Denitrification pathways and rates in the sandy sediments of the Georgia continental shelf, USA

Cynthia Vance-Harris[a] and Ellery Ingall
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332

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Denitrification in continental shelf sediments has been estimated to be a significant sink of oceanic fixed nitrogen (N). The significance and mechanisms of denitrification in organic-poor sands, which comprise 70% of continental shelf sediments, are not well known. Core incubations and isotope tracer techniques were employed to determine processes and rates of denitrification in the coarse-grained, sandy sediments of the Georgia continental shelf. In these sediments, heterotrophic denitrification was the dominant process for fixed N removal. Processes such as coupled nitrification-denitrification, anammox (anaerobic ammonium oxidation), and oxygen-limited autotrophic nitrification–denitrification were not evident over the 24 and 48 h time scale of the incubation experiments. Heterotrophic denitrification processes produce $22.8-34.1\ \mu\text{mole N m}^{-2}\,\text{d}^{-1}$ of N_2 in these coarse-grained sediments. These denitrification rates are approximately two orders of magnitude lower than rates determined in fine-grained shelf sediments. These lower rates may help reconcile unbalanced marine N budgets which calculate global N losses exceeding N inputs. © *2005 American Institute of Physics.*
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I. INTRODUCTION

Recent studies have reported inbalances in global marine fixed N budgets with rates of N loss exceeding rates of N input.[1–3] These inbalanced budgets reflect the difficulties in making estimations given the many uncertainties in the pathways and rates of key N supply and removal reactions. In particular, the relatively few measurements of pathways and rates of denitrification reactions, the largest sink term in the global N budget, confound estimations of global N losses. Denitrification in continental shelf sediments is one of the largest sinks of oceanic N,[2,4,5] accounting for up to 67% of estimates of total global denitrification.[3] Most direct denitrification rate measurements for continental shelves have been made on fine-grained, muddy sediments which cover only 30% of global shelf area.[6] The remaining 70% of continental shelf area is covered by sandy sediments. These sandy sediment environments are generally characterized by low organic matter and high pore water dissolved oxygen concentrations, properties typically considered unfavorable for heterotrophic denitrification. The possibility of alternative pathways to N_2, which may not be limited by organic matter content, oxygen, or observed dissolved inorganic N levels, have not been examined in these widespread environments. This study of denitrification in the coarse-grained, sandy sediments of the Georgia continental shelf provides new information in an often overlooked but potentially significant sediment type.

Heterotrophic denitrification is the process of organic matter oxidation using nitrate (NO_3^-) and/or nitrite (NO_2^-) as electron acceptors [Eq. (1)]. Denitrifying organisms are able to use oxygen as an electron acceptor under aerobic conditions and can switch to the denitrification pathway of organic matter oxidation under suboxic or anoxic conditions. The sandy sediments of the Georgia continental shelf contain very little organic matter, low NO_3^- and NO_2^- concentrations, and are overlain by an oxic water column.[7,8] Dissolved O_2 also penetrates these sediments to variable depths, depending on the season, photosynthetic activity,[8] and light levels at the sea floor[9] and can be circulated throughout the sediment by physical processes related to the interaction of bottom currents and the sediment surface.[10] Typically, these sediments would not be considered an ideal environment for denitrification. Under denitrifying conditions, NO_3^- concentrations would typically decrease with time as a reactant during denitrification [Eq. (1)]. Based on their observations of constant NO_3^- concentrations over time, Marinelli *et al.*[8] suggested that denitrification was not occurring in sediments from the South Atlantic Bight, in which the Georgia continental shelf is located.

$$5CH_2O_{(\text{organic matter})} + 4NO_3^- + H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O, \quad (1)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+. \quad (2)$$

The coupled nitrification–dentrification mechanism has been suggested as an alternative pathway to the classical, heterotrophic denitrification process.[11] Ammonium (NH_4^+) is oxidized to NO_2^- and/or NO_3^- during nitrification [Eq. (2)], and those products can subsequently be reduced to N_2 during denitrification [Eq. (1)]. This coupled process must occur in different zones within the sediment because nitrification is an aerobic process and denitrification is an anaerobic process. Coupled nitrification–denitrification has been used to explain the occurrence of fixed N removal in oxic environments.[12] It

[a]Electronic mail: cynthiav@eas.gatech.edu

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can also be used to explain constant or even increasing NO_3^- concentrations in regions where denitrification is thought to be occurring.[13,14]

