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RESEARCH ARTICLE

The capability of estuarine sediments to remove nitrogen: implications for drinking water resource in Yangtze Estuary

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Abstract Water in the Yangtze Estuary is fresh most of the year because of the large discharge of Yangtze River. The Qingcaosha Reservoir built on the Changxing Island in the Yangtze Estuary is an estuarine reservoir for drinking water. Denitrification rate in the top 10 cm sediment of the intertidal marshes and bare mudflat of Yangtze Estuarine islands was measured by the acetylene inhibition method. Annual denitrification rate in the top 10 cm of sediment was 23.1 μmol m^{-2} h^{-1} in marshes (ranged from 7.5 to 42.1 μmol m^{-2} h^{-1}) and 15.1 μmol m^{-2} h^{-1} at the mudflat (ranged from 6.6 to 26.5 μmol m^{-2} h^{-1}). Annual average denitrification rate is higher at mashes than at mudflat, but without a significant difference (p=0.084, paired t test.). Taking into account the vegetation and water area of the reservoir, a total 1.42×10^8 g N could be converted into nitrogen gas (N_2) annually by the sediment, which is 97.7 % of the dissolved inorganic nitrogen input through precipitation. Denitrification in reservoir sediment can control the bioavailable nitrogen level of the water body. At the Yangtze estuary, denitrification primarily took place in the top 4 cm of sediment, and there was no significant spatial or temporal variation of denitrification during the year at the marshes and mudflat, which led to no single factor determining the denitrification process but the combined effects of the environmental factors, hydrologic condition, and wetland vegetation.

Keywords Denitrification · Estuarine sediment · Nitrogen removal capability · Yangtze estuary · Drinking water reservoir

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Introduction

The rapid expansion of the global economy (fuelled by fossil fuel combustion, creation of synthetic fertilizer, widespread land conversion, and accelerating global trade) has quickly increased bioavailable nitrogen in the environment which has accumulated in both freshwater and coastal marine ecosystems (Galloway et al. 2008). In the past decades, a large amount of nitrogen has been introduced to estuaries by the river (Seitzinger and Kroeze 1998). There are many potential consequences of nutrient enrichment in estuaries from ecological changes to socioeconomic impairments (e.g., fisheries and aquaculture) and serious human health threats (Whitall et al. 2007). Estuarine and coastal wetlands play important roles in the coastal environment by improving water quality through nutrient abatement (DeLaune and White 2012).

Denitrification accounted for the majority of nitrogen loss in estuarine ecosystems (Seitzinger and Sanders 1997), the microbial conversion of bioavailable nitrogen to inert dinitrogen (N_2) (Heip et al. 1995). Researchers have demonstrated that sediment in estuaries could act as an efficient sink of bioavailable nitrogen in the water body and eliminate more than half of the external nitrogen input via rivers (e.g., Trimmer et al. 1998; De Wit et al. 2001; Deutsch et al. 2010; Onken and Riethmüller 2010). For example, 76 % of the estimated watershed nitrogen load was eliminated in Bogue Sound, a temperate estuary (Smyth et al. 2013). In the Yangtze Estuary, the annual average amount of dissolved inorganic nitrogen (DIN) consumed by the sediment was 23.0 % of the total DIN input into the estuary (Wang et al. 2009). Studies in estuaries have shown that denitrification rates have distinct seasonal patterns principally controlled by the salinity and nitrate (NO_3^-) concentration in water (Fear et al. 2005; Seo et al. 2008; Wu et al. 2013), plants (Bastviken et al. 2005; Veraart et al. 2011; Kreiling et al. 2011), temperature (Wang et al. 2007; Wu et al. 2013), and availability of organic carbon (OC) (Wu et al. 2013; García-Ruiz et al. 1998). However, in the environments which these factors vary widely and frequently, their effects on denitrification was complex (Magalhães et al 2005; Wang et al 2006).

A new drinking water reservoir (Qingcaosha) for Shanghai was built in the Yangtze Estuary because of decreasing water quality and shortage. One of the key potential water quality concerns is eutrophication and subsequent algal bloom of the reservoir water body (Shen et al. 2003). External nitrogen deposition will increase the risk of eutrophication and algal bloom. The objectives of this paper are to (1) investigate the denitrification rate in the island intertidal flat sediment of Yangtze Estuary and associated environmental factors, and (2) calculate the capability of sediment to eliminate external nitrogen loading into the drinking water reservoir and examine the role of denitrification in controlling the nitrogen concentrations in the water body.

