

# Denitrification, Anammox, and N<sub>2</sub> Production in Marine Sediments

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## Keywords

nitrogen cycle, nitrogen budget, anoxic sediment, nitrogen isotope

## Abstract

Fixed nitrogen limits primary productivity in many parts of the global ocean, and it consequently plays a role in controlling the carbon dioxide content of the atmosphere. The concentration of fixed nitrogen is determined by the balance between two processes: the fixation of nitrogen gas into organic forms by diazotrophs, and the reconversion of fixed nitrogen to nitrogen gas by denitrifying organisms. However, current sedimentary denitrification rates are poorly constrained, especially in permeable sediments, which cover the majority of the continental margin. Also, anammox has recently been shown to be an additional pathway for the loss of fixed nitrogen in sediments. This article briefly reviews sedimentary fixed nitrogen loss by sedimentary denitrification and anammox, including in sediments in contact with oxygen-deficient zones. A simple extrapolation of existing rate measurements to the global sedimentary denitrification rate yields a value smaller than many existing measurement-based estimates but still larger than the rate of water column denitrification.

#### **Fixed nitrogen:**

nitrogen combined with other elements in forms usable to most organisms, primarily nitrate, nitrite, ammonium, and organic nitrogen; also called combined nitrogen

#### **Nitrogen fixation:**

the conversion of nitrogen gas into fixed nitrogen by microorganisms

#### **Denitrification:**

the conversion of fixed nitrogen to nitrogen gas or nitrous oxide

#### **Suboxic:**

having an oxygen concentration low enough to induce metabolisms such as denitrification, anammox, manganese reduction, and iron reduction

#### **Remineralization:**

the conversion of organic nitrogen to ammonium associated with organic matter oxidation

#### **Heterotrophic**

**denitrification:** the oxidation of organic matter with nitrate, resulting in the production of nitrogen gas, nitrous oxide, and carbon dioxide

## 1. INTRODUCTION

Biologically available nitrogen is an essential element for life in the oceans and is the fourth-most-abundant element in marine plankton. Within seawater, however, it is present in only trace amounts compared with carbon, hydrogen, and oxygen. Consequently, nitrogen limits new marine productivity in many parts of the ocean (Codispoti 1989, Tyrell 1999), and it thereby plays an important role in determining the amount of carbon sequestered in the ocean (Falkowski 1997, Broecker & Henderson 1998). Despite many years of study, however, the marine fixed nitrogen budget is not well quantified (Middelburg et al. 1996, Codispoti et al. 2001, Devol 2008, Gruber & Galloway 2008, Trimmer & Engström 2011, DeVries et al. 2012).

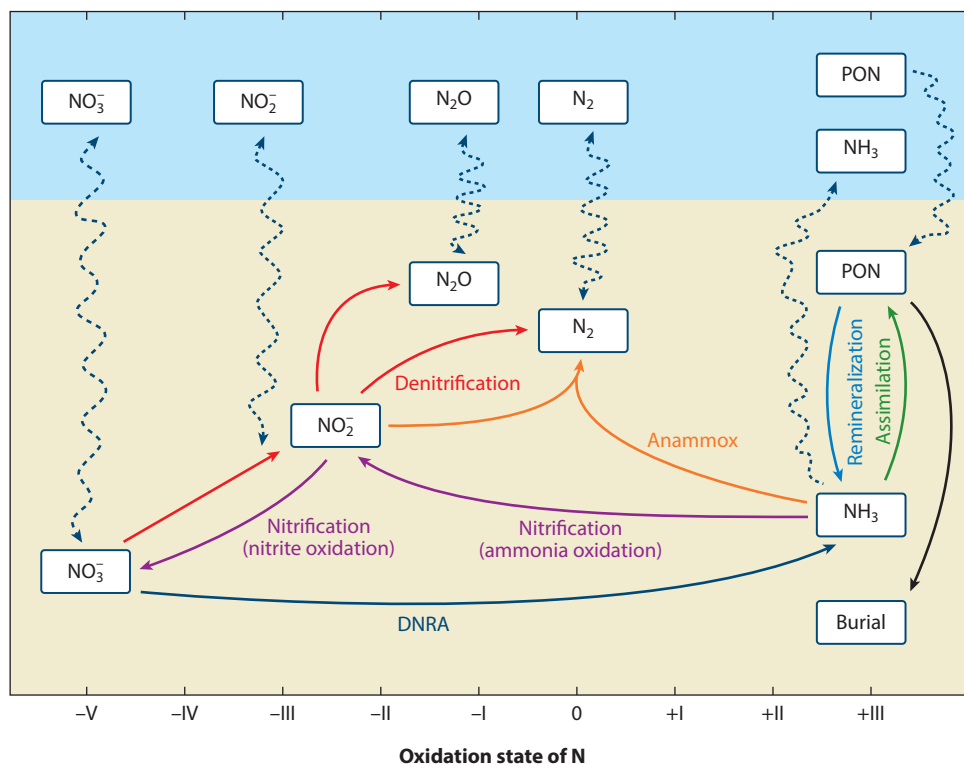
The major sources of fixed nitrogen to the ocean are nitrogen fixation and atmospheric deposition; the major sink is denitrification (Gruber & Galloway 2008). (Here, I use the phenomenological definition of denitrification: the conversion of fixed nitrogen to a gaseous end product.) At present, it is unclear whether sources and sinks are balanced (e.g., Gruber & Galloway 2008) or unbalanced (e.g., Codispoti 2007). An additional complication in the nitrogen cycle is that anthropogenic nitrogen inputs, primarily Haber-Bosch fixation and fossil fuel combustion, are of the same magnitude as biological nitrogen fixation on land or in the ocean (Galloway et al. 2008).

It is critical to understand the marine fixed nitrogen cycle and how it might change as we enter the epoch of the Anthropocene (Crutzen 2002, Gruber & Galloway 2008, Syvitski 2012). As a contribution to that effort, this review focuses on the fixed nitrogen sink in marine sediments. Denitrification in continental shelf sediments has been estimated to constitute 44% of total global denitrification (Seitzinger et al. 2006). Within the marine system, sedimentary denitrification is thought to account for 50–75% of the total marine fixed nitrogen sink; the remainder occurs in the ocean's pelagic oxygen minimum zones (Gruber 2004, Devol 2008).

## 2. THE SEDIMENTARY NITROGEN CYCLE

A simplified schematic of the major nitrogen cycle reactions is given in **Figure 1**. The energy that directly or indirectly drives these reactions is derived from organic matter oxidation. The organic matter oxidation may proceed via aerobic, suboxic, or anaerobic pathways. The decomposition of organic matter is accompanied by the remineralization of the organic nitrogen compounds to ammonium. After all or nearly all of the dissolved oxygen in the sedimentary pore waters is consumed, organic matter decomposition continues via heterotrophic denitrification or dissimilatory nitrate reduction to ammonium (DNRA, also known as nitrate fermentation). Heterotrophic denitrification is carried out mainly by facultative heterotrophic anaerobes that modify their electron transport chains to accommodate N-oxides as terminal electron acceptors. Dissolved oxygen exerts strong control over denitrification, such that heterotrophic denitrification is typically not initiated until dissolved oxygen concentrations are reduced to near-zero values (Tiedje 1988, Zumft 1997, Devol 2008). During heterotrophic denitrification, nitrate is reduced to nitrite, which is followed by a stepwise reduction to nitric oxide, nitrous oxide, and finally nitrogen gas.