Other alternative pathways to heterotrophic denitrification that lead to the production of N_2 have been identified, increasing the difficulty in delineating the processes responsible for fixed N removal in natural systems. NH_4^+ and NO_2^- can react directly in the absence of organic matter to form N_2 in the reaction known as anammox (anaerobic ammonium oxidation) [Eq. (3)]. Anammox has been found to occur in natural systems[15,16] as well as in the wastewater reactor environment, where the reaction was discovered.[17–19] NH_4^+ can also be aerobically oxidized to form N_2 in the absence of organic matter in a two-step reaction termed OLAND (oxygen-limited autotrophic nitrification-denitrification)[20,21] [Eqs. (4a) and (4b)]. The second step of the OLAND reaction [Eq. (4b)] differs from the anammox reaction [Eq. (3)] in that the NO_2^- that is consumed is produced during the first step of the reaction,[20] whereas anammox consumes ambient NO_2^- and/or NO_2^- produced as an intermediate of heterotrophic denitrification.[15–17] Anammox also differs from all of the other processes because it occurs within the cells of the anammox organisms, specifically in the anammoxosome, a special compartment where the reaction takes place.[22] The other processes are known to be extracellular.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O, \quad (3)$$

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+, \quad (4a)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O. \quad (4b)$$

Marine fixed N can be further removed through the anaerobic oxidation of ammonium by manganese dioxide (MnO_2) via two pathways:

$$4MnO_2 + NH_4^+ + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O, \quad (5a)$$

$$3MnO_2 + 2NH_4^+ + 4H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O. \quad (5b)$$

Reaction (5a) indirectly removes fixed N by converting NH_4^+ to NO_3^-, which can be subsequently denitrified to form N_2. The Mn cycle interacts with the N cycle through yet another reaction involving the reduction of nitrate by Mn^{2+}:

$$5Mn^{2+} + 2NO_3^- + 4H_2O \rightarrow 5MnO_{2(solid)} + N_2 + 8H^+. \quad (5c)$$

The coupling of the manganese cycle to the nitrogen cycle has been cited as an alternative means of fixed N removal and N_2 production.[23–27] These reactions were found to occur in fine-grained, deep, continental margin sediments.[26] Although it is important to recognize their potential influence on the N cycle, specific examination of these reactions is beyond the scope of this study.

Beyond discerning the different denitrification pathways, the influence of organic matter quantity and benthic primary production on heterotrophic denitrification is also not clear. Because organic matter is consumed during heterotrophic denitrification, it must be present in order for the reaction to occur. Sandy sediments have been overlooked in some denitrification studies due to their typically low organic carbon (C) content. It has been proposed that the bioreactivity of organic matter is more important than the quantity of organic matter for heterotrophic denitrification.[12,14] Benthic primary production may be able to supply the bioavailable organic matter required to support heterotrophic denitrification in these sediments. However, the utilization of nutrients, such as NH_4^+, by these benthic organisms may effectively block their regeneration to the overlying water, thus limiting processes such as nitrification and denitrification.[8,28] Also, oxygen produced during benthic primary production[29] may influence nitrification [Eq. (2)][28] and OLAND [Eq. (4a)][20,21] reactions. Hence, it is unclear what the net effect of benthic primary production would be on denitrification.

Due to the many reactions that may produce or consume nitrite, nitrate, and ammonium, measurements of N_2 provide the most direct evidence of denitrification.[4,17,30,31] Typically, it is difficult to measure small changes in dissolved N_2 relative to the high ambient concentrations in seawater. Because the sedimentary characteristics of Georgia shelf sediments are not typically conducive for denitrification, it is necessary to employ techniques sensitive enough to detect relatively low denitrification rates. Isotope tracer techniques using ^{15}N-labeled NO_3^- and NH_4^+ during sediment incubation experiments can yield various isotopically heavy N_2 gases depending on the N cycling mechanisms involved. The isotopically heavy N_2 gases produced during incubations are easily observed relative to their low ambient concentrations in seawater[32,33] and can be measured using membrane inlet mass spectrometry. Sediment cores were collected from the Georgia continental shelf and incubated in the presence of labeled NO_3^- or NH_4^+ to determine the presence of denitrification, and if present, the pathways and rates to N_2.