Materials and methods

Study site

The Yangtze Estuary, one of the biggest estuaries in the world, is located in the northern subtropical monsoon zone and has four distinct seasons. Annual mean tide water temperature is approximately 17.5 °C, ranging from the highest in August (~28 °C) to lowest in January (~6.7 °C) (Jin et al 2007). Average multiannual rainfall is 1,122.6 mm (Xu 2004). The Yangtze Estuary has been severely affected by eutrophication and algal bloom problems (Chai et al. 2006), which have increased gradually from the 1970s, and accelerated during the 1990s (Cheng et al. 2012). NO_3^- concentration of the inshore water body increased from 11 μM to about 97 μM, nearly ninefold since the early 1960s because of increasing human population and fertilizer utilization (Shen et al. 2003). Average DIN concentration in the Yangtze Estuarine main channel was 0.83±0.28 mg N L^{-1} from 2005 to 2012 (State Oceanic Administration People's Republic of China 2013); in addition to the upstream water input, precipitation is the other main external source of DIN to the water body (Shen et al. 2003).

The Qingcaosha reservoir was built on two underwater sand beaches, Qingcaosha and Zhongyangsha, which are in the northwest of Changxing Island in the Yangtze Estuary (Fig. 1). The construction of this reservoir was completed in

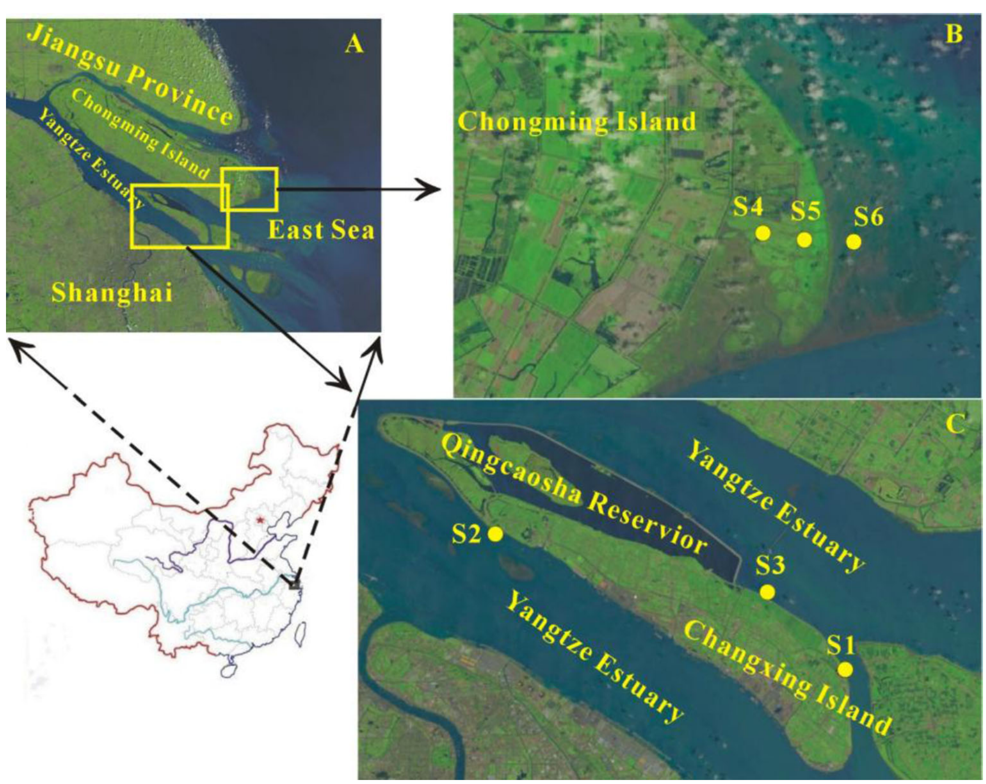

Fig. 1 Location of the sampling sites (*A* Yangtze Estuary, *B* the tidal flat of east Chongming Island, *C* Changxing Island and Qingcaosha reservoir. Sites 1 and 4 are *Phragmites communis* marshes. Site 2 is *Scirpus mariqueter* marsh with some *Phragmites communis*. Site 5 is a single *Scirpus mariqueter* marsh. Sites 3 and 6 are bare mudflat. Background photo is the Landsat 8 OLI/TIRS imagery on August 13, 2013)

2011. Designated total storage capacity of Qingcaosha reservoir is 5.27×10^8 m^3, and available storage capacity is 4.38×10^8 m^3. Average water depth is 7.95 m. The maximum water-delivery pump capacity is 7.19×10^6 m^3 day^{-1}. Salt water intrusion in the Yangtze Estuary is mainly impacted by fresh water discharge from the Yangtze River and the coastal ocean tides. The salinity values are higher during the dry season and decrease with increasing discharge. When the salinity is higher than 0.45‰, water is not fit for drinking. The longest continuous period that the water around Qingcaosha reservoir was not suitable for drinking is 68 days in 2003 and 54 days in 2008 (Zhu et al 2013).

Two research locations were selected in the Yangtze estuary. One area is around Changxing Island, and the other is on the tidal flat of east Chongming Island. In these locations, six sampling sites were established on the marsh areas, *Phragmites communis* (sites 1 and 4) and *Scirpus mariqueter* (sites 2 and 5), and the bare mudflat area (sites 3 and 6), respectively (Fig. 1).

