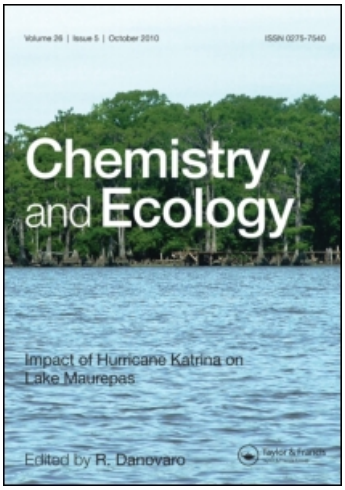


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# Denitrification in bottom sediment near oil production facilities off the Louisiana Gulf Coast

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# Denitrification in bottom sediment near oil production facilities off the Louisiana Gulf Coast

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There is little information on denitrification in Gulf of Mexico bottom sediment. Potential denitrification rates in surface sediment were measured along transects legs extending 0–800 m from two offshore oil production platforms. The average potential denitrification ranged from approximately 50 mg N $m^{-2}$ $d^{-1}$ in surface sediment near the platforms to 15 mg N $m^{-2}$ $d^{-1}$ in sediment 800 m from the platforms. Measured denitrification rates were correlated to a higher organic matter content in sediment nearer the platforms. This research examined only a small component of nitrogen processing in Gulf of Mexico sediment. Additional research should examine the effect of nitrogen loading and temporal and spatial variability on denitrification rate.

*Keywords*: Denitrification; Coastal; Sediment; Gulf of Mexico; Oil platforms

## 1. Introduction

Nitrogen inputs to estuaries and coastal ecosystem have increased significantly [1–3]. Nitrogen addition can increase primary production and eutrophication [4, 5]. Denitrification is an important process in nitrogen removal from coastal systems [6].

Along the Louisiana Gulf Coast, recent attention has focused on problems associated with nutrient loading to coastal water bodies. Gulf coast scientists have documented a large area of low oxygen water sitting along the bottom of the Gulf of Mexico, along the Louisiana Coast [4]. This dead zone has been attributed to the excessive nutrients in the Mississippi River, which ultimately enters the Gulf [7, 8]. The dead zone in the Gulf of Mexico runs from a depth of approximately 10–30 m covering a large area extending from the mouth of the Mississippi River. It is estimated that the dead zone covers an area of several thousand square kilometres. The dead zone generally forms in May, reaching a peak in midsummer and declining during the fall [4].

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In nitrogen-limited oceanic food webs, increased phytoplankton production is reported to be the likely result of increased nitrogen loading [9]. The productivity of coastal plankton in the Gulf Coast region is also reported to be limited by nitrogen [4]. Accordingly, scientists have attributed excessive nutrients from the Mississippi River to the increase in plankton activity in the Gulf of Mexico in the warmer months. Plankton use oxygen from the water while growing and remove more as they die and sink to the bottom.

The amount of nitrate entering the Gulf from the Mississippi River has tripled over the past several decades [10]. Approximately 45% of the nitrate that reaches the mouth of the Mississippi River appears to be entering from the upper portion of the river. Only 19% of the nitrate is from the Lower River Valley. The US Geological Survey reports that once the nitrate enters the river, it apparently remains in the river valley. Nitrate-N in the Mississippi River at New Orleans is in the order of 1 mg N $l^{-1}$ [8].

Coastal zone sediment is a major site for denitrification in oceans [6, 11]. The reported primary source of nitrogen for denitrification in coastal marine sediment is nitrate produced in the sediment rather than nitrate diffused from the overlying water [12]. Denitrification in estuarine sediment is reported to remove an amount of nitrogen equivalent of 20–50% of the total nitrogen input. Denitrification in the continental shelf and slope sediment has been reported to be the most important sink in the marine nitrogen cycle [13].