The heterotrophic denitrification pathway, its intermediates, and the associated enzymes have been well characterized (e.g., Zumft 1997). The capacity for heterotrophic denitrification is present in a wide diversity of bacteria (especially proteobacteria) as well as in archaea (Zumft 1997) and foraminifera (Risgaard-Petersen et al. 2006, Høgslund et al. 2008, Bernhard et al. 2012). Although foraminiferal denitrification has not been well documented, it might be as important as heterotrophic denitrification in marine sediments (Piña-Ochoa et al. 2010, Bernhard et al. 2012, Glock et al. 2013). In addition to heterotrophic denitrification, the production of nitrogen gas from nitrate can also result from chemodenitrification. Both *Thiobacillus denitrificans* and *Thiomicrospira*



**Figure 1**

Simplified sedimentary nitrogen cycle. The light blue section at the top represents the overlying water; the beige section shows nitrogen cycle reactions. Abbreviation: DNRA, dissimilatory nitrate reduction to ammonium.

*denitrificans* are capable of using hydrogen sulfide as an energy source (Zumft 1997, Cardoso et al. 2006). Finally, there is convincing evidence that metal oxides such as manganese dioxide can serve as energy sources for denitrification (Anschutz et al. 2000).

Because the end product of heterotrophic denitrification is nitrogen gas, it constitutes a sink term in the fixed nitrogen budget. The other gaseous sink term in the nitrogen cycle is anammox, a chemoautotrophic process in which ammonium is the energy source and nitrite is the electron acceptor (Strous et al. 1999). During anammox, one unit of ammonium reacts with one unit of nitrite to form one unit of nitrogen gas. Anammox bacteria contain a unique organelle, the anammoxosome. The actual ammonium reduction takes place within the anammoxosome, and its function is to contain the highly reactive intermediates hydrazine and nitric oxide (Kartal et al. 2011). Thus far, all anammox bacteria appear to belong to the phylum Planctomycetes, with most of those found in the marine environment belonging to the genera “*Candidatus Scalindua*” (Lam & Kuypers 2011). Anammox bacteria appear able to tolerate low concentrations of oxygen (<13–20  $\mu\text{M O}_2$ ) (Jensen et al. 2008, Kalvelage et al. 2011). The contribution of the anammox reaction to the total denitrification in marine sediments can range from nearly zero to up to 80% (Dalsgaard et al. 2005), and anammox has been measured in many continental margin sediments and even in deep hemipelagic sediments off the coasts of Great Britain (Trimmer & Nicholls 2009) and Washington State (Engström et al. 2009).

#### Dissimilatory nitrate reduction to ammonium (DNRA):

a nitrate reduction process leading to the production of ammonium; it can be either an autotrophic process driven by reduced inorganic compounds such as sulfides or a heterotrophic process

**Chemodenitrification:** the reduction of reduced inorganic compounds with nitrate, resulting in the production of nitrogen gas

#### Anammox:

the oxidation of ammonium with nitrite, resulting in the production of nitrogen gas

#### Nitrification:

the two-step process of ammonium oxidation, first to nitrite and then to nitrate

The other reactions shown in **Figure 1** are not denitrifying reactions; however, they either produce or consume reactants in the denitrifying reactions. Nitrification is a two-step aerobic reaction in which ammonium is first oxidized to nitrite by specific groups of archaea or bacteria, and the nitrite is subsequently oxidized to nitrate by a different group of bacteria (Ward 2008). Finally, DNRA is important in anoxic sediments (Sørensen 1978a, Gardner et al. 2006). DNRA bacteria populations may be heterotrophic (Tiedje 1988) or autotrophic (e.g., *Thiomargarita* and *Thioploca*). *Thiomargarita* and *Thioploca* bacteria are visible to the naked eye. *Thioploca* bacteria form filaments and live in a thick gelatinous sheath that allows them to move from the surface to depth within sediments, accumulating nitrate at the sediment surface and then using it to oxidize sulfide at depth (Schulz et al. 1996, Jørgensen & Gallardo 1999). *Thiomargarita* organisms are the largest known bacteria and are prevalent in sediments in contact with the oxygen minimum zone of Namibia. DNRA and anammox in anoxic sediments are discussed further in Section 8.

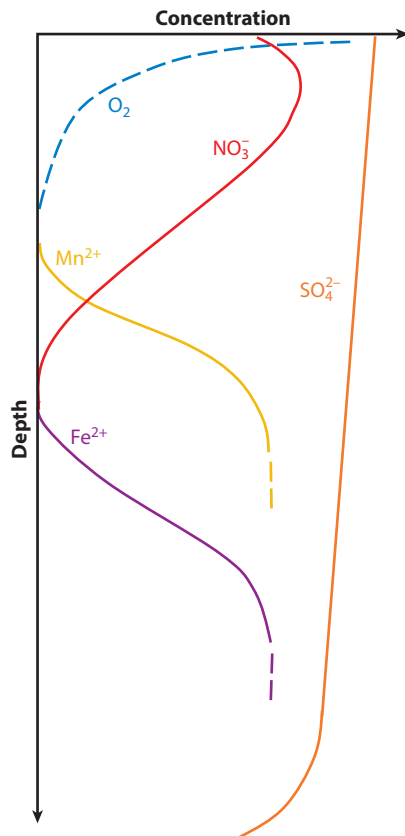
### 3. CONTINENTAL MARGIN SEDIMENTS

Benthic metabolism is driven by the supply rate of sinking organic matter, which is a function of the overlying water primary productivity. Although continental margin sediments constitute only a small fraction of the bottom surface area of the oceans, the waters overlying continental margin sediments have much higher productivity, accounting for ~20% of marine primary production (Huettel et al. 2014). This higher productivity coupled to much shallower average water depths results in high rates of carbon rain to margin sediments, which, in turn, foster high rates of benthic metabolism. Carbon rain rates are commonly high enough that oxygen demand exceeds oxygen supply and anaerobic metabolisms ensue. It is well documented that organic matter oxidation proceeds through a series of electron acceptors in order of decreasing free energy yield:  $O_2 > NO_3^- > Mn^{2+} > Fe^{2+} > SO_4^{2-}$  (Froelich et al. 1979, Burdige 2006, Lam & Kuypers 2011). Thus, continental margin sediments are thought to be the dominant site of benthic denitrification (Middelburg et al. 1996, Codispoti et al. 2001, Devol 2008, DeVries et al. 2012).