II. METHODS

A. Sampling

Measurements of denitrification rates as well as other processes have been limited in sandy sediments because of the difficulty in collecting cores and retaining the pore-water. Sediment cores were collected using a modified spade corer with a metal sleeve designed to fit cylindrical core barrels, which replaced the core box. The acrylic core barrels used in this method (7 cm diameter × 34 cm length × 0.65 cm wall) are fitted with a polyvinyl chloride annulus at the top of the barrel, consisting of two O-rings on the outer surface of the annulus and one O-ring on the inner surface. During retrieval of the sediment core and overlying water, a solid acrylic ball rests upon the O-ring that is placed on the inner surface of the annulus, creating a seal and preventing pore-water leakage. Upon return of the corer from the bottom of the sea floor, a bottom piston containing two O-rings is inserted into the core barrel, the ball-valve system is removed from the top, and the overlying water of the core is open to the atmosphere.[8]

1. W27 cores

Two sediment cores and bottom water samples were collected on 23 July 2002, at W27 site located on the Georgia continental shelf at a depth of 27 m in the South Atlantic Bight (Fig. 1). The cores contained 15.5 cm of sediment with

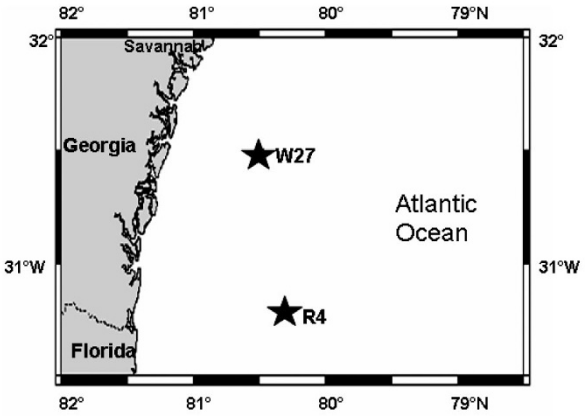

FIG. 1. Sampling sites. Cores were collected from W27 site in July 2002. W27 is along the Wassaw transect and has a depth of 27 m. The Wassaw transect was characterized by Marinelli *et al.* (Ref. 8). Cores were also collected from the R4 Tower site in April 2004, which is among eight platforms that are used to collect oceanographic and meteorological data for the South Atlantic Bight Synoptic Offshore Observational Network (SABSOON). This site is located at a depth of 40 m.

202 mL of overlying water. The overlying water of these cores contained 1 μM NO_3^-, no detectable NO_2^-, and 6–9 μM NH_4^+. This site was characterized in a study conducted by Marinelli *et al.*,[8] which analyzed the sediment biogeochemistry along a transect in the South Atlantic Bight. The porosity of the sediment at all sites is roughly 0.5.[8] The range of O_2 penetration into the sediments is between 6 and 9 cm during the summer months.[8] The incubation experiment conducted on these cores (see Sec. II C 1) was performed on the *R/V Savannah*, and samples were collected and stored on ice during transport back to the Georgia Institute of Technology in Atlanta, GA.

2. R4 cores

Six sediment cores and bottom water samples were collected on 23 April 2004, at R4 Tower, also located on the Georgia continental shelf at a depth of 40 m in the South Atlantic Bight (Fig. 1). These cores contained between 15–18 cm of sediment and 190–215 mL of overlying water. The R4 Tower is one of eight platforms in the South Atlantic Bight off of the Southeastern U.S. The platforms are a part of the South Atlantic Bight Synoptic Offshore Observational Network (SABSOON), which is used to obtain continuous and real-time oceanographic and meteorological data in this region. The core samples were transported back to the Georgia Institute of Technology and stored in an environmental chamber at bottom water temperature (18 °C).

B. Isotope tracer technique

The natural abundance of the isotope ^{14}N is 99.634%. When denitrification occurs [Eq. (1)], the dominant product is $^{28}N_2$. Due to the naturally high concentration of dissolved N_2 in seawater, it is often difficult to observe the small additions of $^{28}N_2$ from denitrification. The other stable isotope of N, ^{15}N, has a natural abundance of 0.366%. Using the isotope tracer technique, nitrate strongly enriched (>98%) in the ^{15}N isotope ($^{15}NO_3^-$) is used as a reactant during denitrification and can react with ambient $^{14}NO_3^-$ molecules to produce $^{29}N_2$. This tracer can also react with other $^{15}NO_3^-$ molecules to produce $^{30}N_2$. The production of these two isotopically distinct end products is much higher than would be observed during natural denitrification.