Nitrogen entering coastal wetland systems can undergo a series of transformations. Coupled nitrification–denitrification in the benthic layer is important in nitrogen transformation [14]. Denitrification in coastal sediments is coupled to nitrification. In "coupled nitrification–denitrification", the ammonium released during organic matter decomposition is first oxidized to nitrate in aerobic portions of sediment. Nitrate then diffuses to the reducing sediment layer, where it is reduced to $N_2$. Influences on this process include macrofaunal bioturbation, which increases the relative thickness of the oxidized surface layer [15], sediment ion-exchange capacity [12], and bottom-water oxygen concentrations [16]. Hypoxic condition can have a major influence on benthic biogeochemical processes, producing an environment in which heterotrophic activity is associated primarily with sulphate-reducing activity [17].

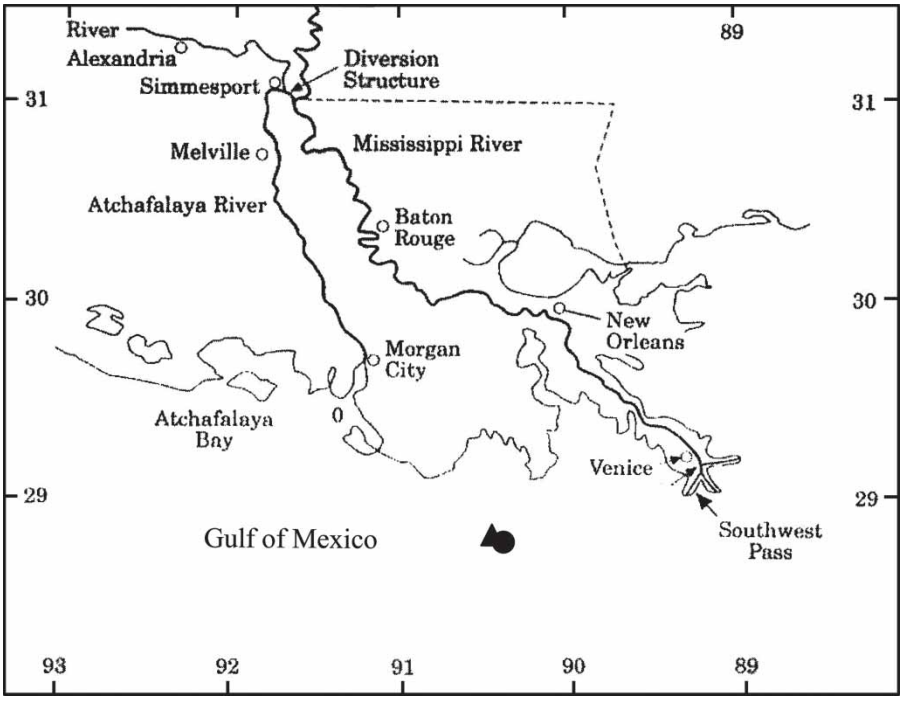
In some cases, nitrate in the overlying water may be present in sufficiently high concentrations such that denitrification in the sediments is not dependent upon the rate of nitrification of ammonium within the sediment [18]. Overall, this process is less important than coupled nitrification–denitrification in many marine environments but may be important when there is a source of nitrate from riverine inputs.

Currently, there is little information on denitrification in surface sediment of Louisiana offshore areas. Quantification of denitrification rates would provide critical information for evaluating the contribution of denitrification to the nitrogen cycle in these offshore ecosystems. In this paper, we examine denitrification in bottom sediment in the Gulf of Mexico along transects extending from several offshore oil-production platforms.

## 2. Materials and methods

### 2.1 *Gradient or transect studies*

Bottom sediment was collected near two oil-production platforms located in the Gulf of Mexico, off the Louisiana Coast. The sites were in areas which experiment with seasonal low oxygen conditions. South Timbalier 53 (C6-B) (Lat. 28° 52.169′ N Long. 90° 28.040′ W) and South Timbalier 53-A (Lat. 28° 51.484′ N Long. 90° 27.551′ W) were sampled on 11 August 2003 (figure 1). South Timbalier 53 is also known as C6-B and is a small four, pile structure, about 8 m wide on each side. Site two (ST-53-A) is a much larger structure consisting of two large independent platforms which are connected. This is a manned structure, unlike ST-53.




