

Denitrification in Qi'ao Island coastal zone, the Zhujiang Estuary in China

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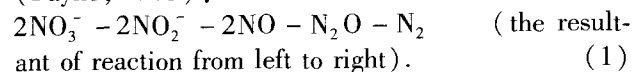
Abstract

Samples of sediments and the overlying water were collected in the Qi'ao Island coastal zone, the Zhujiang (Pearl River) Estuary (ZE). Denitrification rates, sediment oxygen demand (SOD), and fluxes of inorganic nitrogen compounds were investigated with N₂ flux method, using a self-designed continuous flow through and auto-sampling system. The results indicate that the denitrification rates varied between 222 and 908 μmol/(m² · h) with an average of 499 μmol/(m² · h). During incubation, the sediments absorbed dissolved oxygen in the overlying water with SOD ranging from 300 to 2 363 μmol/(m² · h). The denitrification rates were highly correlated with the SOD ($r^2 = 0.77$) regardless of the NO₃⁻ + NO₂⁻ concentrations in the overlying water, organic carbon contents in sediments and water temperature, suggesting that the SOD was probably the main environmental factor controlling the denitrification in the Qi'ao Island coastal zone. There was a net flux of NO₃⁻ + NO₂⁻ into the sediments from the overlying water. The NH₄⁺ flux from sediments into water as the result of mineralization was between 12.3 and 210.3 μmol/(m² · h), which seems limited by both organic carbon content in sediment and dissolved oxygen concentration in the overlying water.

Key words: denitrification, N₂ flux, SOD, inorganic nitrogen compound, Qi'ao Island coastal zone, Zhujiang Estuary

1 Introduction

Nitrogen cycles are one of the key aspects of understanding marine ecosystem. Marine nitrogen cycles include nitrogen fixation, nitrification, denitrification, mineralization, and synthesis of inorganic nitrogenous compounds (Hebert, 1999). Denitrification is a significant process as it removes excess nitrogen in the ocean (Devol and Christensen, 1993; Christensen et al., 1987; Bender et al., 1977), and it is a reductive process, whereby heterotrophic bacteria utilize nitrate or nitrite as a terminal electron acceptor, and reduce it to gaseous products (N₂ or N₂O) under oxygen depleted condition (Payne, 1973):



Denitrification has been studied since the 1970s, and becomes one of the issues of coastal nutrient biogeochemistry study. But the progress is limited by

the difficulty in measuring N₂, the end product of denitrification. Therefore, it is significant to construct reliable methods for measuring denitrification. Some major approaches have been taken to measure denitrification in terrestrial and aquatic environments, such as acetylene inhibition technique (AIT), nitrogen-15 isotope pairing technique, N₂ flux method, and membrane inlet mass spectrometry (MIMS) since the 1970s. However, all these techniques have their own advantages and limitations (Groffman et al., 2006; Cornwell et al., 1999). The most commonly applied method to measure denitrification is based on the ability of acetylene (C₂H₂) to inhibit the reduction of N₂O to N₂. The accumulation of N₂O instead of N₂ is readily measured by gas chromatograph using an electron capture detector and the total N₂O flux is equivalent to the denitrification rate. AIT is relatively easy, sensitive and economical. However the most critical of this method is that C₂H₂ can inhibit the production of

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NO_3^- via nitrification and C_2H_2 cannot inhibit N_2O reductase completely (Koike and Sørensen, 1998; Seitzinger et al., 1993). Therefore, this technique may underestimate denitrification rate (Lohse et al., 1996; Seitzinger et al., 1993). Nitrogen-15 isotope pairing technique is based on adding $^{15}\text{NO}_3^-$ or $^{15}\text{NH}_4^+$ to water or sediment and measuring the production of ^{15}N -labeled N_2 . This approach can partition the denitrification attributable to $\text{NO}_3^- + \text{NO}_2^-$ in the overlying water and $\text{NO}_3^- + \text{NO}_2^-$ supplied by nitrification (coupled nitrification-denitrification) (Nielsen, 1992). The problem with this method is that the added $^{15}\text{NO}_3^-$ or $^{15}\text{NH}_4^+$ might accelerate the denitrification (Nielsen and Glud, 1996; Nishio et al., 1983). N_2 flux method could provide the accurate estimate of denitrification rate as it is based on measuring N_2 directly without adding nitrate or any other chemicals. Shortcomings of this method (Van Lujin et al., 1999; Risgaard-Petersen et al., 1998) are mainly associated with contamination by the large N_2 background in air when N_2 is sampled and measured. On the other hand, a long preincubation time is needed to exhaust the residual pore water N_2 in sediment. MIMS has been applied on the study of denitrification after it was used to measure N_2 in water since 1994 (Pribyl et al., 2005; McCutchan et al., 2003; Laursen and Seitzinger, 2002; Kana et al., 1998; Kana et al., 1994). Even a slight change of N_2 concentration in water can be detected by MIMS, which make measurement of denitrification rate more accurate and easier.