### 4. NITROGEN GAS PRODUCTION IN IMPERMEABLE SEDIMENTS

In a general sense, continental margin sediments can be divided into two broad categories: impermeable sediments (muds/silts), which constitute approximately 40% of continental margins, and permeable sediments (relict sands), which constitute another 50% (Emery 1968, Hall 2002). Sedimentary metabolic reaction rates are controlled by the concentration of labile carbon and the supply of oxidants, with the ultimate source of oxidants being the overlying water. In impermeable sediments, the oxidant transport mechanism is either molecular diffusion or bioirrigation, which results in the general vertical distribution of pore water solutes shown in **Figure 2**. The thickness of each layer is determined by the overall reaction rate of the oxidant. When the rate of carbon rain to the sediments is high, the thicknesses of the layers are thin and the  $O_2$  and  $NO_3^-$  penetration depths are shallow; when this rate is low, the layers are thicker and the penetration depths are greater.

Because productivity generally decreases and depth generally increases as one moves offshore, the reaction zones generally thicken and the penetration depths generally increase in the offshore direction, as **Figure 3** shows for oxygen and nitrate distributions off the coast of Washington State. Importantly, the nitrate maximum that results from sedimentary nitrification evident at depths greater than 2,000 m increases the gradient and thus the downward flux of nitrate that fuels denitrification, such that nitrification within the sediment column is an important source of nitrate for denitrification. This coupled nitrification-denitrification is also important at shallower



**Figure 2**

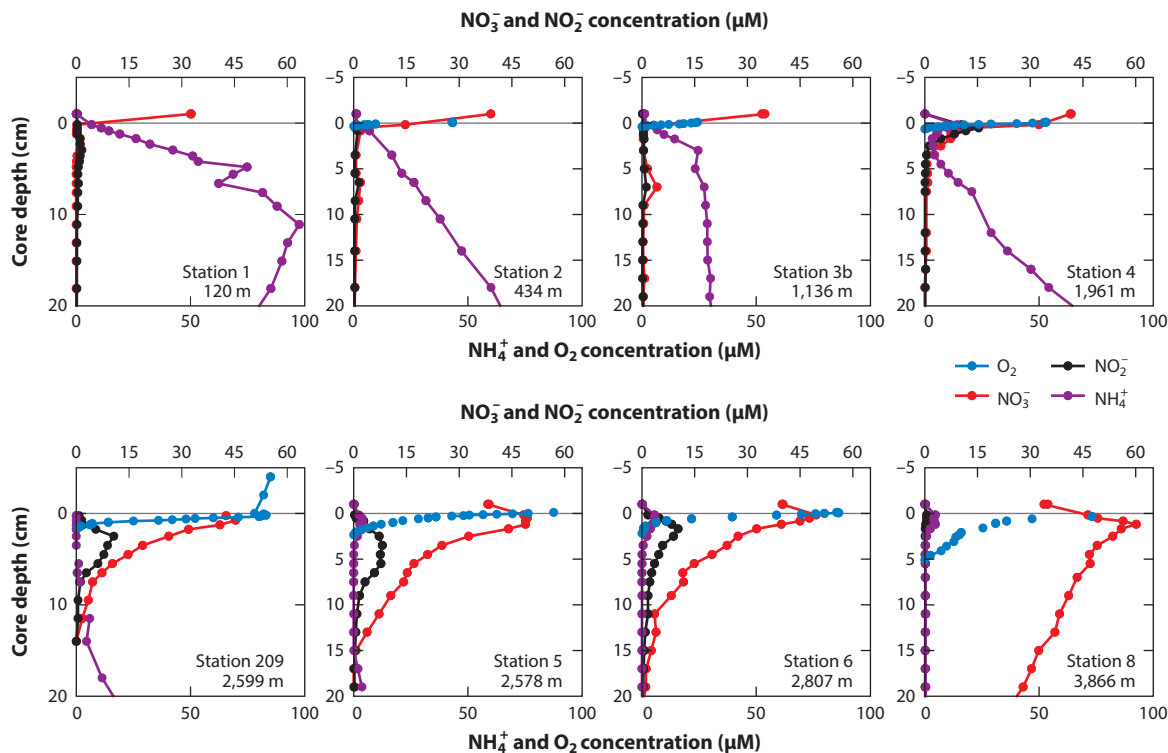
Pore water profiles of dissolved oxygen, nitrate, dissolved manganese, dissolved iron, and sulfate predicted by the thermodynamic yields of various reactions: oxic respiration [ $\Delta G^\circ = -471 \text{ J (mol C)}^{-1}$ ], denitrification [ $\Delta G^\circ = -444 \text{ J (mol C)}^{-1}$ ], manganese reduction [ $\Delta G^\circ = -397 \text{ J (mol C)}^{-1}$ ], iron reduction [ $\Delta G^\circ = -131 \text{ J (mol C)}^{-1}$ ], and sulfate reduction [ $\Delta G^\circ = -76 \text{ J (mol C)}^{-1}$ ]. ( $\Delta G^\circ$  is the standard free energy change of the reaction per mole of carbon; values given here are from Burdige 2006.) Oxic respiration yields the most energy, so oxygen is exhausted first, followed sequentially by nitrate, manganese oxides, iron oxides, and finally sulfate.

depths; however, the denitrification rate is too great to allow the formation of the subsurface nitrate maximum (Suykens et al. 2011). Many studies have documented the importance of sedimentary nitrification as a source for denitrification (e.g., Seitzinger & Giblin 1996). It is frequently equivalent to the nitrate supplied by diffusion (Devol & Christensen 1993) and at times can account for 70–90% of the nitrate supply (Thibodeau et al. 2010, Horak et al. 2013).

In impermeable sediments, where water movements resulting from compaction and burial are negligible, pore water solute profiles can be described by the equation (Boudreau 1997)

$$\frac{d}{dz} \left( \phi (D_s - D_b) \frac{\partial C}{\partial z} \right) + \phi \alpha (C_o - C) + R = \frac{dC}{dt}, \quad (1)$$

where  $C$  is the concentration of the solute,  $C_o$  is the concentration in the overlying water,  $\phi$  is the porosity,  $D_s$  is the molecular diffusivity corrected for tortuosity,  $D_b$  is the biodiffusivity,  $\alpha$  is a macrobenthos irrigation coefficient, and  $R$  is the net rate of production or consumption (Boudreau