NH_4^+ is used as a substrate in some of the alternative pathways to N_2 such as coupled nitrification–denitrification, anammox, and OLAND. In order to detect the presence of these alternative pathways via the production of $^{29}N_2$ and $^{30}N_2$, ammonium enriched (>98%) in the ^{15}N isotope ($^{15}NH_4^+$) can also be used as a tracer. The schematic shown in Fig. 2 shows the potential combination of N isotopes in N_2 gas that would be produced as a result of different N cycling processes during the incubation experiments.

C. Incubation experiment

1. W27 cores

In order to detect the presence of denitrification in the sandy sediments of the Georgia continental shelf, an isotope tracer experiment was conducted on intact cores collected from the W27 site. The overlying water of one core was replaced with an amendment solution containing 50 μM Na $^{15}NO_3$ (>98% ^{15}N), which was made using the bottom water collected from the site. The other core was not amended and was used as a control. A syringe was inserted into self-sealing rubber septa on the core barrels to collect samples of the overlying water[8] of both cores at the start of the experiment and after 24 h. The samples were stored under ice water before dissolved gas analyses.

2. R4 cores

Two different incubation experiments were conducted on intact cores to detect the denitrification pathways in the sandy sediments of the Georgia continental shelf. In order to make a comparison between these experiments and the experiment on W27 cores, 50 μM solutions were also used. In experiment 1, the overlying water in two cores was replaced with a solution containing 50 μM $^{15}NH_4Cl$ (>98% ^{15}N) and 50 μM $NaNO_3$ using the bottom water from the sampling site. Similarly, in experiment 2, the overlying water of two different cores was replaced with a solution containing 50 μM Na $^{15}NO_3$ and 50 μM NH_4Cl. The two remaining cores were used as controls. After replacing the overlying water of the cores, they were sealed with a piston. After 24 and 48 h, the overlying water was sampled by pressing the top pistons down and allowing the water to flow out of a hole that was drilled into the piston and into a long, glass sampling tube. Sampling techniques were designed to minimize exchange of atmospheric N_2 with solution. The samples were then capped and stored under ice water for dissolved gas analyses using membrane inlet mass spectrometry.

3. Core incubation versus in situ benthic landers

Hammond *et al.*[34] recently addressed two common techniques used to study nutrient fluxes: *in situ* benthic landers and core incubations. Overall, the core incubation technique provided similar results to the *in situ* lander results. The core incubation technique, however, was found to have some mi-