In recent several decades, nitrogen fertilizer has been widely used in China, and the loss rate reaches 30%, which results in a rapid increase of inorganic nitrogen in coastal areas (Yang et al., 2003; Wang, 1989). The nitrogen and phosphorus contents of the ZE are seven and three times that of the average level of world estuaries respectively. Its ratio of nitrogen to phosphorus is 21.6, which is much higher than the average (10.3) of world estuaries (Hu et al., 2001). It is estimated that 20%—50% nitrogen loading could be removed by denitrification in estuaries (Hebert, 1999; Seitzinger, 1988). However, there are very few studies on denitrification in the estuaries and coastal areas of China and the measurement technique and incubation setup were all limited to AIT and static incubation (Wang et al., 2006; Xu et al., 2005). The effect of denitrification on nitrogen removal, transfer, and red tides is not clear (Compilation Committee of China Bay Records, 1998), which

will hinder our comprehensive understanding of environmental disasters such as red tides and hypoxia, and affects the establishment of marine environment protection policies and some relative rules and regulations.

In this study, denitrification in sediments of the Qi'ao Island coastal zone was investigated applying N_2 flux method and a self-designed continuous flow through and auto-sampling system. Manual sampling and injecting of gases being avoided, this system surmounts the limitations of N_2 flux method. The present study was also made to illuminate the change of dissolved inorganic nitrogen (DIN) in the overlying water during denitrification and to provide insight into factors controlling denitrification rates in the Qi'ao Island coastal zone.

2 Materials and incubation system

2.1 Sampling

Qi'ao Island has an area of 20 hm^2 , with mud-flat along the west and north coast, while sandy sediment along the east and south coast. Sample sites were situated northwest of Qi'ao Island (see Fig. 1) as denitrification rate in muddy sediment is obviously higher than in sandy sediment, which is related to the high availability of organic matter in muddy sediment.

Muddy sediment cores and the overlying water were collected from February to December 2004, using transparent perspex tubes (diameter 7.4 cm, length 60.0 cm). Sample details were shown in Table 1. There was obvious bioturbation only at Sta. 5, with many macrophytes and caves left by macrofauna. After samples were transported to ship, 0—8 cm sediments were chosen and kept at 4°C and taken to laboratory in 12 h. The overlying water was collected and filtrated through a pre-rinsed glass fiber filter of pore size 0.45 μm , and kept at -20°C until incubation.

2.2 Incubation system

The end product of denitrification, N_2 , was usually sampled using syringe, then injected into gas chromatograph. However, the air contamination is inevitable and the measuring accuracy and precision are not high. To address these issues, we have designed a continuous flow-through and auto-sampling system (see Fig. 2). By connecting incubation system to a gas spectrometry via a six-port valve, gas products (N_2/O_2) can be sampled automatically and measured on line. In addition, sediment samples would be purged with inertia gas (helium) to reduce

the N_2 background in sediment before incubation without disturbing sediment surface. This can reduce

the preincubation time effectively.