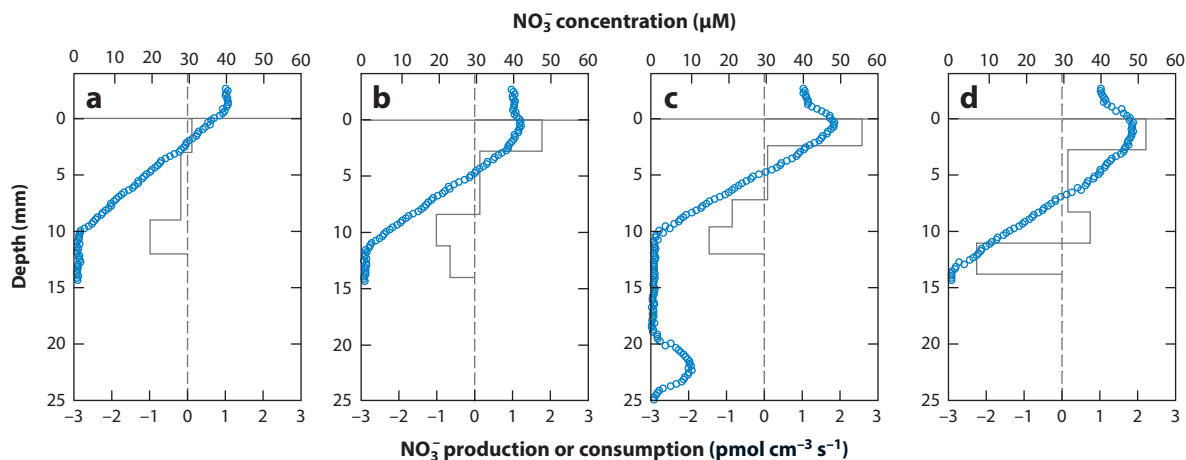
**Figure 3**

Pore water profiles of oxygen (blue), nitrate (red), nitrite (black), and ammonium (purple) for an area extending 740 km west off the coast of Washington State along 46°47'N. Stations are numbered in order of increasing distance from the coast with the exception of station 209, which was situated between stations 4 and 5. At the shallower stations, the reaction rates are high enough to exhaust the oxygen and nitrate supply within a few millimeters. It is likely that nitrification is taking place in the oxygenated zone, but denitrification occurs rapidly enough to prevent the accumulation of nitrate at these shallow stations. Farther offshore, at station 5 and beyond, the oxygen and nitrate penetration depths begin to separate significantly, and sedimentary nitrification is manifested by the subsurface nitrate maximum.

1997, Berg et al. 1998). Macrobenthic organisms often construct tubes or burrows, which many organisms then actively ventilate. The activities of these organisms can physically mix the sediments, and burrow and tube structures provide additional surface area and allow for enhanced solute exchange with the overlying water (Aller 1980, Kristensen et al. 1985). Additionally, the molecular diffusive flux of a solute across the sediment-water interface, or across any depth plane in the sediments, can be calculated from Fick's first law:

$$\frac{dC}{dt} = \phi DS \frac{dC}{dz} \quad (2)$$

Both of these equations have been used in combination with pore water profiles to estimate denitrification rates in sediments (e.g., Berg et al. 1998, Chang & Devol 2009, Glud et al. 2009, Lehmann et al. 2009, Thibodeau et al. 2010, Gao et al. 2012, Horak et al. 2013). Glud et al. (2009) provide a good example of using Equation 1 to determine denitrification rates. Here, the authors used the freely available PROFILE model developed by Berg et al. (1998) to fit nitrate profiles from a 1,450-m-deep station in Sagami Bay, Japan. **Figure 4** shows the results, which clearly illustrate the importance of coupled nitrification-denitrification.



**Figure 4**

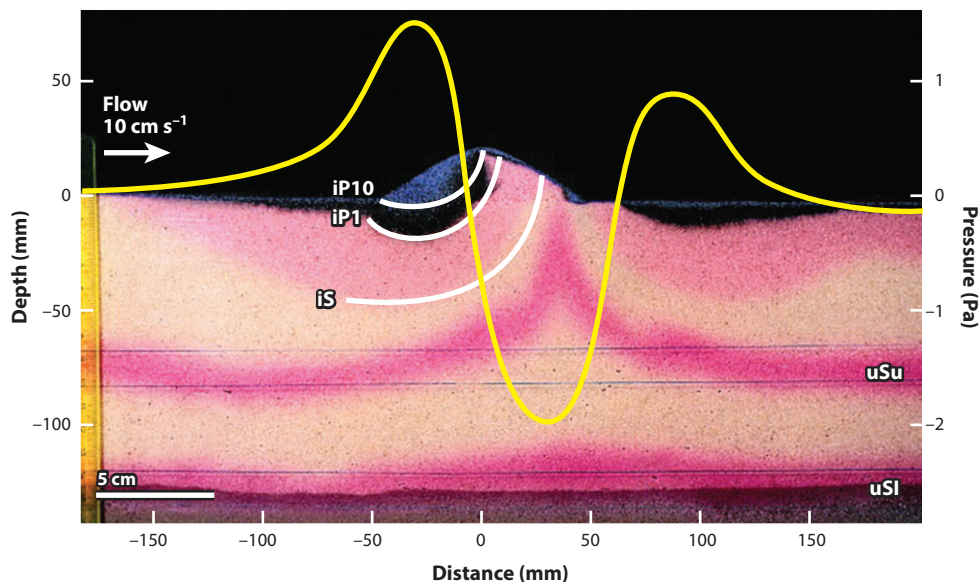
Nitrate profiles from a 1,450-m-deep station in Sagami Bay, Japan, fit with the freely available PROFILE model developed by Berg et al. (1998). The open circles are the nitrate data; the solid lines show the nitrate production or consumption rates resulting from the model fit. The model-determined denitrification rate was  $1.4 \text{ mmol N m}^{-2} \text{ d}^{-1}$  (mean of all estimates). All of the rate profiles show positive nitrate production (nitrification) in the upper portions of the profiles, and in panels *b*, *c*, and *d*, the production is coincident with the subsurface nitrate maximum. Note that in all model fits, nitrate production (nitrification) is a source for denitrification. Figure adapted from Glud et al. (2009), copyright 2014 by the Association for the Sciences of Limnology and Oceanography, Inc.

One of the original techniques for measuring denitrification was acetylene inhibition, in which acetylene is added to a sediment slurry to block the conversion of nitrous oxide to nitrogen gas and the rate of nitrous oxide accumulation is then monitored (Sørensen 1978b). Denitrification rates in impermeable sediments have also been measured by on-deck whole-core incubation (Berelson et al. 1996, Glud et al. 1998, Hartnett & Devol 2003, Chang & Devol 2009) as well as through in situ benthic flux chamber deployments (Devol & Christensen 1993, Hartnett & Devol 2003, Prokopenko et al. 2006, Glud et al. 2009). In both whole-core incubation and benthic flux chamber incubation, the rates of nitrate, nitrite, and ammonium exchange are estimated from the change in the overlying water concentration over time. These fluxes can then be either modeled or used in conjunction with mass balance equations to estimate the denitrification rate (Hartnett & Devol 2003, Prokopenko et al. 2006, Chang & Devol 2009). A comparison of whole-core incubation with benthic flux chamber incubation showed that the two methods give comparable results, with whole-core incubation potentially providing slightly lower values (Hammond et al. 2004). More recently, the adoption of membrane inlet mass spectrometry (Kana et al. 1994) has facilitated the direct measurement of nitrogen gas evolution (Fulweiler et al. 2007, Prokopenko et al. 2011, Horak et al. 2013). Direct measurement of nitrogen gas flux avoids the uncertainty associated with model and mass balance approaches.

Finally, isotope tracer experiments, in which  $^{15}\text{N}$ -labeled nitrate, nitrite, and ammonium are typically added to sediments either singly or in combination, can be used to estimate rates. Two experimental techniques have generally been used. The first is isotope pairing, which uses intact cores to determine the denitrification rate (Nielsen 1992, Rysgaard et al. 1993, Rysgaard-Petersen et al. 2003). The second uses homogenized sediment or sediment-water slurries to determine the rates of both anammox and heterotrophic denitrification (Dalsgaard et al. 2003).