Sampling

Triplicate sediment cores (10-cm long) were collected seasonally at each site in 2012 by the perspex tubes (3.4 cm inner diameter×30 cm long). Two caps were used to cover the two ends of each tube and the tubes were stored vertically in a box then transported back to the laboratory. In addition, one large sediment core (7 cm inner diameter×30 cm long) was collected at each site for measurement of the sediment properties.

Sediment properties

The large sediment cores were sliced into 2-cm layer subsamples, which were weighted to determine wet weight. A portion of each wet subsample was dried at 70 °C until constant weight. Moisture content was calculated by the ratio of the loss of wet subsample and the weight of dried subsample. Dry bulk density (BD) was calculated for each subsample according to the wet weight, moisture content data, and volume. About 5 g of wet sediment sample was extracted by 2 mol L^{-1} KCl for determination of extractable nitrogen (NO_3^- and ammonium (NH_4^+)). Extractable NO_3^- was measured by a continuous flow analyzer (FUTURA, Alliance Co.), and extractable NH_4^+ was measured by a standard colorimetric method (Grasshof et al. 1983). Dried sediment subsamples were ground and passed through a 60-μm sieve, for sediment OC content determination by $K_2Cr_2O_7$–H_2SO_4 oxidation method (Nelson and Sommers 1996).

Denitrification rate measurement

About 10 g each of fresh sediment subsample was put into a 250-ml perspex tube, with two hollow screwed caps at both ends with a silicon rubber septum. An outlet needle was inserted into the septum of one end to vacuum the tube and another needle into the opposite end of the tube, which was connected to compressed high purity mixed gas, 10 % *v/v* ($C_2H_2/(C_2H_2+N_2)$). After 20 min of flushing, a 20-ml gas sample was collected and then the needles were withdrawn. Tubes were incubated at field temperature for 2 h (from 8 °C in winter to 33 °C in summer). At the end of incubation, 20-ml gas samples were collected and injected into a gas chromatograph (GC) (HP7890A) equipped with an electron capture detector (ECD) for N_2O analyses.

Denitrification rate calculation

Denitrification rate was calculated by change of N_2O concentration in the headspace during the incubation as follows:

$$D_{\mathrm{Rate}} = \left(C_{\mathrm{End}} - C_{\mathrm{Beginning}}\right) \times V/W/T$$

Where D_{Rate} is the denitrification rate in sediment (ng N g^{-1} h^{-1}); $C_{\mathrm{Beginning}}$ and C_{End} are the N_2O concentration in the tube at the beginning and end of incubation (ng N L^{-1}); V is the volume of tube (L); W is the weight of the sediment sample put into tube (g); T is the incubation time (h).

Total denitrification rate of the 10-cm depth sediment per m^2 ($D_{\mathrm{Rate\text{-}m2}}$) was calculated according to the bulk density of sample as follows:

$$D_{\mathrm{Rate-m2}} = \left(\left(D_{\mathrm{Rate}}/14\right)/1000\right) \times \mathrm{BD} \times 10^6 \times \mathrm{Depth}$$

Where $D_{\mathrm{Rate\text{-}m2}}$ is the denitrification rate in sediment per m^2 (μmol m^{-2} h^{-1}), BD is the bulk density of sediment sample (g cm^{-3}), and Depth is the thickness of sediment layer (m).

Statistical analyses

SPSS (18.0) was used for statistical analyses of the correlation between denitrification rates and environmental factors, difference between denitrification rates at marshes and mudflat, and the spatial and temporal deviation of denitrification rate at the α=0.05 level of significance.

Results

Area calculation of Qingcaosha reservoir

The vegetation and water area of the Qingcaosha reservoir were calculated by using ESRI ArcGIS software. Given the plane shape of the study area, firstly, we manually delineated the vegetation and water body area from remote sensing imagery (Landsat 8 OLI/TIRS imagery on August 13, 2013) through digitization. Note that the spatial referencing should be fully explored to avoid biased area measurement. We used a local projected coordinate system based on Gauss-Kruger coordinate system. Then the area of the vegetation and water in the reservoir was obtained through the Calculate Geometry tool in Spatial Statistics toolbox of ESRI ArcGIS 10.1. Total area of Qingcaosha reservoir is 66.3 km^2, and the water and vegetation areas are 47.1 and 19.2 km^2, respectively.

Nitrogen loading into Qingcaosha reservoir

Precipitation and river water input are the two main sources of nitrogen loading into Qingcaosha reservoir. From 2005 to 2012, DIN in Yangtze Estuary water body was 0.83±0.28 mg N L^{-1} (State Oceanic Administration People's Republic of China 2013). According to the maximum water-delivery pump capacity (7.19×10^6 m^3/day), there is 2.62×10^9 g N imported into reservoir with river water every year. Total area of Qingcaosha reservoir is 66.3 km^2, and the average annual precipitation is 1,122.6 mm (Xu 2004). In our other study, DIN concentration in precipitation was 1.95 mg N L^{-1} (unpublished data). Hence, the nitrogen input through precipitation is 1.45×10^8 g $year^{-1}$.