▲ = Platform C6B (Lat. 28 deg. 52.169'N, Long. 90 deg. 28.040'W )
● = Platform St53A (Lat. 28 deg. 51.484'N, Long. 90 deg. 27.551'W)

Figure 1. Sampling sites.



Three legs or headings were taken from each platform, leg one was at 0° North, leg two was at 120° SE and leg three was 240° SW from the platform. Sediment sample was taken at 0 m, 25 m, 50 m, 200 m, 400 m, and 800 m from each platform and on each heading.

The samples were taken from 20 m depth using a ponar dredge with 9 inch (23 cm) scoops, which was dropped to the bottom and then pulled up using the A-frame davit and a winch. Samples collected were placed in 32 oz (907 g) wide-mouth glass jars and labelled. The collected sediment samples were placed in a refrigerator until analyses were performed.

### 2.2 *Denitrification measurements*

Denitrification in sediments from offshores legs 1, 2, and 3 positioned 0, 25, 50, 200, 400, and 800 m from the platform St-53-A and platform St-53 (C6-B) were measured using the acetylene ($C_2H_2$) inhibition technique [19, 20]. Field moist sediment (10 g) was placed into 45 ml glass vials (EnviroWare Cat. #03-339-14A, Fisher Scientific), 5 ml of 20 ppm $NO_3$-N solution added and the mixture swirled. This amount of $NO_3$-N added was equivalent to 10 $\mu g\, N\, g^{-1}$. The vials were sealed with silicon-backed Teflon caps, and the headspace (ml) of the vial was purged with $N_2$ gas (ultra pure) to remove $O_2$. For treatment with $N_2$ plus $C_2H_2$, 10 ml of $N_2$ was replaced with acetylene ($C_2H_2$), resulting in 25% concentration in the head space. The samples were then incubated in the dark under laboratory conditions (23–25 °C).

After 24 h, the concentration of $N_2O$ in the headspace of sample vials was measured using a Shimadzu gas chromatograph (GC-14A) equipped with a 10 mCi $^{63}$Ni electron capture detector (ECD). A 1.8 m × 2 mm ID stainless steel column packed with porapak Q (80–100 mesh) was used in this gas chromatograph. The injector, column (isothermal), and

detector temperatures were 45, 80, and 290 °C, respectively. The carrier gas $N_2$ (UHP) flow rate was 30 ml $min^{-1}$. Working standard consisted of 101.1 ppm $N_2O$ diluted in $N_2$ gas (Scott Specialty Gases). Standard curve was prepared by injecting 25, 50, and 100 µl of the standard gas to the GC, and peak heights were recorded. The peak heights were then plotted against concentration in nanograms of $N_2O$ injected, which were 4.64, 9.27, and 18.54 ng of $N_2O$ for 25, 50, and 100 µl, respectively.

The basic calculations to quantify the amount of $N_2O$ evolved or produced by sediments involved multiplying the concentration of $N_2O$ in the headspace of vial at during a 24 h period by volume of head space and then divided by the weight (wet or dry) of sediments [20]. For denitrification rate in a shaken assay such as this experiment, it is necessary to account for $N_2O$ dissolved in solution using Bunsen coefficients that predict the amount of gas dissolved in the liquid phase from the concentration in the gas phase [19]. Organic matter was determined by acid-dichromate oxidation followed by spectrophotometry [21].

## 3. Results and discussion

Potential denitrification rates varied among the various legs of the platform sites (table 1). For platform St-53-A, denitrification (using all legs) ranged from $1.01 \pm 0.60$ µg N $g^{-1}$ $d^{-1}$



Table 1. Denitrification rate and organic-matter content of sediment with distance from the legs of the two platforms.