Many measurements of sedimentary denitrification have been made, but the majority were from estuarine settings (for a recent review, see Joye & Anderson 2008). Denitrification rates measured





**Figure 5**

Photograph of tracer intrusion in a flume experiment. Initially, pore waters in the layers at mid-depth (uSu) and near the bottom of the sandy sediment (uSI) were dyed red between the horizontal lines. The overlying water also contained red dye, along with 10- $\mu\text{m}$  (blue) and 1- $\mu\text{m}$  (black) particles. iP10, iP1, and iS signify the intrusion of the 10- $\mu\text{m}$  particles, 1- $\mu\text{m}$  particles, and red solute dye, respectively, into the sediment at the end of the experiment (16.5 h), with tracer fronts marked by curved lines. Also shown is the approximate pressure distribution produced by the flow (yellow line). Areas of positive pressure produced flow into the sediments, whereas areas of negative pressure resulted in outflow. This flow through the sediment is clearly visible from the penetration of dye from the overlying water into the sediment and the upwelling of the mid-depth layer behind the mound. Figure adapted from Huettel et al. (1996), copyright 2014 by the Association for the Sciences of Limnology and Oceanography, Inc., and from Huettel et al. (1998) with permission from Elsevier.

in estuarine sediments range from a low of approximately  $0.01 \text{ mmol m}^{-2} \text{ d}^{-1}$  to as high as  $18 \text{ mmol m}^{-2} \text{ d}^{-1}$ , but the majority fall between 0.5 and  $5.0 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Joye & Anderson 2008). Rate estimates from continental shelf and slope environments are less common, but a number of them are available; many of these are summarized in **Supplemental Table 1** (follow the **Supplemental Material** link from the Annual Reviews home page at <http://www.annualreviews.org>). Rates vary by approximately two orders of magnitude, from 0.02 to  $6 \text{ mmol m}^{-2} \text{ d}^{-1}$ . Part of this wide range is due to depth variation because the tabulated rates cover a depth range of approximately 20–1,000 m. Despite the wide range, most rates fall between 0.5 and  $2.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ .

## 5. PERMEABLE SEDIMENTS

Although permeable sediments cover more of continental margins than impermeable sediments, denitrification rates in permeable sediments are much less well studied than those in impermeable sediments. In sediments, burrowing or foraging benthic organisms generate mounds and trails, while horizontal sediment transport driven by currents creates ripples. If the sediments are




permeable (permeability  $> 10\text{--}12\text{ m}^2$ ), current flow over topography induces differential pressure gradients, resulting in advection of overlying water through the sediments (Huettel et al. 2014). These advective fluxes are easily visualized in flume studies where dye is used to track the advective flow.

**Figure 5** shows a photograph of an actual flume experiment with flow over a small mound (Huettel et al. 1996). The flow-induced pressure gradient results in advection of overlying water into the sediments before and at the upstream face of the mound, advection of water out of the downstream face, and advection in again downstream of the mound. The advection of water also results in the accumulation of particles with the sandy sediments, which means that sandy sediments can act as particle filters, accumulating organic particles from the water column and increasing potential decomposition rates in these areas. Also shown is the approximate pressure field caused by the small mound (Huettel et al. 1998; see also Huettel & Rush 2000).

Denitrification rate measurements in permeable sediments are few; **Supplemental Table 2** summarizes most of them. In general, the range of rates is approximately the same as for impermeable sediments:  $0.5\text{--}2.0\text{ mmol m}^{-2}\text{ d}^{-1}$ . In sublittoral sands from the Gulf of Mexico, advection of overlying water increased denitrification rates 17-fold (Gihring et al. 2010a). Cardenas et al. (2008) found that denitrification rates varied over a range of permeabilities, with the highest denitrification rate at an intermediate permeability ( $0.5 \times 10^{-10}\text{ m}^2$ ). Nitrification rates increased with increasing permeability, but coupled nitrification-denitrification never accounted for more than 15% of the remineralized nitrogen. Likewise, Kessler et al. (2012) observed weak coupling between nitrification and denitrification. However, a study of lugworm (*Arenicola marina*) irrigation in permeable sediment found that increasing irrigation-driven advection increased the importance of coupled nitrification-denitrification (Na et al. 2008). Similarly, in sandy sediments of the South Atlantic Bight, Rao et al. (2008) found that the nitrate for denitrification was supplied mainly by nitrification.

Quantitative modeling of pore water solutes and reactions in permeable sediments is in its infancy. Because of the multidimensional natures of advection and reaction, gridded numerical models have been employed (Meysman et al. 2007). The theory of flow through permeable media is relatively well developed (Boudreau 1997). In these models, fluid flow is described by a conservation-of-momentum equation and Darcy's law. The flow field is then coupled to a reaction-transport model such as that given by Equation 1 to solve for two-dimensional solute distributions. In only a few instances have these models been applied to denitrification in permeable sediments. Cook et al. (2007) modeled denitrification in a stirred, cylindrical benthic chamber. They compared modeled total denitrification rates with those determined by measuring nitrogen gas fluxes during flux chamber incubations, and experimentally determined the coupled nitrification-denitrification rate, i.e., the total denitrification rate and the amount of that which was coupled to nitrification, using the isotope pairing technique ( $^{15}\text{NO}_3^-$  tracer experiments; Rysgaard et al. 2004). There was general agreement between modeled results and experimental measurements made during chamber incubations. The authors observed that the total denitrification rate increased by up to 5 times as the flushing rate increased from  $3.5$  to  $85\text{ L m}^{-2}\text{ d}^{-1}$ , while simultaneously the fraction of total denitrification that was supported by coupled nitrification decreased by a factor of 6. Additionally, modeled fluxes differed significantly from measured ones for up to five days after changes in the flushing rate or overlying water nitrate concentration. Both modeled results and experimental observations showed that it took up to one day for isotope pairing experiments to reach a steady state, suggesting that short-term incubations in sandy sediments underestimated true denitrification rates.

 **Supplemental Material**

## 6. MACROBENTHIC IRRIGATION

Many studies have concluded that macrobenthic irrigation is an important process promoting solute exchange in both impermeable and permeable sediments, typically increasing denitrification by a factor of 2–10 over that supportable by molecular diffusion alone (e.g., Devol & Christensen 1993, Aller et al. 1998, Kristensen 2000, Glud & Blackburn 2002, Berelson et al. 2003, Welsh 2003, Wenzhöfer & Glud 2004, and references therein). In sediments, benthic macrofauna construct tubes and burrows, and some organisms actively ventilate these structures. In impermeable sediments, these burrows and vents act as structures that connect the interior sediment with the overlying water and allow for diffusion through walls—i.e., they increase the effective surface area for solute exchange. For example, on the Pakistani margin, *Linopherus* sp. nov. constructs semipermanent burrows 0.5–2 mm wide and 1 cm long. An average burrow of 1 mm  $\times$  1 cm has a surface area of approximately 0.03 cm<sup>2</sup>. At 700–800-m depth on the Pakistani margin, burrow densities vary between 1 and 16 cm<sup>-2</sup>, which effectively increases the surface area for solute exchange by 3–50% (Jeffreys et al. 2012). The importance of macrobenthic irrigation has been well studied, and it is typically as important as (if not more important than) molecular diffusion in promoting denitrification.

