calculations for mean N-fixation and only prorate for the summer (when we see high rates of N-fixation), then Providence River Estuary sediments can add 0.85 million moles of N while the rest of Narragansett Bay sediment can add 38–60 million moles of N. Therefore, when net N-fixation does occur, it can increase the total N load to Narragansett Bay by up to 13%—just slightly more than N loading from urban runoff or between 25% and 40% of the total N load from direct sewage discharge (Krumholz, 2012).

Of course, these new estimates are based on the simple average of our data set. If we look at any given year, the variability is high and, in some cases, much more N is removed (up to 25%) while in others much more N is added (up to 38%). Additionally, these high rates are temporally separated, with some years experiencing substantial N removal and others N addition (Figure 3). Regardless, these calculations suggest that net removal is still dampened in Narragansett Bay. This finding is not limited to this ecosystem alone. In nearby Waquoit Bay, denitrification rates are 80% less than those measured 25 years ago (Foster, 2012). Such findings call into question the fate of anthropogenic N entering this and perhaps other temperate estuaries. If the sediments no longer remove as much N as they did in the past, does this N enter continental shelf waters? And if so, what are the impacts?

GLOBAL OCEAN N BUDGET

Although some estimates have suggested that the oceanic fixed N budget is balanced, they are plagued with gross uncertainties (Gruber, 2008, and references therein). Still, many estimates indicate that the budget is unbalanced with

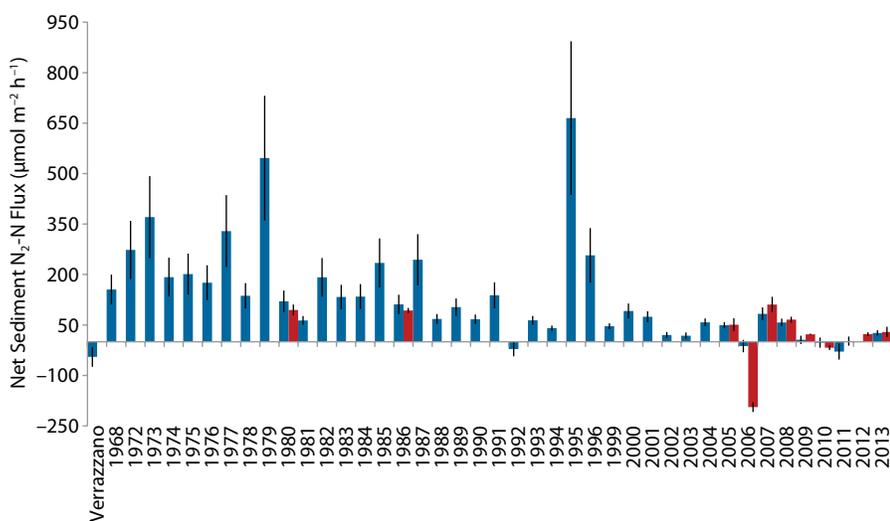


Figure 7. Long-term mean (\pm standard error) summer net sediment N_2 flux rates in Narragansett Bay. Blue bars = predicted rates. Red bars = measured rates. The predicted rates shown here are the average of the rates predicted from the three different relationships between mean summer (June, July, August) surface water column chlorophyll and measured sediment N_2 fluxes (Table 1: All, 2005–2013 all, and 2005–2013 net denitrification only) (\pm standard error of the three different predictions).

a substantial N deficit (Codispoti et al., 2001; Deutsch et al., 2007, and references therein). This deficit is driven by larger denitrification rates, as denitrification in both the water column and sediments is thought to be the dominant N_2 controlling process (Codispoti, 2007). However, several lines of recent evidence highlight that N-fixation may be underestimated in marine systems. For example, in open ocean water columns, unicellular nitrogen-fixing organisms are now known to be more abundant and diverse than previously thought (Hamersley et al., 2011; Rahav et al., 2013). In coastal systems, sediment N-fixation at rates equal to or greater than observed denitrification rates have been reported for a range of systems (Gardner et al., 2006; Vieillard and Fulweiler, 2012). Thus, a new paradigm is slowly emerging in which N fixation plays an important role in the nitrogen cycle and may provide a key to balancing the oceanic N budget.

