

# Remediation of Coastal Sediments by Addition of Calcium Nitrate and Presence of Benthos in a Muddy Tidal Flat

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## Abstract

This study investigated the change in denitrification rate in muddy tidal flats sediment by chemical and biological remediation. Column experiments were conducted to determine the dependence of denitrification rate on the redox potential. Filtered seawater was fed continuously to the pipe filled with sediment from the muddy tidal flats. An increase in the redox potential from  $-198$  mV to  $21$  mV with bioturbation led to increases in the denitrification rate from  $24.2$  mg/m<sup>2</sup>/day to  $29.8$  mg/m<sup>2</sup>/day. The increase in denitrification was explained by the acceleration of mass transfer in the sediment. Redox-potential increased from  $-400$  mV to  $-200$  mV by the addition of  $10$  g calcium nitrate, acid volatile sulfide was below the detection limit to  $20$  cm depth, and denitrification rate was increased from  $21.3$  mg/m<sup>2</sup>/day to  $36.4$  mg/m<sup>2</sup>/day. It is considered that the increased nitrogen concentration led to an increase in microbial activity.

## Keywords

Redox Potential, Muddy Tidal Sediment, Denitrification, Bioturbation, Calcium Nitrate

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## 1. Introduction

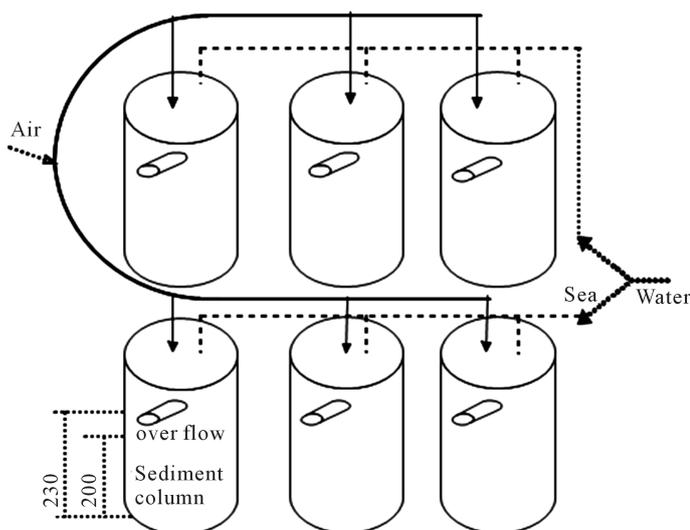
Bioremediation is the process of a return to the original state that does not contain harmful compounds by using plants, fungi, microorganisms or their enzymes. Bioremediation has mainly been used to treat hydrocarbons, hexavalent chromium, aromatic hydrocarbons, diesel and crude oil in contaminated soils [1]-[5]. Despite many environmental remediation technologies being reported for land-based contamination, few studies have been conducted in aquatic environments. The removal of nitrogen from the aquatic environment will lead to the suppression of occurrences of red tide. Pore water exchange is lower in the muddy tidal flats compared with the

sandy tidal flats to contain organic matter and fine particles of mud [6]. One of the important purification functions of tidal flats is nitrogen removal by nitrification and denitrification. At the tidal flat, the water depth is shallow, active biological motion and seawater exchange takes place, and enough ammonia and oxygen are supplied to nitrifying bacteria. Simultaneously, nitrate and organic matter are supplied to denitrifying bacteria [7] [8]. As a feature of the sediments of tidal flats, the environment is very different between the surface and the internal environment of the sediment. In the deeper part of the sediment, oxygen does not penetrate and an anaerobic environment is formed. In the environment, anaerobic, denitrifying bacteria are responsible for denitrification. In this study, we targeted the remediation of muddy tidal flat sediments that are generally an anoxic environment. Fine muddy sediments are under very strong reducing conditions and, permeability is small, but the environment can promote repair by creating different states. If mass transfer of oxygen and nitrate can be promoted, it is possible to reduce the acid-volatile sulfide and nitrogen by environmental remediation. Burrows of benthos contribute to oxygen transfer in tidal flats. The oxidation zone can be increased by penetration of fresh seawater to the nest holes of benthos. The sediment around a burrow will be oxidized but oxidation will be reduced with increased distance from the burrow. The denitrification process in this case is referred to as bioturbation [8]. Raymundo *et al.* (1992) measured the denitrification activity in the bottom sediment using the acetylene block method, and reported the changes in relation to time and depth [9]. In this study, particle sizes are classified as fine muddy sediment rather than Raymundo [9]. The method for enhancing the activity of denitrifying bacteria by supplying nitrate ions as well as changing the reduction state of mud flats with an oxidizing agent containing nitrates at the same time has been studied. Nitrate calcium hydrate is one of the oxidizing agents being used to improve sediments [10]. Addition of this compound to sediments could improve the oxidation of the sediment and accelerate denitrification activity [11]. We have also considered the effect of calcium nitrate on characteristics of muddy sediments in this study.