Permeable sediments will be affected by the same types of mechanisms that operate in impermeable sediments. Additionally, water pumped into burrows can return to the overlying water via advective flow through the sediment interior. The lugworm (*Arenicola marina*) is a well-studied example of this (Riisgård & Banta 1998; Meysman et al. 2005, 2006).

## 7. ANAMMOX RELATIVE TO HETEROTROPHIC DENITRIFICATION AS A SOURCE OF NITROGEN GAS PRODUCTION

The first report of anammox in the marine environment was by Thamdrup & Dalsgaard (2002), who used <sup>15</sup>N-labeled compounds to trace the conversion of ammonium to nitrogen gas in sediments from the Skagerrak. At all three sampling locations, they detected both heterotrophic denitrification and anammox. However, there was a clear trend showing an increase of the fraction of nitrogen gas production by anammox as depth increased, despite the decrease in both rates with depth. At the shallowest station (16 m), anammox accounted for only a few percent of the total nitrogen production, whereas at the deepest location it accounted for 50–67%. Engström et al. (2005) extended the study to seven locations (including the original three) and saw similar trends, with anammox accounting for 4–79% of total nitrogen production. They concluded that the fraction of total nitrogen production attributable to anammox was inversely related to remineralized solute production (e.g., NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>), the benthic oxygen consumption rate, and surface sediment chlorophyll *a* content. Dalsgaard et al. (2005) tabulated the then-available data and concluded that the relative importance of anammox to total nitrogen gas production increased with water depth as a result of higher organic loading to shallower sediments, which favored heterotrophic denitrification. They concluded that at depths greater than the deepest studied at the time (700 m), anammox would be responsible for two-thirds or more of the total nitrogen production.

Since the Dalsgaard et al. (2005) study, several other studies, conducted mainly in estuaries, have quantified the fraction of total nitrogen production attributable to anammox (many are included in **Table 1**). Among those studies, the fraction of total nitrogen production by anammox (ra%) ranged from 0% to 79%, with several reporting that anammox was unimportant. However, if one looks at **Table 1** as a whole, it appears that ra% might typically constitute on the order of 10–40% of the nitrogen production. Interestingly, only a few of the studies drew conclusions about

**Table 1** Relative importance of denitrification and anammox [ $ra\% = (\text{anammox rate})/(\text{total nitrogen gas production rate})$ ]

Study	ra%	Study area
Brandsma et al. 2011	23–47%	Gullmar Fjord (Sweden)
Dong et al. 2011	Anammox unimportant	Southwest Pacific island estuaries
Engström et al. 2005	4–79%	Long Island Sound (United States) and the Skagerrak
Engström et al. 2009	42% (average)	Cascadia Basin (northeast Pacific)
Fernandes et al. 2010	Anammox unimportant	Goa Estuary (India)
Gihring et al. 2010b	5–23%	Arctic fjords
Glud et al. 2009	37%	Sagami Bay (Japan)
Hietanen & Kuparinen 2008	10–15%	Gulf of Finland
Jantti et al. 2011	Anammox unimportant	Gulf of Finland
Neubacher et al. 2011	10–20%	North Sea
Nicholls & Trimmer 2009	1–11%	United Kingdom estuaries
Rich et al. 2008	0–22%	Chesapeake Bay (United States)
Rooks et al. 2012	2–37%	Medway Estuary (United Kingdom)
Teixeira et al. 2012	17–77%	Cávado Estuary (Portugal)
Trimmer & Nicholls 2009	33% (average)	North Atlantic shelf-slope transect
Trimmer et al. 2013	0–77%	Norwegian Trench

the factors controlling the importance of anammox. Of these, two found nitrate concentration to be important, with a higher  $ra\%$  at higher nitrate concentrations (Rich et al. 2008, Teixeira et al. 2012), and one found that, in slope sediments,  $ra\%$  was positively related to the overall rate of nitrogen production, whereas on the slope itself, there was no such relationship (Trimmer & Nicholls 2009). Recently, Brin et al. (2014) found that both organic matter and nitrate are important factors regulating  $ra\%$ . Despite 10 years of study, the factors controlling the partitioning of anammox and denitrification in sediments remain unclear.

Returning to the hypothesis that, in the deep ocean ( $> \sim 1,000$  m), anammox would be responsible for two-thirds or more of the total nitrogen gas production, only a few studies have estimated rate measurements of anammox and total nitrogen production below 1,000 m. At 1,450-m depth in Sagami Bay, Japan, Glud et al. (2009) used a combination of benthic flux estimates and  $^{15}\text{N}$  tracer experiments to determine that anammox contributed 37% to total nitrogen production, with heterotrophic denitrification (59%) and foraminifera-based denitrification (4%) making up the remainder. On a shelf-to-slope transect in the North Atlantic, Trimmer & Nicholls (2009) found that  $ra\%$  was generally lower in shelf sediments than in slope sediments, and across the slope (500–2,000 m),  $ra\%$  increased linearly from approximately 35% to 68% with increasing depth. On average, over the slope,  $ra\%$  was 52%. Engström et al. (2009) determined  $ra\%$  for eight stations in the Cascadia Basin (eastern North Pacific) for which the depth ranged from 2,750 m to 3,110 m. They used both  $^{15}\text{N}$  isotope tracer experiments and pore water flux calculations to calculate  $ra\%$ , with the result that  $ra\%$  determined from tracer experiments averaged 40% (range 12–51%) and  $ra\%$  determined from flux calculations averaged 42% (range 36–50%). Although high  $ra\%$  is occasionally observed in deep sediments, the results from the three studies discussed above do not generally support the earlier suggestion that the relative importance of anammox increases with water depth and that anammox should therefore dominate over denitrification at depths greater than 1,000 m.

### Oxygen-deficient

**zone (ODZ):** an area of the ocean where the water column oxygen concentration is so low (low nanomolar range) that oxygen respiration is precluded and denitrification and other low-oxygen (suboxic) metabolisms predominate

## 8. ANOXIC SEDIMENTS IN CONTACT WITH OXYGEN-DEFICIENT OVERLYING WATERS

It is well known that reduced sulfur compounds can be used as an energy source for denitrification. A classic example is *Thiobacillus denitrificans* (Shao et al. 2010), which couples the oxidation of reduced sulfur compounds directly to the reduction of nitrate to nitrogen gas. However, an indirect coupling of reduced-sulfur-driven denitrification involving DNRA and anammox is an important pathway to nitrogen gas in sediments in contact with oxygen-deficient zones (ODZs) as well as those in anoxic basins.