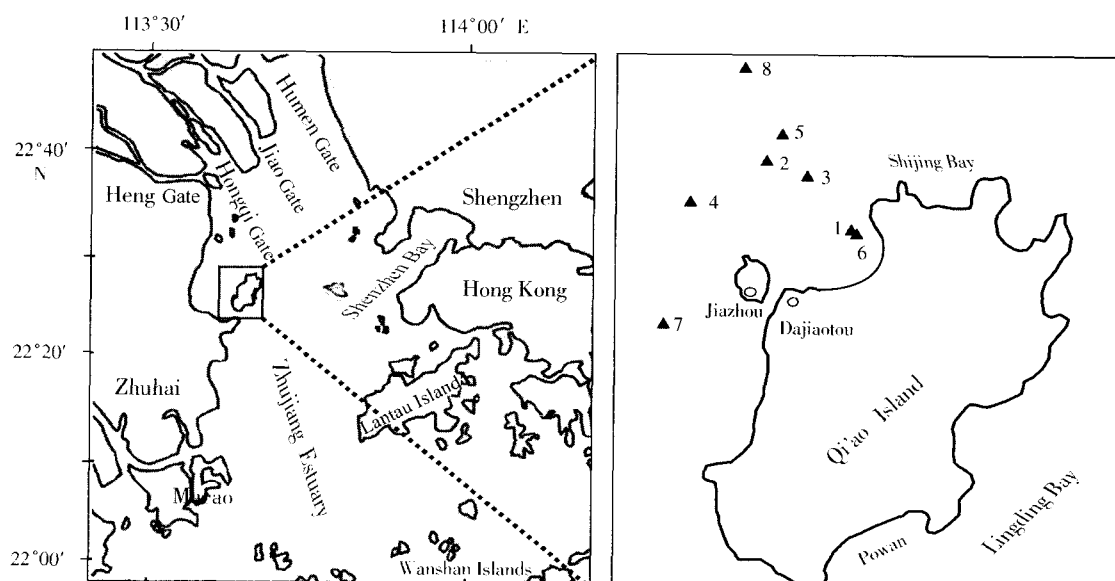


Fig. 1. Map of sampling sites.

Table 1. Sample characteristics and incubation results (denitrification rate, SOD and fluxes of dissolved inorganic nitrogen)

| | Station | | | | | | | |
|--|------------------------|--------|--------|-------|--------|--------|-------|--------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | sample characteristics | | | | | | | |
| Sampling time | Feb. | Apr. | Apr. | Aug. | Sep. | Nov. | Dec. | Dec. |
| Water temperature/°C | 20 | 19 | 19 | 28 | 28 | 18 | 20 | 20 |
| Depth/m | 0.5 | 1.5 | 1.3 | 1.0 | 1.3 | 0.5 | 1.2 | 1.4 |
| TOC in sediment(%) | 2.11 | 1.21 | 1.70 | 1.50 | 1.47 | 1.01 | 1.19 | 1.30 |
| $NO_3^- + NO_2^-$ concentration in overlying water/ $\mu\text{mol} \cdot \text{dm}^{-3}$ | 49.3 | 113.5 | 138.2 | 65.1 | 69.5 | 100.9 | 94.8 | 110.7 |
| NH_4^+ concentration in overlying water/ $\mu\text{mol} \cdot \text{dm}^{-3}$ | 13.4 | 3.8 | 8.89 | 0.9 | 1.8 | 11.4 | 1.3 | 0.9 |
| | results | | | | | | | |
| $F_{N_2}/\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | 401 | 222 | 666 | 426 | 908 | 699 | 240 | 429 |
| $F_{O_2}/\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | 1 988 | 2 363 | 1 808 | 1 998 | 300 | 1 696 | 2 221 | 1 861 |
| $F_{NO_3^- + NO_2^-}/\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | -136.5 | -276.5 | -325.2 | -99.7 | -236.1 | -151.5 | -43.0 | -191.0 |
| $F_{NH_4^+}/\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | 210.3 | 112.9 | 143.3 | 68.6 | 12.3 | 55.4 | 130.6 | 96.8 |

Notes: F means flux; “-” means concentration in effluent is lower than in influent.

The incubation system consists of four parts, gas-supplying, water-supplying, incubation and sampling-measuring setup (see Fig. 2). (1) Gas-supplying setup: reservoir C for storing the overlying water was bubbled with mixed gas free of N_2 ($CO_2 + O_2 + He$) in specific ratio for the purpose of lowering

the N_2 background and adjusting O_2 concentration in the water. (2) Water-supplying setup: the overlying water was supplied by means of peristaltic pumps (D_1, D_2) from C and E. The flow rate was 16.3 mL/h. This relative low flow rate was chosen to optimize the sensitivity of the flux measurement. (3) Incuba-

tion setup; the incubation chamber (H) was a glass cylinder (diameter 7.4 cm, height 14.3 cm) with sediment in the bottom and filled with the overlying water in the upper space stirred by a teflon-coated magnet (G). The stirring rate should be adjusted not to resuspending the sediment. H, covered with aluminum foil to keep dark, was put in a thermostated water bath (I) so that the experiments could be done at in situ temperature. (4) Sampling and measuring setup; water samples for analyzing DIN contents before and after incubation were withdrawn from sampling ports F₁ and F₂ using glass syringes. Gas samples (N₂/O₂) dissolved in water were ex-

tracted in the 51 mL degassing flask (J). First, valve K₁ and K₂ and K₃ were closed, and water (about 20 mL) in J was heated to approximately 70°C while stirring the water vigorously. N₂/O₂ escaped to the upper space of J. Second the tube between K₃ and K₄ including sample loop (0.25 mL) was pumped into vacuum after it was flushed with helium. Then valve K₃ was opened, N₂/O₂ in the upper space of J entered into sample loop of six-port valve (M) under low pressure. By rotating the M, N₂/O₂ in the loop were carried into the gas chromatograph (O) and analyzed.