Sediment properties at marsh and bare mudflat sites

The intertidal flat is narrow around Changxing Island, and only small patches extend out from the dike. While at the east of Chongming Island, the intertidal flat is well developed in the past 10 years (Fig. 1). Because of the difference in sedimentation dynamic and vegetation density, the properties of the sediments at these two sampling areas are different (Table 1). Extractable NO_3^- and NH_4^+ contents were low at all the sites, especially NO_3^- which would be a limitation for denitrification in sediment.

Denitrification rate in sediment and the spatial and temporal change

On the whole, the vegetation area had higher denitrification rates than the mudflat, especially at the *S. mariqueter* area. *S. mariqueter* area is located on the intertidal flat between the bare mudflat and *P. communis* area and has a longer submerging time during tide cycling than *P. communis* area. During the tidal cycling, more NO_3^- was brought into *S. mariqueter* area by tidal water. The annual average denitrification rates in the top 10 cm of sediment at the *S. mariqueter*, *P. communis*, and bare mudflat area of Chongming Island were 32.1±9.1, 24.8±6.3, and 17.1±11.5 μmol m^{-2} h^{-1}, respectively, which are higher than at *S. mariqueter* area (23.2±6.4 μmol m^{-2} h^{-1}), *P. communis* area (12.5±4.8 μmol m^{-2} h^{-1}), and bare mudflat area (13.2±6.0 μmol m^{-2} h^{-1}) of Changxing Island (Fig. 2). However, there is no significant spatial difference between them.

There was no uniform seasonal variation pattern of the sediment denitrification rates at Chongming and Changxing Island. At the vegetation sites, denitrifications in spring and autumn are higher than in winter, indicating the effect of temperature on the activity of denitrifiers (Zimmerman and Benner 1994). But at the *S. mariqueter* area of Changxing Island, the denitrification rate was higher in winter (Fig. 2). Denitrification rates at the bare mudflat were low in summer at both Chongming and Changxing Islands (Fig. 2), indicating that denitrification was not only controlled by temperature but by multiple factors, including the plant species which identity influenced the activity, abundance, and communities' composition of denitrifier (Bremer et al. 2007; Dassonville et al. 2011). Denitrification mainly occurred in the top 4 cm of the sediment at Yangtze Estuary, same with other estuaries (e.g., Barnes and Owens 1998; Livingstone et al. 2000) except during summer at *P. communis* and *S. mariqueter* area at Changxing Island. At these two sites, denitrification was low in summer likely linked to low NO_3^- concentrations restricting the activity of denitrifiers. In summer, the deeper layer sediment (6–10 cm) of *P. communis* and *S. mariqueter* area at Changxing Island had higher denitrification rates than surface sediments; however, this phenomenon was not found at Chongming Island sites (Fig. 3).

Table 1 Properties of the 0–10 cm sediment interval at sampling sites (average ± standard deviation, here standard deviations are the seasonal change range)

Site	Area	MC (%)	BD (g cm^{-3})	OC (mg kg^{-1})	NO_3^- (mg kg^{-1})	NH_4^+ (mg kg^{-1})
P	CM	35.6±5.58	1.38±0.12	7.32±1.12	0.12±0.21	110.9±82.1
	CX	38.4±9.65	1.19±0.14		0.31±0.25	113.5±53.9
S	CM	47.8±7.90	1.05±0.22	5.72±0.84	0.47±0.61	102.2±81.7
	CX	48.8±12.7	0.99±0.19		0.20±0.21	164.2±124.8
M	CM	48.2±13.8	1.10±0.18	2.94±1.46	0.30±0.39	162.8±123.5
	CX	31.4±9.44	1.34±0.24		0.02±0.01	64.7±50.1

P Phragmites communis, *S Scirpus mariqueter*, *M* mudflat, *CM* Chongming Island, *CX* Changxing Island, *MC* moisture content, *BD* bulk density, NH_4^+ and NO_3^- are the extractable nitrogen of sediment