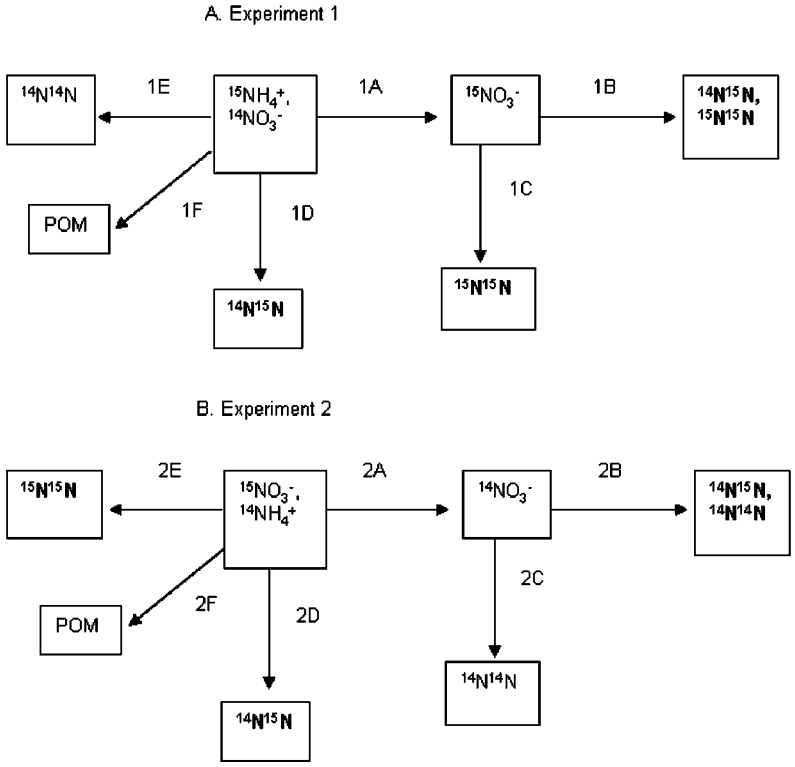

FIG. 2. Possible outcomes of amendment experiments. 1A = aerobic nitrification of $^{15}NH_4^+$; 1B = heterotrophic denitrification with $^{14}NO_3^-$ and/or $^{15}NO_3^-$; 1C = OLAND with $^{15}NH_4^+$ or partial nitrate reduction to nitrite followed by anammox with $^{15}NH_4^+$; 1D = same as 1C except with standard nitrate; 1E = heterotrophic denitrification with standard nitrate; 1F = assimilation. 2A = aerobic nitrification of standard ammonium; 2B = heterotrophic denitrification with $^{14}NO_3^-$ and/or $^{15}NO_3^-$; 2C = OLAND with standard ammonium or partial nitrate reduction to nitrite followed by anammox with standard ammonium; 2D = same as 2C except with $^{15}NO_3^-$; 2E = heterotrophic denitrification of $^{15}NO_3^-$; 2F = assimilation.

nor drawbacks. During the incubation experiment nitrate uptake was observed to be ~34% lower than the observed *in situ* rates. They concluded that denitrification rates may be underestimated by incubation studies.[34] Given that the objective of this paper is to identify denitrification rates and pathways in an environment that is often overlooked, an underestimation of measured denitrification would suggest that the results are a lower limit of the actual denitrification rates in these sandy sediments.

D. Membrane inlet mass spectrometry

Investigation of denitrification in all marine environments has been hampered by the complexity of measuring dissolved N_2 in natural waters. Previous investigations of denitrification rates have utilized a variety of techniques including stoichiometric calculations, gas chromatography, acetylene block, and *in situ* measurements using benthic chambers.[4,8,14,35–41] Membrane inlet mass spectrometry, or MIMS, is another approach to dissolved gas measurement developed by Kana *et al.*[30] Some advantages of MIMS include: no separate degassing step (a source of error in other methods), small sample size (8–10 mL), measurements can be made in a timely fashion (≈15 samples/h), and high precision (<0.05% error for N_2/Ar analyses).[30] The instrument can detect masses 28, 29, and 30, which can be attributed to various combinations of the stable isotopes of N (^{14}N, ^{15}N) in N_2. Other gases with these masses are removed before analysis with a cryogenic trap. It has been noted that the ability of the MIMS to detect $^{30}N_2$ can be influenced by dissolved O_2 concentration.[42] O_2 can react with N_2 in the ion source of the mass spectrometer to form NO^+, which also has a mass of 30. When calculating the concentration of $^{30}N_2$, this O_2 effect is taken into consideration using the approach described in Eyre *et al.*[42] Further information on the MIMS technique can be obtained in Kana *et al.*[30]

III. RESULTS AND DISCUSSION

A. Heterotrophic denitrification and alternative pathways

1. W27 cores

MIMS analyses on samples obtained from the core amended with 50 μM $^{15}NO_3^-$ showed increases in both $^{29}N_2$ and $^{30}N_2$, while the control samples did not show an increase in either of the dissolved gases (Fig. 3). Because $^{15}NO_3^-$ was the only significant source of ^{15}N–N, it is clear that the production of $^{29}N_2$ and $^{30}N_2$ was the result of the reduction of the $^{15}NO_3^-$ tracer. These results indicate that some form of denitrification occurs in Georgia continental shelf sediments.

2. R4 cores

Experiment 1 used a solution amended with $^{15}NH_4^+$ and standard NO_3^-. MIMS gas analyses on samples from this experiment, obtained 24 and 48 h after the start of the incubation, showed no increase in $^{30}N_2$ or $^{29}N_2$ (Fig. 3). According to Fig. 2, the absence of detectable $^{29}N_2$ and $^{30}N_2$ indi-