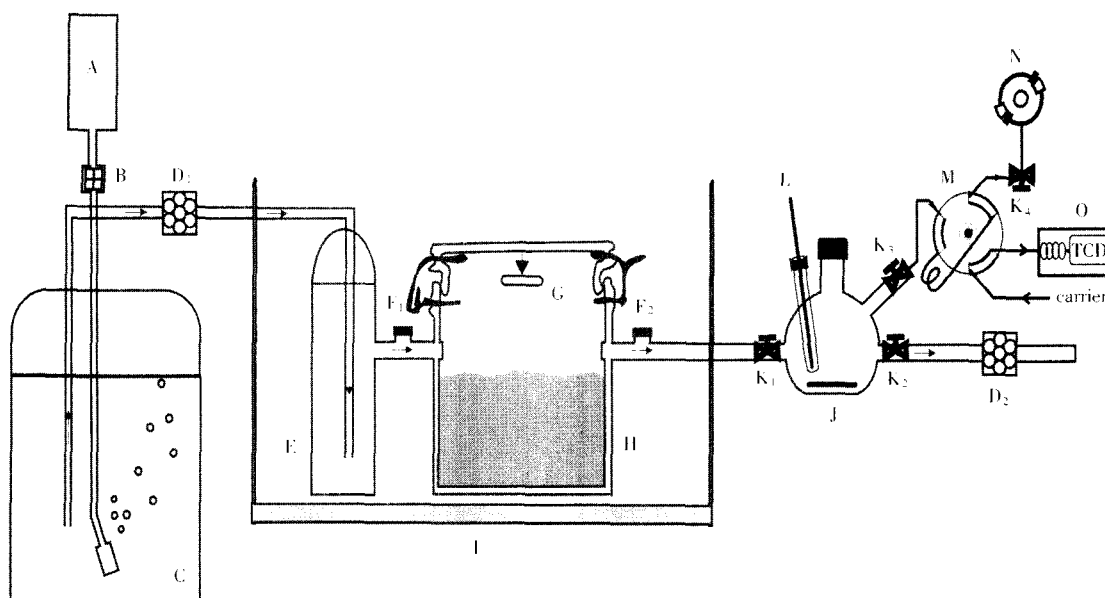


Fig. 2. The continuous flow through and auto-sampling system for sediment incubation. A represents gas mixture, B flowmeter, C 10 L reservoir, D1 and D2 peristaltic pump, E bottle for supplying water, F1 and F2 sampling port, G Teflon-coated magnet, H incubation chamber, I thermostated water bath, J degassing flask, K1–K4 valve, L thermometer, M six-port valve, N vacuum pump, and O gas chromatograph.

Samples of water and gases were collected every 12 or 24 h, and every experiment run for about 10 d. The control experiments without sediment would be also made to insure and check the gas tightness and stability of the incubation system, N₂ background and oxygen concentration in the overlying water being acquired simultaneously.

3 Methods

N₂ produced via denitrification and O₂ in the overlying water were analyzed by a gas chromatograph of HP6820 equipped with a TCD. The chromatograph and analyzing condition are as follow: 3 m × 1/8 molsieve 5A (60/80) packed column; high

purified helium as the carrier, TCD temperature was 250°C; column temperature was 60°C. Three kinds of main dissolved inorganic nitrogen (NH₄⁺, NO₂⁻, NO₃⁻) in water were analyzed by colorimetry, NO₃⁻ was analyzed with autoanalyzer A II. The detailed steps were after *China Specification for Oceanographic Survey* (State Bureau of Quality and Technical Supervision, 1994). For analyzing total organic carbon contents using elemental analyzer, carbonate in sediments was removed with 10% HCl. Every sample was measured twice, and the average was accepted. The standard deviation (σ) is ± 0.02 ($n = 5$).

Fluxes of N₂, NH₄⁺, NO₃⁻, NO₂⁻ and SOD across the sediment-water interface were calculated

by the general flux equation according to the concentration change between the effluent and influent water.

$$F = \frac{c_e - c_i}{A} r_f, \quad (2)$$

where F is flux; c_e and c_i are the concentrations in the effluent and influent water; r_f the flow rate; and A is the surface area of the sediment.