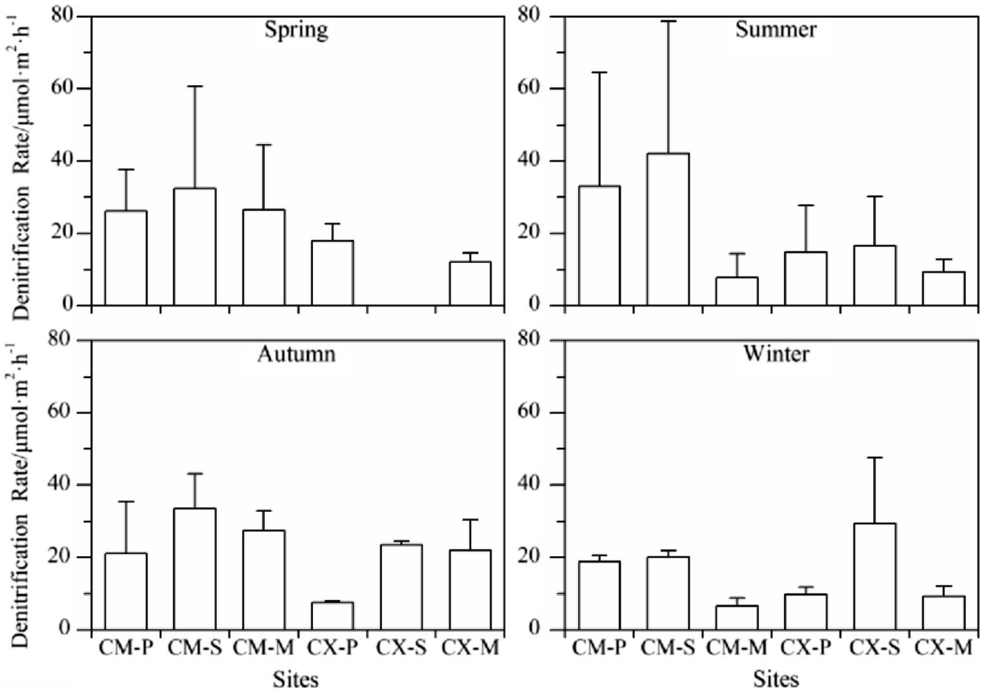

Fig. 2 The spatial and temporal deviation of denitrification in Yangtze Estuarine intertidal sediment (*CM* Chongming Island, *CX* Changxing Island, *P Phragmites communis*, *S Scirpus mariqueter*, *M* mudflat. *Error bar* is the standard deviation, n=3)

Discussion

Effect of environmental factors on denitrification

At estuarine and coastal areas, controlling factors of denitrification include salinity and NO_3^- concentration (Cornwell et al. 1999; Fear et al. 2005; Seo et al. 2008; Wu et al. 2013), temperature (Wang et al. 2007; Wu et al. 2013), overall rates of sediment carbon metabolism and the depth of oxygen penetration (Cornwell et al. 1999), the presence/absence of aquatic vegetation (Cornwell et al. 1999; Bastviken et al. 2005; Veraart et al. 2011; Kreiling et al. 2011), and availability of OC (García-Ruiz et al. 1998; Wu et al. 2013). We expected spatial and temporal variability in sediment denitrification rates varying with environmental factors. However, in our research, ANOVA analysis indicated that there was no significant spatial or temporal difference (p>0.05) in denitrification rates between sites and seasons.

Temperature is a fundamental factor affecting the denitrification rate. Denitrification rates increased with sediment

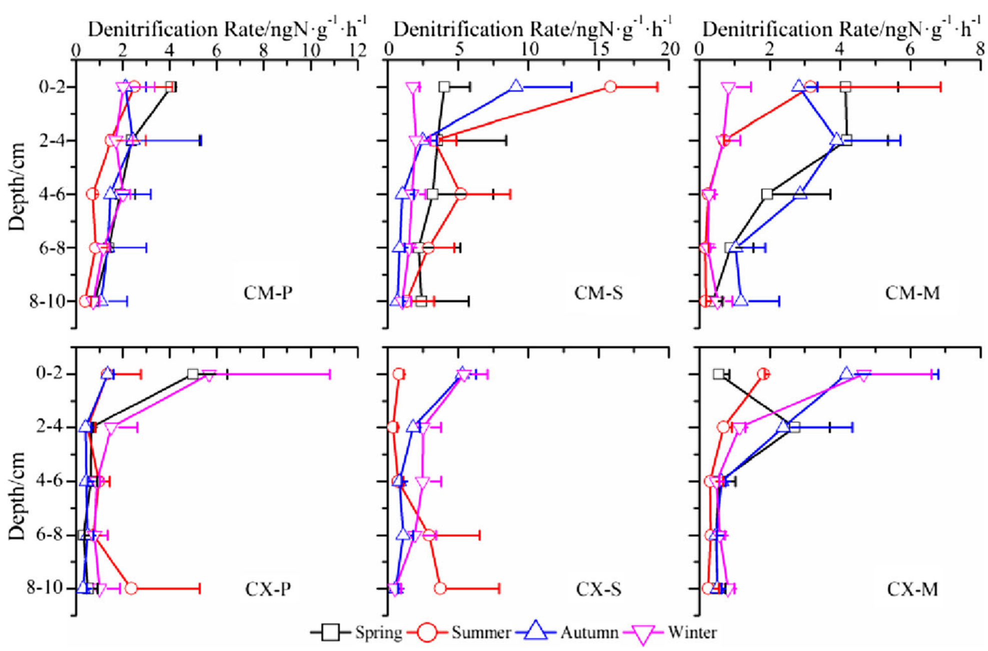

Fig. 3 The vertical profile of denitrification rate in Yangtze Estuarine intertidal sediment (*CM* Chongming Island, *CX* Changxing Island, *P Phragmites communis*, *S Scirpus mariqueter*, *M* mudflat. *Error bar* is the standard deviation, n=3)