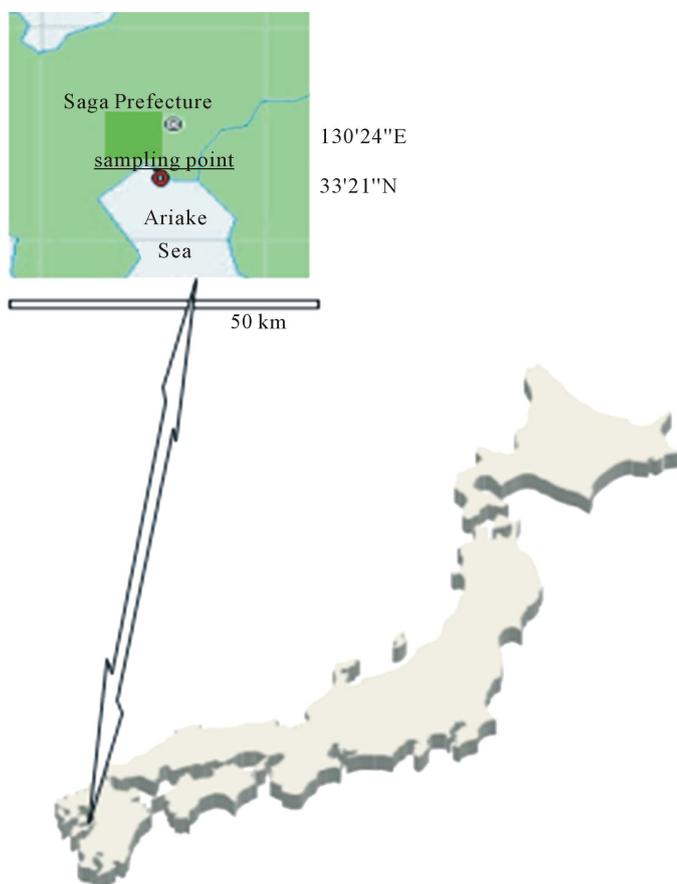
## 2. Materials and Methods

### 2.1. Effects of Bioturbation on Denitrification

To avoid the influence of original benthic organisms living in the sediment, they were excluded using a sieve. Introduced polychaetes were obtained from the same environment as the sediment samples as much as possible. Sediment samples were taken from the 0 - 2 cm layer. Sediment samples were processed through a 1 mm sieve by pouring seawater. Filtered Sediment was filled to a height of 20 cm into columns that had rubber stoppers on the bottom. Oxygen was slowly supplied into bulk seawater on sediments by an air pump. **Figure 1** shows the experimental apparatus. The seawater was collected from the estuary tidal flat region (**Figure 2**). The sampling position was in Sagaprefecture Kyushu, Japan (130°E and 33°N). The seawater was replaced with newly filtered



**Figure 1.** Experimental setup (RUN and Control).



**Figure 2.** Sampling point in Kyushu, Japan (130°24'E, 33°21'N).

seawater once a week. Six columns were prepared. Six polychaetes of 0.8 - 1.5 g were added to each of three columns. These columns were defined as RUN and the other three columns were defined as controls. Control and RUN columns were dismantled at days 15 and 30. Sediment COD and denitrification activity were analyzed.

## 2.2. Effects of Calcium Nitrate on Denitrification

In a separate experiment, calcium nitrate (5, 10 and 30 g) was added to each of three columns filled with sediment. A similar experiment procedure was conducted as in [Figure 1](#), except that oxygen was not supplied in this experiment.

## 2.3. Analyses

Denitrification rate was measured by the acetylene block method [7] [10] [12]. Nitrous oxide was measured using a gas chromatograph (Hitachi GC-14, Tokyo Japan) with ECD detector. Redox potential of the sediment was measured using a platinum electrode (Eh portable meter PRN-41/Fujiwara Scientific Co. Ltd., Tokyo, Japan) with a diameter of 0.5 mm at a depth of 1 cm from the surface layer on the sampling time. Acid volatile sulfide was measured using the Sulfides Measuring Kit (Hydrotec-S, Gas Tech Corporation, Kanagawa Japan).