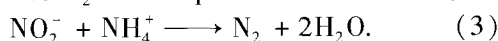
4 Results and discussion

4.1 Overlying water DIN concentrations

The concentrations of dissolved inorganic nitrogen (DIN = $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) in the overlying water were very high, and varied from 62.7 to 147.1 $\mu\text{mol}/\text{dm}^3$ with an average value of 98.0 $\mu\text{mol}/\text{dm}^3$ (see Table 1), indicating the high nitrogen loading and anthropogenic pollution in the Qi'ao Island coastal zone, the ZE. NO_3^- was the main existing form of DIN, and comprised over 70% of the DIN. NH_4^+ concentrations at Stas 1, 3 and 6 were higher than at other stations. This is probably related to the drainage of domestic sewage because Stas 1, 3 and 6 are nearer to the Qi'ao Island coastal line. As the concentration of NO_2^- was low ($<4 \mu\text{mol}/\text{dm}^3$) and its change during incubation was very small, we combined NO_3^- and NO_2^- as a whole.

4.2 Denitrification rate

Since anaerobic ammonium oxidation (anammox) was found [Eq. (3)], it had been thought as one of the two N_2 sources produced in sediment:



Anammox is a strict anaerobic process, and is correlated with sediment mineralization rate and water depth. Many studies have showed that anammox is accelerated by mineralization in shallow estuaries. However, N_2 from anammox is a minor part of total N_2 production except in marine environment with great depth, where Anammox would be responsible for 1/3–1/2 of the N_2 production in sediments (Dalsgaard et al., 2003; Thamdrup and Dalsgaard, 2002; Strous et al., 1997). Rysgaard et al. (2004) found that N_2 production via anammox was from 35% to 1% of the total N_2 production in sediments of east and west Greenland as the water depth decreased from 100 to 36 m. Therefore we deduced that the N_2 production in the sediments was mainly from denitrification in our study.

According to the previous studies (Pribyl et al., 2005; McCutchan et al., 2003; Risgaard-Petersen et al., 1998), about 10 d of preincubation

time was needed to exhaust the large pool of N_2 initially dissolved in sediment pore water, depending on the sediment thickness. In this study, the preincubation time was reduced to 4–5 d because the sediments were initially purged with helium. To take the sediment incubation at Sta. 1 as an example, concentrations of N_2 and O_2 in the effluent water achieved steady state within 4 d (Fig. 3). The results of other incubation experiments are analogous to this.

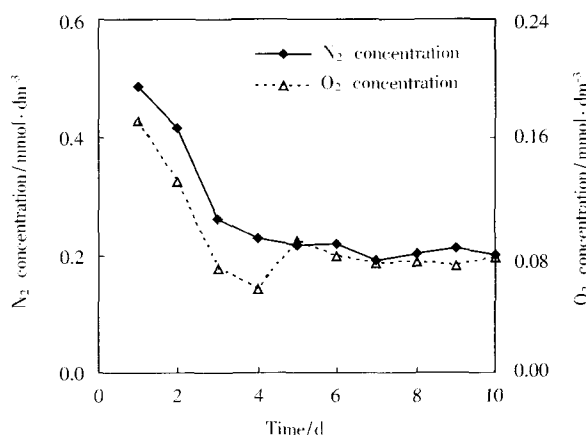


Fig. 3. Concentrations of N_2 and O_2 in the effluent water during incubation of sediment at Sta. 1.

When the outflow concentration of N_2 was stable, the N_2 production (denitrification) was estimated from Eq. (2). The results were listed in Table 1. The denitrification rates were significantly different, and varied from 222 to 908, 499 $\mu\text{mol}/(\text{m}^2 \cdot \text{h})$ on average. Comparison of denitrification rates is somewhat difficult given the complicated coastal environments, even samples were collected in the same season (e.g., Stas 2 and 3, Stas 7 and 8). In Section 4.4, the main environment factor controlling denitrification would be discussed in detail.

The denitrification rates in Qi'ao Island coastal zone were obviously higher than those in most other estuaries reported previously (see Table 2), but are consistent with that in polluted estuaries receiving excess waste such as the Narragansett Bay and the Tama Estuary (Usui, 2001; Seitzinger and Nixon, 1985). For recent 20 a, the nitrogen, phosphorous and organic matter loading of the ZE have increased rapidly, and the eutrophication become worsened with the development of economy and rapid growth of population (Wang and Peng, 1996), which largely accelerated the denitrification. However, we could not assess the importance of denitrification in nitro-

gen loss in the Qi'ao Island coastal zone as we have no data of nitrogen input there. The measured denitrification rates were most representative of the Qi'ao Island coastal zone, not the ZE. But with these high denitrification rates and nitrogen load, we have reason to deduce that denitrification might play a more

significant role in nitrogen budget in the ZE than in other estuaries. Future studies on seasonal change and spatial distribution of denitrification at large scale are urgently needed in the ZE, which will help to fill a vacancy in our knowledge of China's estuaries.