From our long-term study of Narragansett Bay, a clear picture emerges of the dynamic nature of sediment N_2 fluxes. Though such long-term data sets unfortunately are not yet available for continental shelf systems, these data suggest that perhaps our oceanic N budgets should also reflect this variability. In fact, in a recent study measuring net sediment N_2 fluxes on the inner continental shelf offshore of Narragansett Bay, Heiss et al. (2012) found mean net denitrification rates to be highly variable (19 to $76 \mu\text{mol m}^{-2} \text{h}^{-1}$) over the seasonal cycle). By applying the Seitzinger and Giblin (1996) model to historic and more recent measurements of water column productivity, these authors estimated a 70% decrease in denitrification rates of the inner shelf off of Rhode Island. This is critical because changes in surface water productivity have had

dramatic impacts on the benthic metabolism (Fulweiler et al., 2010; Fields, 2013) and the N removal capacity of Narragansett Bay and perhaps the neighboring continental shelf. If other areas are also experiencing a decrease in water column productivity, then we suspect similar decreases in sediment denitrification could be occurring elsewhere.

Recent work on ocean phytoplankton productivity reported a 1% decline in global median chlorophyll concentration and a decline in eight out of 10 ocean regions (Boyce et al., 2010). This research has come under intense criticism (Mackas, 2011; McQuatters-Gollop et al., 2011; Rykaczewski and Dunne, 2011). Despite this criticism, it is useful to use this concept of declining productivity to examine potential changes to ocean N cycling. From the work presented here, and numerous other studies, we know that organic matter is a strong driver of sediment nitrogen cycling and that the sediments respond rapidly to pulses of carbon deposition. If ocean productivity is declining, then we may balance our N budget briefly until, or if, sediment N-fixation becomes important and the budget swings in the other direction.

However, it is also important to remember that 20% to 40% of ocean N loss is thought to occur not in sediments but in oxygen minimum zones (OMZs; Codispoti et al., 2001; Gruber, 2008). OMZ development is controlled by high rates of oxygen consumption due to decomposition of surface water column productivity. If this productivity declines, as e Boyce et al. (2010) suggest could be a possibility, will we also see a decline in N removal? We suspect yes, as less organic matter would not only reduce oxygen consumption rates but also production of the substrates

(e.g., ammonium, nitrate, nitrite) needed for denitrification and anammox. There is precedent for such declines. For example, a 225,000-year reconstruction of the Arabian Sea OMZ found periods of weakened or nonexistent OMZ when productivity declined and water column mixing was strong (Reichart et al., 1998). The future of N loss in OMZs and throughout the global ocean is complicated by the predicted decrease in ocean dissolved oxygen conditions due to climate-induced warming (Keeling et al., 2010). The fate of nitrogen in a future ocean with less organic matter and lower oxygen concentrations is unknown. If Narragansett Bay can serve as model for decreased organic matter, then we propose the future ocean may remove less nitrogen via denitrification, and, over time, N-fixation may become a more important process in both sediments and the water column.

CONCLUSION

The coupled nature of the nitrogen and carbon cycles suggests that as we fundamentally alter one, we will simultaneously alter the other. Just as nitrogen helps regulate ocean primary productivity, the resulting organic matter helps control nitrogen cycling processes. In this period of oceanic change, including increased water temperature, lower concentrations of dissolved oxygen, and perhaps decreases in phytoplankton production, we can be assured the N cycle will respond in dynamic and perhaps unpredicted ways. To capture the changing chemistry of the ocean N cycle, long-term measurements in critical areas coupled to ocean modeling are necessary steps.

It is humbling to read Johnstone's words quoted at the beginning of this article and realize that many of the same

questions scientists were contemplating over a century ago remain unanswered. It is also motivating, because in the rapidly changing ocean we have much more work to do to better understand, predict changes in, and hopefully protect our ocean.

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