| Distance (m) | Leg | Organic matter (%) | Denitrification rate (µg N g dry sediment$^{-1}$ d$^{-1}$) | Organic matter (%) | Denitrification rate (µg N g dry sediment$^{-1}$ d$^{-1}$) |
|---|---|---|---|---|---|
| | | | Platform St-53-A | | Platform C6-B |
| 0 | 1 | 0.50 | 1.09 | 3.32 | 9.31 |
| 0 | 2 | 3.26 | 8.34 | 1.37 | 4.16 |
| 0 | 3 | 3.29 | 3.66 | 3.50 | 3.49 |
| Average | | 2.35 | 4.36 | 2.73 | 5.65 |
| S.D. | | 1.61 | 3.67 | 1.18 | 3.19 |
| 25 | 1 | 0.80 | 3.83 | 2.97 | 5.54 |
| 25 | 2 | 0.40 | 2.66 | 2.86 | 6.03 |
| 25 | 3 | 2.26 | 3.49 | 3.79 | 7.03 |
| Average | | 1.15 | 3.33 | 3.21 | 6.20 |
| S.D. | | 0.98 | 0.60 | 0.51 | 0.76 |
| 50 | 1 | 0.38 | 2.98 | 3.47 | 4.18 |
| 50 | 2 | 1.82 | 2.04 | 3.58 | 3.54 |
| 50 | 3 | 2.65 | 3.93 | 3.63 | 3.87 |
| Average | | 1.62 | 2.98 | 3.56 | 3.86 |
| S.D. | | 1.15 | 0.95 | 0.08 | 0.32 |
| 200 | 1 | 1.86 | 4.05 | 2.61 | 2.37 |
| 200 | 2 | 0.90 | 1.11 | 2.05 | 1.97 |
| 200 | 3 | 0.84 | 0.97 | 3.82 | 6.13 |
| Average | | 1.20 | 2.04 | 2.83 | 3.49 |
| S.D. | | 0.57 | 1.74 | 0.90 | 2.30 |
| 400 | 1 | 0.87 | 1.47 | 3.02 | 4.57 |
| 400 | 2 | 1.03 | 1.22 | 1.43 | 1.82 |
| 400 | 3 | 0.42 | 0.86 | 2.60 | 4.56 |
| Average | | 0.78 | 1.18 | 2.35 | 3.65 |
| S.D. | | 0.32 | 0.31 | 0.82 | 1.59 |
| 800 | 1 | 0.90 | 1.56 | 1.62 | 2.06 |
| 800 | 2 | 1.02 | 1.10 | 0.76 | 1.77 |
| 800 | 3 | 1.71 | 0.37 | 1.23 | 2.23 |
| Average | | 1.21 | 1.01 | 1.20 | 2.02 |
| S.D. | | 0.44 | 0.60 | 0.43 | 0.23 |

dry sediment at 800 m to $4.36 \pm 03.67\ \mu g\ N\ g^{-1}\ d^{-1}$ dry sediment at sites nearest to the platform. For platform C6B, the measured average potential denitrification ranged from $2.017 \pm 0.23\ \mu g\ N\ g^{-1}\ d^{-1}$ dry sediment at 800 m to $5.65 \pm 3.18\ \mu g\ N\ g^{-1}\ d^{-1}$ dry sediment at 0 m. For each of the platform sites, sediment within 0, 25, and 50 m of the platform had higher potential denitrification rates than to more distance sites (200, 400, and 800 m). The sites nearer the platform also had a higher amount of organic matter content than sites with distance from the platform.

Figures 2 and 3 show the relationship of organic matter and denitrification with distance from the platform. The organic matter–distance relationship is shown by the $r$ of 0.936 ($P < 0.001$) and $r$ of 0.985 ($P < 0.001$). The correlation analysis between percentage organic matter and denitrification (figure 4) was statistically significant ($r = 0.716$, $P < 0.001$). We attribute this to higher fish densities near the platform. Standing platforms harbour about 0.1 fish $m^{-3}$ (average fish size 0.5 kg) where open water fish densities are 0.0001–0.001 fish $m^{-3}$ (Chuck Wilson, personal communication). The higher fish densities and dense growth of encrusting organism on platform legs lead to a high organic rain on sediment in the vicinity of the platform. The results clearly demonstrate that the higher organic matter found in sediment near the platform supports a more active rate of denitrification.