## 3. Results and Discussion

### 3.1. Effects of Bioturbation on Denitrification

[Tables 1-3](#) show the results of denitrification rate, Eh and COD. Denitrification rate increased over time in the control. Redox potentials were  $-201 \text{ mV} \pm 40 \text{ mV}$  in the control. Denitrification rate reached maximum values

**Table 1.** Changes in the denitrification rate.

Elapsed time [day]	Denitrification rate [mg/m <sup>2</sup> /day]	
	Control	RUN
0	21.2	21.2
15	25.2	29.8
30	29.8	18.7

**Table 2.** Changes in the redox potential.

Elapsed time [day]	Eh [mV]	
	Control	RUN
0	-172	-172
15	-258	21
30	-203	128

**Table 3.** Changes in the COD.

Elapsed time [day]	COD [mg/L]	
	Control	RUN
0	1.4	1.4
15	1.5	2.1
30	1.5	2

At 15 days, because of the large mass transfer and limited increase in oxidation state. The redox potential reached 120 mV at 30 days, and denitrification was reduced. Wang *et al.* [12] [13] reported that DO was inversely related to sediment denitrification rate.

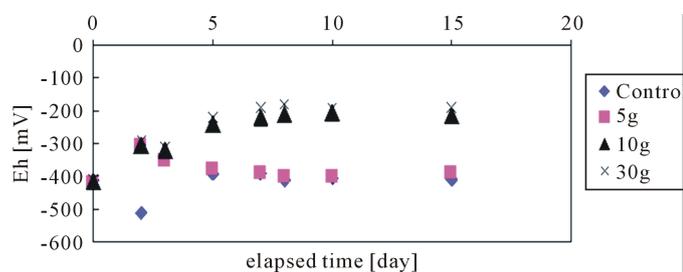
Remediation of this sediment could be improved by using an oxidizing agent in the oxidation state from reduced state. Activities of benthos increased COD in sediment, but did not affect denitrification rate in this study.

### 3.2. Effects of Calcium Nitrate on Denitrification

**Figure 3** shows the redox potential of the sediment column surface. Redox potentials were maintained at about -400 mV in columns with addition of 0 and 5 g calcium nitrate. In columns with 10 g and 30 g addition of calcium nitrate, the redox potential increased to -200 mV. **Table 4** shows the nitrate nitrogen of interstitial water and denitrification rate of the surface layer. The denitrification activity was proportional to the nitrogen concentration [12]. Addition of calcium nitrate reduced sulfide content over the entire layer and strongly reducing conditions were improved. Yamamoto (2012) reported that crushed oyster shells contribute to oxidization of marine sediments, and acid volatile sulfide was reduced by addition of this powder [13].

## 4. Conclusion

The muddy sediment in tidal flats has significant purification capacity, but the current situation is not optimal with low permeability and low redox potential. This study examined the environmental remediation of these conditions using biological and chemical treatments. We used polychaetes and chemical oxidation of calcium nitrate. Bioturbation altered the redox potential in muddy sediments to oxic conditions, and caused an increase in the denitrification rate. Redox potential increased with the amount of calcium nitrate added, but did not increase enough to reach an oxidized state. By addition of calcium nitrate to muddy tidal sediment, sediment COD



**Figure 3.** Changes in redox potential.

**Table 4.** Effects of calcium nitrate addition.

Denitrification rate [mg/m <sup>2</sup> /day]				
Depth [cm]	Control	5 g Calcium nitrate	10 g Calcium nitrate	30 g Calcium nitrate
0 - 10	21.3	25.2	36.4	46.1
Nitrate in Pore water/NO <sub>3</sub> -N [mg/L]				
Depth [cm]	Control	5 g Calcium nitrate	10 g Calcium nitrate	30 g Calcium nitrate
0 - 10	0.58	8.53	5.62	2.67
10 - 20	0.68	0.19	7.75	1.27
Nitrate in bulk water/NO <sub>3</sub> -N [mg/L]				
	Control	5 g Calcium nitrate	10 g Calcium nitrate	30 g Calcium nitrate
	0.6	4.2	6.1	18.2
Acid-volatile sulfide (AVS) [%]				
Depth [cm]	Control	5 g Calcium nitrate	10 g Calcium nitrate	30 g Calcium nitrate
0 - 10	0.00002	N.D.	N.D.	N.D.
10 - 20	0.004	0.0006	N.D.	N.D.

and acid volatile sulfide were also reduced, but because nitric acid remains in the bulk we will also consider the synergistic effects of bioturbation.

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