temperature due to the increased metabolic activity that occurs at higher temperatures (Lindau et al. 2008; Song et al. 2012; Wu et al. 2013). In Zimmerman and Benner's study (1994), temperature was the most important factor controlling denitrification, exceeding NO_3^- concentration and salinity. Denitrification rates are positively related to temperature in the littoral sediments, where temperature explained 66 % of the variation in denitrification alone (Saunders and Kalff 2001). Other studies, however, do not always show a positive temperature effect on denitrification. For example, a study by Hasegawa and Okino (2004) showed that denitrification rate began to decrease when temperature continuously increased while Piña-Ochoa and Álvarez-Cobelas (2006) and Poulin et al. (2007) showed that there was no significant correlation between denitrification rate and temperature. Winter peak of denitrification and may be attributed to, firstly, the higher NO_3^- load stimulating rates of sedimentary denitrification (Pfenning and McMahon 1996; Ogilvie et al. 1997; Fear et al. 2005) and, secondly, low environmental temperature increasingly selecting a denitrifying benthic microflora at the expense of nitrate ammonifiers (King and Nedwell 1984). Although temperature had significant positive correlation with sediment denitrification in Wang et al.'s (2007) study on the whole Yangtze Estuarine coastal sediment. Another study by Wang et al. (2006) also found that denitrifications in summer and winter were higher than in spring and autumn at Chongming Island intertidal flat, the same location as our present study. Pearson correlation did not show significant relationships between denitrification rate and other single environmental factors (e.g., temperature). The Yangtze Estuary is one of the largest estuaries in the world (more than 1,000 km^2) and is located in the subtropical monsoon area. Seasonal change of hydrology and environmental factors and the spatial variation at intertidal sites is complex. In a hydrologically dynamic environment such as the intertidal flat, with wide variation among environmental factors, the weak relationships may be the result of confounding effects of these factors on denitrification rates.

The denitrification process mainly took place in the top 4 cm sediment (Fig. 3). We divided the denitrification rate and extractable NO_3^- data into two groups, from 1 to 4 cm and from 5 to 10 cm. There is a significant difference ($p<0.05$) between average extractable NO_3^- of 1–4 cm and 5–10 cm sediment. Average extractable NO_3^- of 1–4 cm sediment was 0.41 mg kg^{-1}, which is greater than 5–10 cm sediment (0.19 mg kg^{-1}). A direct proportionality between sediment denitrification rate and overlying water column NO_3^- concentration has been reported in many studies (Seitzinger et al. 1993; Pelegri et al. 1994; Nielsen et al. 1995; Kana et al. 1998). Sediment NO_3^- concentration decreases rapidly down to the deeper layer indicating that denitrification rate is controlled by the rate of diffusion across the layer separating the mixed water column from the anoxic areas where denitrification occurs (Kana et al. 1998). Availability of NO_3^- determined the denitrification occurring in sediment (Cornwell et al. 1999). There was a significant ($p<0.01$) correlation with extractable NO_3^- and denitrification rate at Changxing and Chongming Islands sediment (Fig. 4). Denitrification rates in 1–4 cm sediment are significantly ($p<0.01$) greater than 5–10 cm sediment, where the average denitrification rates are 2.87 ng N g^{-1} h^{-1} and 1.13 ng N g^{-1} h^{-1} in 1–4 and 5¯10 cm sediment, respectively. In summer, nitrification within the rhizosphere could be enhanced by the oxygen exuded from roots thus promoting denitrification (Caffrey and Kemp 1992; Yu et al. 2012). The deeper sediment of *P. communis* and *S. mariqueter* area at Changxing Island had higher denitrification rates. At Chongming Island sites, which have a rapid deposition rate and where the depth of the vegetation roots were deeper, denitrification rates in surface sediment were always higher than in 6–8 cm layers.