If we assume that the average bulk density of surface sediment is $1.0\ g\ cm^{-1}$, the top 1 cm of surface of sediment is the active zone of nitrification–denitrification, and the average denitrification rate is $5\ \mu g\ N\ d^{-1} g^{-1}$ dry sediment 0 m from the platform, the denitrification rate per $m^2$ of surface sediment would be approximately $50\ mg\ N\ m^{-2}\ d^{-1}$ ($3.571\ mmol\ N\ m^{-2}\ d^{-1}$). Based on an average denitrification at 800 m of $1.5\ \mu g\ N\ g^{-1}\ d^{-1}$ dry sediment, the denitrification rate would be $15\ mg\ N\ m^{-2}\ d^{-1}$ or $1.071\ mmol\ N\ m^{-2}\ d^{-1}$.



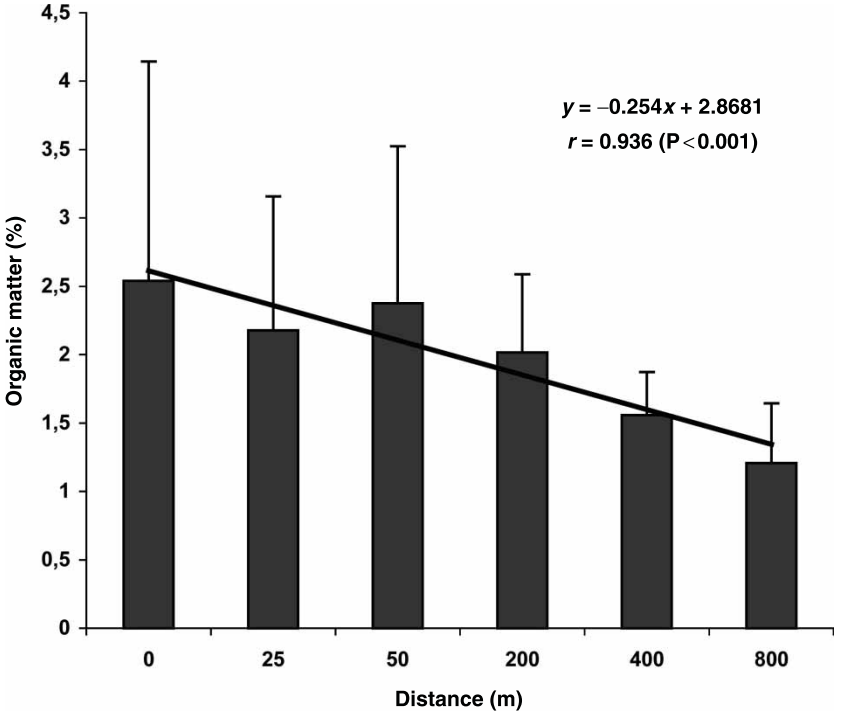



Figure 2. Change in sediment organic matter content with distance from two platforms (average of two platforms, $n = 18$).

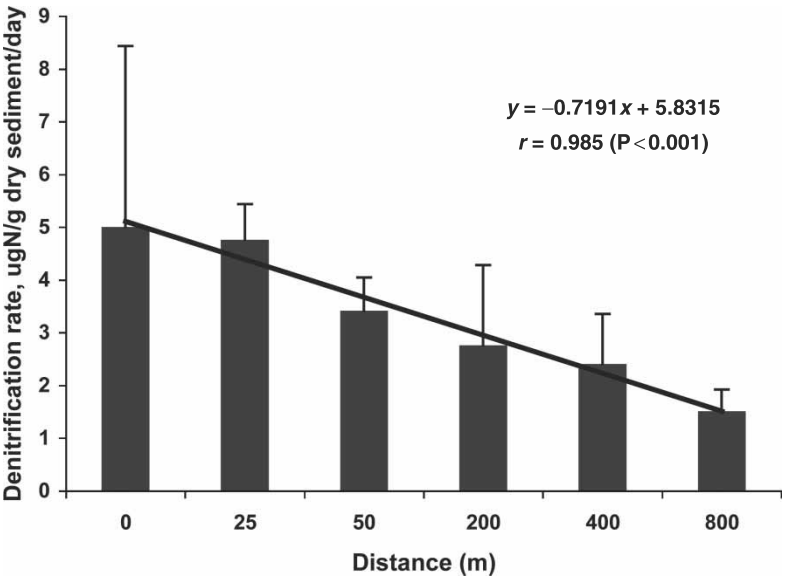



Figure 3. Denitrification in sediment with distance from the two platforms (average of two platforms, $n = 18$).