The oceans contain three large ODZs (Gruber 2004, Codispoti et al. 2005, Devol 2008), in which the dissolved oxygen concentration is drawn down to a few nanomoles per liter (Jensen et al. 2011, Thamdrup et al. 2012). These ODZs span a depth range from approximately 100 m to 500–800 m, such that off the coasts of western Mexico, Peru-Chile, and Oman-Iran-Pakistan-India, the dissolved oxygen concentration is accordingly low in waters overlying sediments. Likewise, in anoxic basins such as the Santa Monica Basin off California and the Soledad Basin off the western Baja California peninsula (Mexico), the dissolved oxygen concentration is zero or nearly so in the waters overlying the sediments. In these areas, the low oxygen precludes macrobenthic organisms, and solute exchange has been thought to occur through diffusive processes only. Because of the lack of any oxygen supply mechanism to these sediments, they can be considered anoxic sediments. In anoxic sediments, not only is there no potential for carbon oxidation by aerobic metabolisms, but also the denitrification rate is limited by the diffusive supply of nitrate from the overlying waters. Given that these sediments often underlie highly productive waters, sulfate reduction becomes a major carbon degradation pathway, and free sulfide is common within the upper 10 cm.

In anoxic sediments, *Thioploca* bacteria are common nitrogen cycle organisms (Fossing et al. 1995, Teske et al. 2009). These bacteria form trichomes surrounded by a sheath within which they can navigate between electron donors (reduced sulfur) and electron acceptors (nitrate) (Høgslund et al. 2010). Additionally, they have the capacity to accumulate nitrate in intracellular vacuoles at concentrations up to approximately 500 mM (Fossing et al. 1995, Schulz et al. 1999). In 1999, the giant sulfur bacterium *Thiomargarita namibiensis*, individual cells of which are visible to the naked eye, was discovered in the anoxic sediments off Namibia (Schulz et al. 1999). This organism is related to *Thioploca* and can accumulate nitrate in intercellular vacuoles at concentrations up to 800 mM. Both *Thioploca* and *Thiomargarita* bacteria oxidize reduced sulfur compounds via the DNRA pathway (Schulz & de Beer 2002, Høgslund et al. 2009).

Chong et al. (2012) investigated five basins off the coasts of California and Baja California, some of which were oxic and some of which were anoxic. Macrobenthic irrigation was not a significant solute transport mechanism in any of these basins. Fluxes of nitrogen gas, nitrate, and ammonium were measured in whole-core incubations, and pore water profiles were used to calculate diffusive fluxes across the sediment-water interface. Nitrogen mass balance calculations showed that the diffusion of nitrate into the sediments was sufficient to balance the outward flux of nitrogen gas at the oxic sites. At the suboxic sites, however, diffusion alone could not support the nitrogen gas efflux from the sediments, and a biological nitrate transport mechanism was necessary to achieve balance. In addition to the mass balance calculations, the biological transport mechanism was supported by the observation that the suboxic basins had subsurface maxima in nitrate, nitrite, and nitrous oxide that were likely caused by nitrate sequestered by infaunal microbiota that were able to access nitrate in the overlying water and transport it to depth. In the Soledad Basin (the most reducing basin), the authors observed not only a large flux of nitrogen gas out of the sediments, indicative of active nitrogen production, but also a flux of ammonium out of the sediments that

was of nearly identical magnitude and was much higher than could be supported by organic matter oxidation alone.

Because sediments of the Soledad Basin support populations of *Thioploca* bacteria, Chong et al. (2012) suggested DNRA as the source of this ammonium. Earlier, Prokopenko et al. (2006) had proposed that anammox bacteria living in symbiosis with *Thioploca* could be responsible for significant denitrification, but because nitrous oxide production—an intermediate in denitrification—was observed, Chong et al. (2012) suggested a denitrifying symbiont instead. Prokopenko et al. (2013) subsequently investigated the Soledad Basin in detail. They collected individual *Thioploca* sheaths and stained them with 4',6-diamidino-2-phenylindole (DAPI) to reveal any associated microorganisms. Samples from the 4–6-cm depth interval showed three morphological types of organisms: filamentous bacteria, cocci, and donut-shaped organisms, the latter being characteristic of anammox bacteria owing to the large nonstaining anammoxosome within the cell (Kuenen 2008, Prokopenko et al. 2013). Investigation with an rDNA probe specific for marine anammox bacteria confirmed that the donut-shaped bacteria were indeed anammox bacteria, most likely “*Candidatus Scalindua*.” Further identification was provided by a polymerase chain reaction of extracted DNA using primers for the hydrazine oxidoreductase gene specific to anammox bacteria. The activity of the anammox bacteria was confirmed by  $^{15}\text{N}$  tracer experiments, and a nitrogen mass balance model for Soledad Basin sediments suggested that approximately 50% of the nitrogen production could be associated with anammox (Prokopenko et al. 2013).

In addition to bacteria, certain foraminifera appear to be capable of respiratory denitrification. Prokopenko et al. (2006) noticed high nitrate concentrations in pore water at depth in the anoxic sediment of the San Pedro Basin in the California borderlands. They attributed this to breakage of the vacuoles of nitrate-accumulating organisms and, owing to an absence of *Thioploca*, suggested that these organisms were tubular agglutinated foraminifera of the genus *Hyperammina*. Prokopenko et al. (2006) were not the first to show that eukaryotic benthic foraminifera can store and reduce nitrate; Risgaard-Petersen et al. (2006) found nitrate-accumulating, denitrifying foraminifera in anoxic sediments in contact with the oxygen-deficient waters off Chile and Peru. They were unable to demonstrate any significant symbiosis with denitrifying prokaryotes, and thus concluded that the foraminifera were responsible for the denitrification. Høglund et al. (2008) observed similar denitrifying foraminifera in Chile margin sediments. To date, more than 60 foraminiferal species have been shown to accumulate nitrate and respire through denitrification (Piña-Ochoa et al. 2010).

Bohlen et al. (2011) measured pore water profiles and benthic fluxes across a complete depth transect through the anoxic waters in contact with the ODZ off Peru at 11°S. The measurements were interpreted in the context of a one-dimensional reaction-transport model for each station. Clear trends in the rates of nitrification, denitrification, anammox, and DNRA were discernible across the section. On the shelf and upper slope (80–260 m), DNRA dominated nitrogen cycling, and this zone coincided with extensive mats of filamentous bacteria (*Beggiatoa* and *Thioploca*). In this zone, DNRA was responsible for >65% of the nitrogen cycling. Bohlen et al. (2011) therefore concluded that shelf and upper-slope sediments were not a significant sink for combined nitrogen, but rather were a recycling site where DNRA and remineralization recycled ammonium back to the overlying water. Below this zone, at depths between approximately 300 and 1,000 m, heterotrophic denitrification was the dominant nitrogen cycle reaction, removing 55–73% of the nitrate and nitrite taken up by the sediments. Anammox was unimportant in the upper zone, where DNRA dominated, but became important in the deeper sediments.