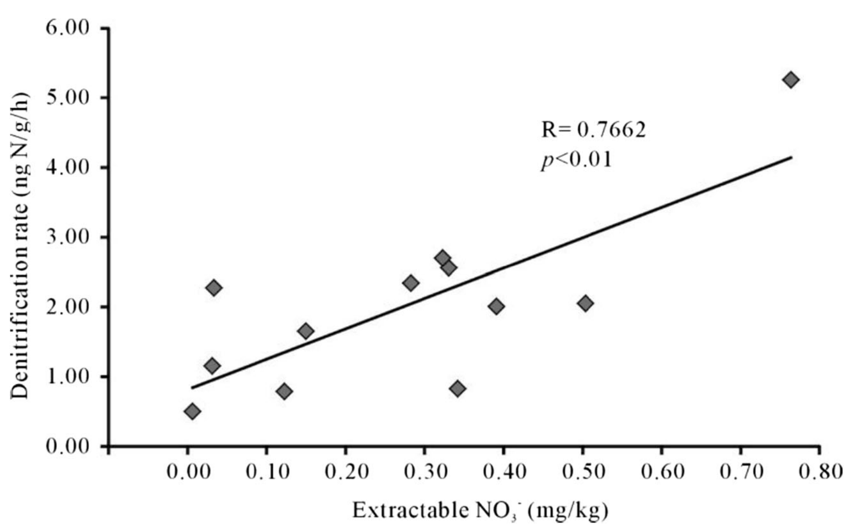

Fig. 4 The correlation between the average data of extractable NO_3^- and denitrification rate in 1–4 cm and 5–10 cm sediment

Table 2 Denitrification rates reported for estuaries (μmol N m^{-2} h^{-1}, units have been converted from the units in the references)

No.	System	Denitrification rate	Reference
1	Estuaries in southern Texas	8.0–142.2	Yoon and Benner 1992
2	Colne Estuary	19–1,317	Ogilvie et al. 1997
3	Great Ouse Estuary	4–228	Trimmer et al. 1998
4	Humber Estuary	50-416.6	Barnes and Owens 1998
5	Yorkshire Ouse	131–575	García-Ruiz et al. 1998
6	Wetland in Breton Sound estuary	0–2.8	DeLaune and Jugsujinda 2003
7	Louisiana Barataria Basin	92–214	DeLaune et al. 2005
8	Neuse River Estuary	0–275	Fear et al. 2005
9	Yangtze estuary	1.12–33.3	Wang et al. 2006
10	Estuaries of the northern Baltic Sea	3.75–37.9	Silvennoinen et al. 2007
11	Yangtze estuary and coast	0.2–36.4	Wang et al. 2007
12	Atchafalaya River Estuary	0.18–14.2	Lindau et al. 2008
13	Estuary of Northern Arabian Gulf	1.88±0.63	Al Ghadban et al. 2012
14	Liaohe Estuary	0.61–116.8	Guan et al. 2013
15	Yangtze estuary Islands	6.6–42.1	This study

Capacity of sediment in removing nitrogen in the drinking water reservoir

Sediment OC is one of the key factors controlling the activity of denitrification microbes (Piña-Ochoa and Álvarez-Cobelas 2006). During plant growth, the labile exudation or the detritus of root provides the carbon source for denitrification (Saunders and Kalff 2001). The decomposition of plant material can also supply the carbon for denitrification (Bastviken et al. 2005; Veraart et al. 2011; Kreiling et al. 2011). For example, at the shallow water bog (Lindau et al. 2008) and coastal lagoon (Rysgaard et al. 1996), plant areas had higher denitrification rate than areas without plants. A comparison of NO_3^- reduction rates in vegetated and nonvegetated marsh soils indicated that the rate of denitrification increased tenfold in vegetated soils versus unvegetated (VanZomeren et al. 2013). Average denitrification rate in mudflat was 15.1 μmol m^{-2} h^{-1}, which is lower than the vegetation area (23.1 μmol m^{-2} h^{-1}) even there was no significant correlation between denitrification rate and OC. Average denitrification rates in *P. communis* and *S. mariqueter* sediment at Changxing and Chongming Islands are used as the denitrification rate in vegetation area, and the average of denitrification rates in mudflat sediment at these two Islands is used as the unvegetated area of the reservoir. From this, we conclude that the sediment in Qingcaosha reservoir could remove about 1.42×10^8 g N every year, which means that sediment can efficiently remove 97.7 % of DIN loading through precipitation, but cannot decrease the DIN concentration in Qingcaosha reservoir water body loaded by the river.