Table 2. Denitrification rates reported for estuaries

| Location | Rate/ $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ | Method | Reference |
|---|---|--------|--------------------------------|
| Ochlockonee Bay in Florida | 0–210 | a | Seitzinger (1987) |
| Galveston Bay in Texas | 0–47 | a | Zimmerman and Benner (1994) |
| Narragansett Bay | 305–888 | a | Seitzinger and Nixon (1985) |
| Tama Estuary in Japan | 214–1 260 | b | Usui et al. (2001) |
| Aarhus Bight | 350–470 | b | Nielsen and Glud (1996) |
| Neva Estuary | 0.4–50 | b | Gran and Pitkänen (1999) |
| River Colne Estuary | 0–6 250 | b | Dong et al. (2000) |
| St. Lawrence Estuary | 19.2–51 | b | Poulin et al. (2007) |
| Landrup Vig | 12–213 | c | Andersen et al. (1984) |
| Great Bay, Long Island | 3–16 | c | Slater and Capone (1987) |
| Chongming east tidal flat, Changjiang Estuary | 1.12–34.09 | c | Wang et al. (2006) |
| Zhujiang Estuary | 30–840 | c | Xu et al. (2005) |
| Raritan Bay, New Jersey | 158–308 | d | Hartnett and Seitzinger (2003) |
| Neuse Estuary | 0–275 | d | Fear et al. (2005) |
| Qi'ao Island, Zhujiang Estuary | 222–908 | a | This study |

Notes: a represents N_2 flux method, b nitrogen-15 isotope pairing technique, c acetylene inhibition technique and d membrane inlet mass spectrometry.

$\text{NO}_3^- + \text{NO}_2^-$ in the overlying water did not appear to be the only source of $\text{NO}_3^- + \text{NO}_2^-$ supporting denitrification. $\text{NO}_3^- + \text{NO}_2^-$ uptaken by the sediment accounted for less than 50% of the $\text{NO}_3^- + \text{NO}_2^-$ and needed to support the measured denitrification rates except at Sta. 2 (see Fig. 4). Nitrification of NH_4^+ released during mineralization of organic nitrogen in sediment appeared to be another $\text{NO}_3^- + \text{NO}_2^-$ source. Xu et al. (2005) also found that there were simultaneously processes of nitrification, denitrification and nitrate reduction in sediment of the ZE using AIT technique. But the magnitude of coupled nitrification-denitrification and denitrification supported by the overlying water $\text{NO}_3^- + \text{NO}_2^-$ should be quantified by nitrogen-15 isotope pairing technique. At Sta. 2, denitrification rate was smaller than $\text{NO}_3^- + \text{NO}_2^-$ uptaken by the sediment. Processes of anammox and/or assimilatory nitrate reduction might consume more $\text{NO}_3^- + \text{NO}_2^-$ into the sediment than at other stations, while further evidence is needed to

support this.

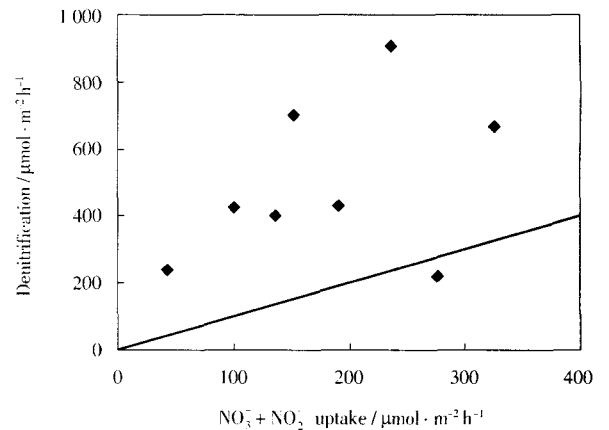


Fig. 4. Denitrification rates as a function of the rate $\text{NO}_3^- + \text{NO}_2^-$ uptaken ($F_{\text{NO}_3^- + \text{NO}_2^-}$) by the sediments from the overlying water. Line is the 1:1 ratio between denitrification rate and $\text{NO}_3^- + \text{NO}_2^-$ uptake; points above the line represent sediments in which denitrification rates were greater than net $\text{NO}_3^- + \text{NO}_2^-$ flux into sediments from the overlying water.