The acetylene technique used in this study blocks the reduction of $N_2O$ to $N_2$, and accumulation of $N_2O$ is equated to the denitrification rate. The method has several limitations, since acetylene inhibits nitrification and methanogenesis, and growth of sulpate-respiring bacteria. In addition, acetylene is not always an effective block [22]. The above may affect the denitrification rates measured. The measured potential denitrification rates in this study, however, are in the range for other reported studies. Reported denitrification rates in various estuaries and coastal marine sediment range between 33.6 and 168 mg N $m^{-2}$ $d^{-1}$ [23]. By comparison, denitrification rates in stream and river sediment range from 0 to 238 mg N $m^{-2}$ $d^{-1}$. Henriksen *et al.* [24] reported denitrification rates of 10–40 mg N $m^{-2}$ $d^{-1}$ for sediment off the Danish coast. Denitrification rates are generally higher in systems from riverine sources receiving nitrogen input [25].

Even though nitrate loading to the Gulf of Mexico by Mississippi river discharge is a major source of nitrate for denitrification, in most systems including coastal marine sediments, nitrate produced in the bottom sediment, rather than nitrate diffusing from the diverging water, is the

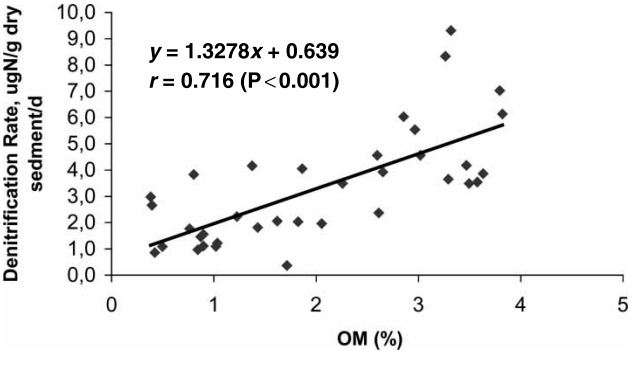



Figure 4. Correlation between organic matter (OM %) and denitrification rate in sediment receiving 10 μg $NO_3$-N $g^{-1}$ ($n = 36$).

source for denitrification [13, 26]. In this study, in which we added $NO_3$-N, the measured denitrification is likely to have been higher than the actual denitrification rates occurring in the sediment.

Even though our potential denitrification measurement may have been overestimated, this transect study clearly demonstrates the relationship of organic matter to the process and of organic matter to the distance from the platforms. It also suggests the possible influence of fish density effects on biogeochemical processes in the vicinity of offshore production platforms. The measured potential denitrification rate in the bottom sediment is only one aspect of the benthic nitrogen cycling in coastal area off the Louisiana Gulf Coast. It was once thought that denitrification was the only process converting nitrogen to gaseous $N_2$. It has recently been discovered that anaerobic oxidation of ammonium with nitrite (Anammox reaction) may also be a source of $N_2$ production in anoxic coastal basins [27, 28]. Additional research is needed for quantifying nitrogen accumulation, organic matter mineralization, nitrification and the importance of regenerated ammonium nitrogen to the nitrogen budgets. Since the coupled nitrification–denitrification reaction is related to the amount of oxygen penetrating into the surface sediment, the hypoxic conditions (dead zones) may strongly influence nitrification of ammonium nitrogen in the surface sediment. A reduction in the rate of nitrification associated with low oxygen levels would in turn reduce the denitrification rates.



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