Interestingly, although Bohlen et al.’s (2011) interpretation that ammonium recycling dominated the shelf and upper slope may be correct for the sedimentary system, it may not apply to the entire sediment–water column system. Kalvelage et al. (2013) recently constructed a dissolved

inorganic nitrogen budget for the Peruvian oxygen minimum zone in which they suggest that ammonium flux from the sediments could fuel up to 50% of their measured anammox in the coastal part of the oxygen minimum zone. Thus, within the entire oxygen minimum zone system, sedimentary DNRA may serve simply as the first step in the ultimate conversion of combined nitrogen to nitrogen gas.

## 9. ISOTOPIC EFFECTS OF SEDIMENTARY DENITRIFICATION

As with most biological reactions, denitrification reactions proceed with a kinetic isotope effect favoring the lighter isotope of nitrogen. This increases the  $^{15}\text{N}/^{14}\text{N}$  ratio in the reaction products relative to the reactants. The enrichment in the heavy isotope of nitrogen is typically expressed as the parts-per-thousand change in the ratio relative to air or as  $\delta^{15}\text{N}$  change (in units of ‰). The degree of fractionation in similar units, or the fractionation factor, is typically expressed as  $\epsilon$ , where  $\epsilon = 1,000(\alpha - 1)$  and  $\alpha$  is the ratio of the rate constants for the light and heavy isotopes.

Laboratory cultures of heterotrophic denitrifying bacteria typically express fractionation factors of 17–30‰ (Delwiche & Steyn 1970, Mariotti et al. 1982, Barford et al. 1999, Granger et al. 2008); however, values as low as approximately 10‰ have been reported (Kritee et al. 2012). Similarly, estimates of the fractionation factor in open-ocean pelagic ODZ water columns are typically between 22‰ and 30‰ (Cline & Kaplan 1975, Brandes et al. 1998, Altabet et al. 1999, Voss et al. 2001). These water column fractionation factors have been derived from the change in  $\delta^{15}\text{N}$  of the remaining nitrate, and they therefore represent a community fractionation for all processes that remove nitrate (denitrification plus anammox).

Only a few estimates of nitrogen isotope fractionation in sediments have been published. Brandes & Devol (1997) used a benthic lander to measure the change in the  $^{15}\text{N}$  composition of nitrogen gas during sedimentary denitrification and found an effective (as opposed to biological) fractionation factor of basically zero. Lehmann et al. (2004, 2007) and Sigman et al. (2001) have observed similar near-zero fractionations.

Because the effective fractionation factors are different for the water column and sediments, it is possible to evaluate the relative importance of sedimentary and water column denitrification in the global marine combined nitrogen budget. As a simple example, assume the marine budget is in a steady state. Inputs of combined nitrogen, principally via nitrogen fixation, must then be balanced by losses through denitrification. Nitrogen fixation has a negligible isotopic fractionation (Capone et al. 1997), so the newly fixed nitrogen has approximately the same  $\delta^{15}\text{N}$  as air, which is 0‰. This means that the total nitrogen gas loss caused by denitrification (water column plus sedimentary) must also have a  $\delta^{15}\text{N}$  of 0‰. If the mean ocean  $\delta^{15}\text{N}$  of combined nitrogen is 5‰ and we assume a water column fractionation of  $\epsilon = 25\text{‰}$ , a loss of 50% of the combined nitrogen entering ODZs, and Rayleigh fractionation, then the isotopic composition of the accumulated nitrogen gas would be on the order of  $-12\text{‰}$ . For the net of water column and sedimentary denitrification to equal the input from nitrogen fixation, 0‰, the sedimentary denitrification rate would have to be approximately 2.4 times that of the water column denitrification.

Several recent studies have reported sedimentary denitrification fractionation factors of 3–6‰ (Granger et al. 2011, Alkhatib et al. 2012). If a fractionation factor of this magnitude were representative of marine sediments in general, then a much larger fraction of sedimentary denitrification relative to water column denitrification would be required compared with the fraction calculated above. This implies that the higher fractionations are not the general rule; that the simple, steady-state model of the nitrogen budget is not sufficient; or that our understanding of the isotope systematics of the nitrogen cycle is incomplete.




## 10. SEDIMENTARY DENITRIFICATION AND THE GLOBAL MARINE NITROGEN BUDGET

The ocean's combined nitrogen budget consists of inputs, mainly biological nitrogen fixation, riverine input, and atmospheric deposition, and losses, mainly denitrification, sediment burial, and losses to the atmosphere (Gruber & Galloway 2008). However, it is thought that by far the largest terms in the budget are nitrogen fixation and denitrification, so as a first approximation, the marine nitrogen budget is simply the balance between the two (Codispoti et al. 2001, Devol 2008, DeVries et al. 2012). At present there have not been enough measurements of either to accurately define the budget, and there is an active debate about whether it is indeed balanced (Gruber 2004) or unbalanced (Codispoti 2007).

Ocean sediments are only one site of denitrification, albeit the largest. Additionally, denitrification takes place in the three large pelagic ODZs (Gruber & Sarmiento 1997, Devol 2008). These ODZs are located in the eastern tropical North Pacific and South Pacific as well as in the Arabian Sea at intermediate water depths (100–800 m), where ventilation rates are not high enough to meet oxygen demand. Owing to the isotopic constraints discussed above, it is thought that the sedimentary denitrification is 2–4 times greater than pelagic denitrification (Brandes & Devol 2002, Deutsch et al. 2004, DeVries et al. 2012).

Based on limited data and global extrapolations, early estimates of total sedimentary denitrification varied widely, ranging from approximately 100 to 400 Tg a<sup>-1</sup> (Middelburg et al. 1996; Codispoti 1997, 2007; Gruber & Sarmiento 1997; Codispoti et al. 2001). Since that time, the number of direct measurements of open shelf marine sedimentary denitrification has increased substantially (e.g., **Supplemental Tables 1** and **2**). Although measurements are still scarce, the data suggest a denitrification rate of approximately 1 mmol m<sup>-2</sup> d<sup>-1</sup> for impermeable sediments (**Supplemental Table 1**). There are even fewer data for permeable sediments, but the value appears to be similar for them (**Supplemental Table 2**). A continental shelf area of approximately  $27 \times 10^{12}$  m<sup>2</sup> (Emery 1968) and a rate of 1 mmol m<sup>-2</sup> d<sup>-1</sup> would yield a total continental shelf denitrification rate of 140 Tg a<sup>-1</sup>. To this we need to add the denitrification rate in slope sediments, which, based on very few measurements, appears to be on the order of 0.5 mmol m<sup>-2</sup> d<sup>-1</sup>. This rate and an upper-slope (200–1,000 m) area of  $25 \times 10^{12}$  m<sup>2</sup> (Emery 1968) would add another 63 Tg a<sup>-1</sup>. Although denitrification undoubtedly occurs in deeper sediments, the paucity of measurements precludes meaningful extrapolation. Thus, based on observations, a reasonable minimum rate of sedimentary denitrification would be approximately 200 Tg a<sup>-1</sup>. This value is in reasonable agreement with recent mass balance estimates of approximately 180 Tg a<sup>-1</sup> (Gruber 2004, 2008) as well as the global model estimate of 164 Tg a<sup>-1</sup> (DeVries et al. 2012).

 Supplemental Material

## DISCLOSURE STATEMENT

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**Errata**

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