N_2O is a byproduct of denitrification. Many studies showed that N_2O in estuary water is supersaturated, and it is one of the sources of atmosphere (Seitzinger and Kroeze, 1998; Law et al., 1992; Jørgensen et al., 1984). However N_2O production is not the main process of nitrogen loss in estuaries. The ratio of N_2O : N_2 flux from benthic sediments is generally within the range of 0.1%–0.5% in rivers and estuaries, only in heavily polluted sediments yields up to 6% were observed (Seitzinger, 1988; Jensen et al., 1984; Nishio et al., 1983). Therefore, the deviation of denitrification rates is small in the current study, though denitrification rates may be underestimated.

4.3 Fluxes of inorganic nitrogen compounds across sediment-water interface and SOD

Dissolved oxygen in the overlying water was absorbed by sediments with SOD ranging from 300 to 2 363 $\mu\text{mol}/(\text{m}^2 \cdot \text{h})$ (see Table 1). Probably the oxygen was consumed via nitrification and organic nitrogen mineralization (ammonification). The DIN contents in the overlying water obviously changed. There was a net flux of $\text{NO}_3^- + \text{NO}_2^-$ into the sediments from the overlying water, with its flux ranging

from 325.2 to 43.0 $\mu\text{mol}/(\text{m}^2 \cdot \text{h})$. $\text{NO}_3^- + \text{NO}_2^-$ into the sediments consumed via denitrification and other processes (e. g., assimilatory nitrate reduction). On the contrary, NH_4^+ was released from the sediments into the overlying water as the result of mineralization, with its flux between 12.3 and 210.3 $\mu\text{mol}/(\text{m}^2 \cdot \text{h})$. Regression analysis showed that there was a weakly positive relationship ($r^2 = 0.37$) between NH_4^+ flux and sediment organic carbon content (Fig. 5a). On the other hand, NH_4^+ fluxes decreased with the increase of dissolved oxygen concentration in the overlying water except at Sta. 2 (Fig. 5b), as was the result of oxidation of NH_4^+ by O_2 and forming NO_3^- or NO_2^- (Kemp et al., 1990; Nedwell et al., 1983). Therefore, NH_4^+ flux from sediment to the overlying water was limited by both dissolved oxygen concentration in the overlying water and the organic carbon content in sediment. It should be noted that, to some extent, the increase of NH_4^+ in the overlying water might be relative to the incubation conditions because the microbe activity was possibly inhibited in dark.

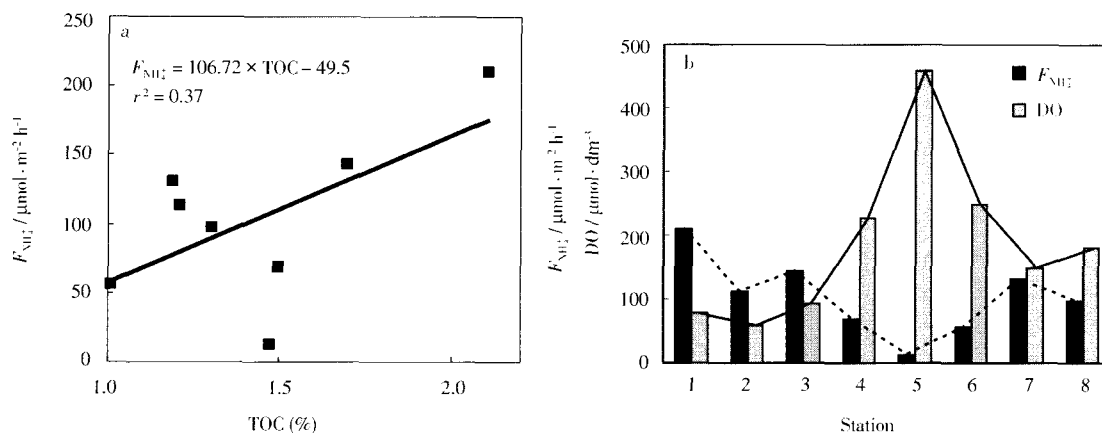


Fig. 5. The correlation between flux of NH_4^+ ($F_{\text{NH}_4^+}$) and total organic carbon content in sediment (a) and dissolved oxygen concentration (DO) in the overlying water (b).