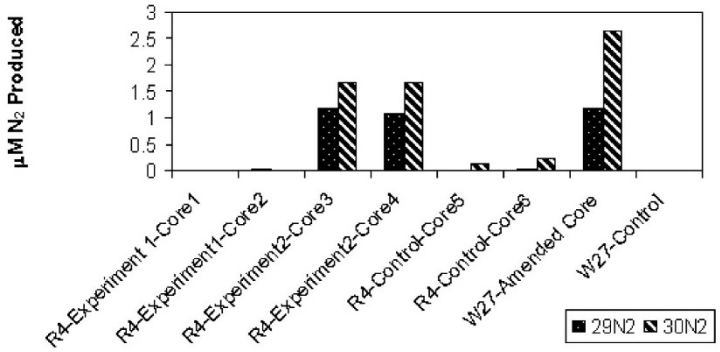

FIG. 3. Concentrations of dissolved $^{29}N_2$ and $^{30}N_2$ in core incubations after 48 h in R4 cores and 24 h in W27 cores. R4-experiment 1 was amended with $^{15}NH_4^+$ and standard NO_3^-. R4-experiment 2 was amended with $^{15}NO_3^-$ and standard NH_4^+. W27-amended core was amended with $^{15}NO_3^-$. The omission of a bar indicates that the production of that gas was negligible.

cates that alternative pathways such as coupled nitrification–denitrification, anammox, and OLAND are not significant on the time scale of these experiments.

Experiment 2 used a solution amended with $^{15}NO_3^-$ and standard NH_4^+. MIMS gas analyses on these samples after 48 h showed an increase in both $^{29}N_2$ and $^{30}N_2$ (Fig. 3). As seen in Fig. 2, the only source of ^{15}N was the $^{15}NO_3^-$ tracer, thus the increase in $^{30}N_2$ must be due to heterotrophic denitrification. Also, according to Fig. 2, the increase in $^{29}N_2$ can be explained by a number of possibilities such as the presence of OLAND or anammox reactions or the coupled nitrification–denitrification mechanism. However, those possibilities can be eliminated due to the lack of evidence for an alternative pathway to N_2 as observed in experiment 1. Therefore, the increase in $^{29}N_2$ suggests that a fraction of the ambient $^{14}NO_3^-$ was denitrified with the $^{15}NO_3^-$ tracer to produce the heavy gas.

The fraction of ambient $^{14}NO_3^-$ denitrified with the $^{15}NO_3^-$ tracer can be estimated. Given the area, depth, and volume of water (including porewater) of the cores, and the porosity of the sediment, the average amount of ^{14}N and ^{15}N was calculated for W27 and R4-experiment 2 as 1.1 and 10.4 μmol, respectively. The N in the system was therefore composed of 10% ^{14}N and 90% ^{15}N. Using the amount of $^{29}N_2$ and $^{30}N_2$ that was produced in the cores (Fig. 3), it was estimated that 48%–53% of the total ^{14}N in the system was used to produce $^{29}N_2$ and 37%–56% of the total ^{15}N in the system was used to produce both $^{29}N_2$ and $^{30}N_2$. These calculations suggest that the $^{29}N_2$ produced during the two experiments could have been the result of heterotrophic denitrification of ambient $^{14}NO_3^-$ with the $^{15}NO_3^-$ tracer.

The sandy sediments of the Georgia continental shelf contain very little organic C (0.03%–0.12%) in comparison to typical continental shelf sediments (0.7%).[9] The presence of heterotrophic denitrification in these sediments suggests that organic matter quantity is not a good indication of the potential of a particular sediment to support denitrification. Benthic primary production in these sediments is significant and comparable to water column primary production,[29] thus providing a source of fresh, bioavailable organic matter, which may be easily oxidized during heterotrophic denitrification. Although the influence that benthic organisms have on heterotrophic denitrification with regards to O_2 and nutrient dynamics was not directly measured as a part of the current study, the results indicate that benthic primary production has a net positive effect in supporting heterotrophic denitrification in Georgia shelf sands.

B. Denitrification rates

The concentrations of $^{29}N_2$ and $^{30}N_2$ measured in samples from W27 and R4-experiment 2 were used to obtain the rate of heterotrophic denitrification in these sediments. The gas production fluxes were calculated using