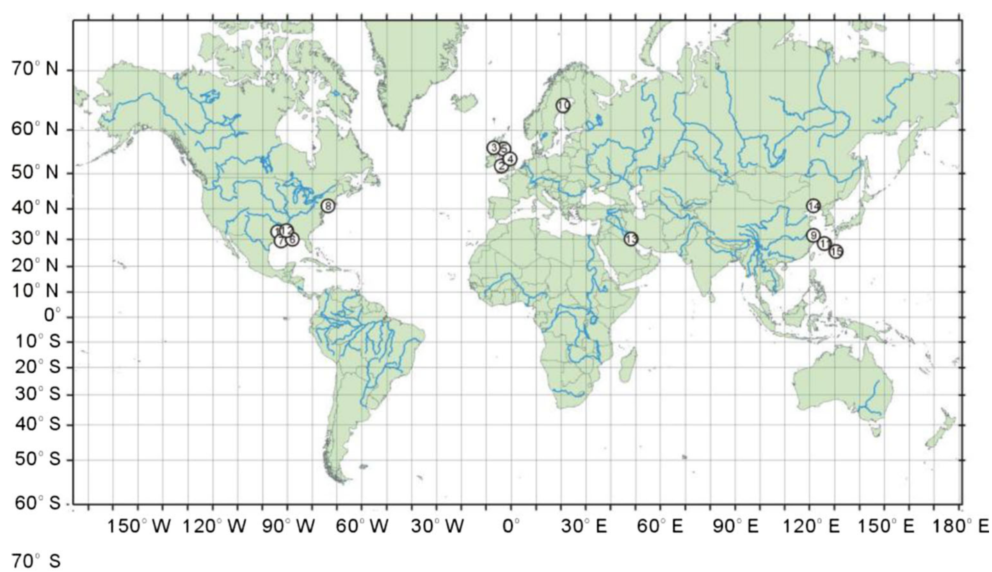

Fig. 5 The distribution of the locations of the research cited in Table 2 (locations 12, 14, and 22 are in Yangtze Estuary)

Furthermore, we did not measure the dissolved organic nitrogen in precipitation, and nitrogen fixation is also a potential contribution of external nitrogen loading (Howarth and Marino 1988). Therefore, there is a potential increase of bioavailable nitrogen concentration in water body and eutrophication risk in Qingcaosha reservoir.

The potential nitrogen removal capability of sediment

Denitrification rates in many studies have been measured in the top several centimeter of the sediment because of the hypothesis that the NO_3^- will be quickly exhausted from the surface to the deep layer of sediment (e.g., Vanderborght and Billen 1975). In this study, we found that denitrification still happens in deeper layer of sediment, especially the higher rate that was found in the deep rhizosphere. The denitrification rate was calculated as the sum of the top 10 cm sediment, which ranged from 6.6±2.2 μmol m^{-2} h^{-1} to 42.1± 36.6 μmol m^{-2} h^{-1}. Our results (32.1±9.1 μmol m^{-2} h^{-1} at *S. mariqueter* area and 17.1±11.5 μmol m^{-2} h^{-1} at mudflat, respectively) are higher than Wang et al.'s study (2007) at Chongming Island in which denitrification rates in the top 3 cm sediment were 18.2±12.3 μmol m^{-2} h^{-1} (*S. mariqueter* area) and 15.1±9.45 μmol m^{-2} h^{-1} (mudflat).

Compared to other studies in estuaries in China and around the world, denitrification rates in the Yangtze River estuary belongs to the lower range of the data (Table 2 and Fig. 5). Low NO_3^- concentration (~60 μM) and complex environmental factors variation would be the reason of low denitrification rate in Yangtze Estuarine intertidal sediment. For example, in the Mississippi Delta, denitrification rates were low (0.18–14.2 μmol m^{-2} h^{-1}) at the sites with low NO_3^- in flood water (<1.4 μM) (Lindau et al. 2008), and high (92–214 μmol m^{-2} h^{-1}) at the sites with high NO_3^- concentration (143–286 μM) (Delaune et al. 2005). At the River Colne estuary which had very high NO_3^- concentration (1,200 μM), denitrification rate reached 1,317 μmol m^{-2} h^{-1} (Ogilvie et al. 1997). This implies that there is a potential for increased denitrification at the Yangtze Estuary. On the other hand, the samples used in this research were collected from the natural intertidal zone out of the dike, where the tidal water submerges the tidal flat twice during the day making the NO_3^- supplement from water to sediment discontinuous and aerobic and anaerobic condition shift in the top sediment. While in the reservoir, water covers the sediment all the time and thus the calculated nitrogen removal in this paper may be underestimated. Future investigation in this reservoir should be undertaken to quantify the nitrogen removal capability of the sediment of Qingcaosha reservoir. Moreover, the in situ denitrifying bacteria respond rapidly to the increase in the NO_3^- concentration in the overlying water (Kana et al. 1998), which means that the sediment microbial population remains poised to utilize available NO_3^- and that the denitrification rate is modulated by short-term temporal changes in the NO_3^- concentration in the overlying water. More studies need to be taken to determine the factors that affect the slope of the NO_3^- versus denitrification relationship (Cornwell et al. 1999).

Conclusion

Because of the insufficiency of NO_3^-, annual average denitrification rate in the top 10 cm sediment of intertidal flat at Yangtze Estuary was 23.1 μmol m^{-2} h^{-1} at the marshes and 15.1 μmol m^{-2} h^{-1} at the mudflat, which are relatively lower than the sediments of other estuaries of the world. Sediments of the reservoir could efficiently remove the DIN loaded through precipitation, but cannot reduce the inorganic nitrogen level of the water body in the reservoir. Results of this study may underestimate the total nitrogen removal capability of the reservoir sediment. There is no significant correlation between denitrification rate and single environmental factors indicating a joint effect on the rate. Further investigation is needed to probe the effects of environmental factors on sediment denitrification.

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