4.4 Environmental factors controlling denitrification

Many factors can influence denitrification, including the supply of NO_3^- and organic matter, water temperature, dissolved oxygen concentration, SOD and bioturbation by benthic infauna and submersed plants (Cornwell et al., 1999; Nockiw, 1994; Seitzinger, 1988; Slater and Capone, 1987). In the last decade, many field observations and laboratory

incubation experiments have been performed to identify the main environmental factors that control denitrification in different aquatic environments (Kana et al., 1998; Rysgaard et al., 1994; Caffrey and Kemp, 1992). All the results show that the influences of environmental factors on denitrification are often different for coupled nitrification-denitrification and denitrification supported by overlying water $\text{NO}_3^- + \text{NO}_2^-$.

In this study, there was no definite relationship

found between denitrification rate and water column NO_3^- concentration, organic matter content in sediment and water temperature, though previous studies showed a direct proportionality between them (Nielsen et al., 1995; Pelegri et al., 1994; Caffrey et al., 1993). It is possibly due to the high loadings of NO_3^- and organic matter and high water temperature ($\geq 18^\circ\text{C}$), which did not limit denitrification. However, the linear regression analysis showed denitrification rate was highly correlated ($r^2 = 0.77$) with SOD (Fig. 6), suggesting that SOD is one of the principal factors controlling the denitrification rates

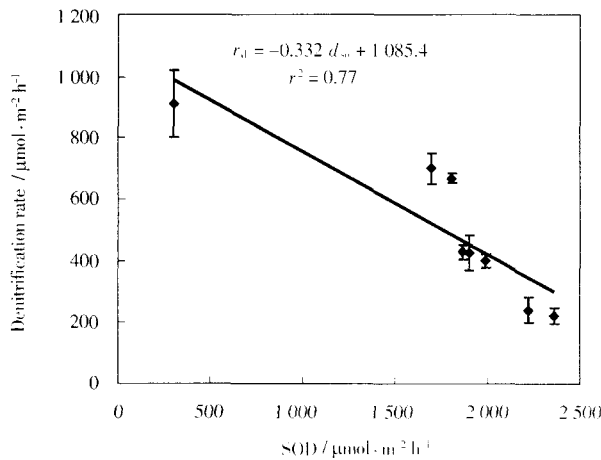


Fig. 6. The correlation between denitrification rate and SOD (d_{so}). Error bars represent standard error of five samples.

(r_d) in the Qi'ao Island coastal zone.

$$r_d = -0.332r_{so} + 1085.4. \quad (3)$$

The correlation with O_2 consumption had been demonstrated in a variety of aquatic sediments (Seitzinger, 1990) and riparian wetlands (Seitzinger, 1994) as well. There are a number of possible explanations for this correlation. In this study, the negative correlation with SOD might reflect control of denitrification by the availability of nitrogen sources from the overlying water. When SOD increases, coupled nitrification-denitrification will increase because higher oxygen conditions will stimulate nitrification and mineralization, however, denitrification supported by the overlying water $\text{NO}_3^- + \text{NO}_2^-$, even total denitrification, will decrease because it is more difficult for NO_3^- and NO_2^- in the overlying water into the anaerobic denitrification zone. This was also supported by Rysgaard et al. (1994) and Risgaard-Petersen et al. (1994).

The highest denitrification rate at Sta. 5 might be also associated with the bioturbation, where there

are many macrophytes and caves left by macrofauna. Submersed plants can stimulate nitrification and mineralization by increased O_2 input into the sediment, and burrows can increase flux of NO_3^- from water column to the sediment (Pelegri et al., 1994; Caffrey and Kemp, 1992), which was then denitrified.

5 Conclusions

(1) In the Qi'ao Island coastal zone, the concentrations of DIN in water were very high, with an average of $98.0 \mu\text{mol}/\text{dm}^3$, and NO_3^- was the main existing form of DIN, which exceeded 70% of the total inorganic nitrogen.

(2) Denitrification rates in the Qi'ao Island coastal zone varied from 222 to $908 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$, with $499 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$ on average. Dissolved oxygen in the overlying water was absorbed by the sediments with SOD value ranging from 300 to $2363 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$.

(3) There was a net flux of $\text{NO}_3^- + \text{NO}_2^-$ into the sediments from the overlying water, while NH_4^+ was released from the sediments into the overlying water as a result of mineralization, with its flux between 12.3 and $210.3 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$. The flux of NH_4^+ seemed limited by both organic matter content in sediment and dissolved oxygen concentration in water.

(4) The denitrification rates were highly correlated with the SOD ($r^2 = 0.77$) regardless of $\text{NO}_3^- + \text{NO}_2^-$ concentrations in the overlying water, organic carbon contents in sediments and water temperature. SOD might be the main environmental factor controlling the denitrification in the Qi'ao Island coastal zone.

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