$$r = \frac{([N_2]_f - [N_2]_i)}{A * t} * (V_{ow} + \phi * V_{sed}), \quad (6)$$

where $[N_2]_f$ = final concentration of N_2 gas in the overlying water of the core, $[N_2]_i$ = initial concentration of N_2 gas in the overlying water, A = area of sediment, t = length of time of the experiment, V_{ow} = volume of overlying water, V_{sed} = volume of sediment, ϕ = porosity of the sediment. To estimate ambient denitrification rates based on the gas fluxes obtained in isotopically amended core incubations, the method of Nielsen was used.[33] Denitrification estimates based on these calculations yield a range of 22.8–34.1 μmol N m^{-2} d^{-1} for Georgia continental shelf sediments. Also, the rates obtained from the W27 experiment (34.1 μmol N m^{-2} d^{-1}), which used an amendment solution of 50 μM $^{15}NO_3^-$, are slightly higher than those obtained from R4-experiment 2 (22.8 and 23.2 μmol N m^{-2} d^{-1}), which used a solution of 50 μM $^{15}NO_3^-$ and 50 μM standard NH_4^+. If an alternative denitrification pathway existed in these sediments, the rates obtained from R4-experiment 2 should have been higher than those obtained in the W27 experiment, which was not observed. These results further suggest that the $^{29}N_2$ that was produced during R4-experiment 2 was a result of ambient $^{14}NO_3^-$ being denitrified with the tracer $^{15}NO_3^-$.

C. Comparison to literature

In a study conducted by Laursen and Seitzinger,[14] denitrification rates in various continental shelf sediments were reported from other studies. Laursen and Seitzinger,[14] using the dissolved inorganic N concentrations and N:P ratios determined by Hopkinson *et al.*[7] for Georgia Bight sediments,

obtained an average denitrification rate of 3200 μmol N m^{-2} d^{-1} for the Georgia Bight (compared to 22.8–34.1 μmol N m^{-2} d^{-1} from this study). However, the data were collected from Gray's Reef, a site in the Georgia Bight that has a unique benthic organism community and contains a heterogeneous sediment type throughout the site.[7] Gary's Reef is a hard bottom habitat, which consists of biological assemblages of a variety of organisms that are attached to hard surfaces on the sea floor. There are regions within the reef of high epifaunal biomass that correlated with high nutrient regeneration rates. Organic C levels were also substantially higher in the sediments at Gray's Reef than in the surrounding sandy sediments.[7] The sampling location of this study is very different from the environment of Gray's Reef, which may contribute to the markedly different denitrification rates obtained in these two studies.

In comparison to the rates determined by this study, higher rates were also obtained by other studies of continental shelf sediments (700–3200 μmol N m^{-2} d^{-1}).[14,37,39] These lower rates are not surprising when considering the differences between the sedimentary characteristics of the Georgia continental shelf and those of the continental shelves in which the above denitrification rates were measured. These other study sites contain fine-grained, muddy, organic-rich sediments as opposed to the coarse-grained, sandy, organic-poor sediments of the Georgia continental shelf. Although Georgia Bight sediments are receiving a fresh supply of reactive organic matter from benthic primary production, there is still very little organic matter (0.03%–0.12% organic C by weight compared to 0.7% for typical shelf sediments[9]) to be oxidized during heterotrophic denitrification. The O_2 present in these sediments may also have some inhibitory effect on denitrification rates because heterotrophic denitrification is typically an anaerobic process.

The marine fixed nitrogen budget has been the subject of much controversy over the past 20 years. Some studies have shown that the N budget is balanced and that the ocean is in steady state with respect to N.[13,43] Other studies have shown that fixed N is being removed from the ocean at a higher rate than it is being supplied, suggesting that the ocean is losing fixed N.[1–3] One of the sources of this ongoing debate is the uncertainty in many of the denitrification estimates that have been made. Direct measurements of denitrification have been made at relatively few locations throughout the world's oceans.[44] The global budgets that have been proposed are dependent upon both direct and indirect measurements of denitrification that have been extrapolated to larger regions.[2,39]

IV. CONCLUSIONS

The data obtained during this study suggest that heterotrophic denitrification, occurring at a rate of 22.8–34.1 μmol N m^{-2} d^{-1}, is the only pathway to N_2 in Georgia shelf sediments. These direct estimates of denitrification rates, if representative of coarse-grained, sandy sediments worldwide, would lower the denitrification sink term for fixed N in continental shelf sediments. These results show that N_2 produced from isotope tracers at relatively low rates can be detected by MIMS on reasonable experimental time scales. Further studies of the Georgia continental shelf examining potential spatial and temporal trends as well as the influence of benthic primary production on denitrification are necessary. A better-constrained range of denitrification rates in these sediments will allow this region and perhaps other regions dominated by coarse-grained, sandy sediments to be better represented in global N budgets.

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