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Dissimilatory nitrate reduction to ammonium conserves nitrogen in anthropogenically affected subtropical mangrove sediments in Southeast China

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ABSTRACT

In this study, basic sediment properties, nutrient flux, and nitrogen cycle (including denitrification, anaerobic ammonium oxidation [anammox], nitrification, and dissimilatory nitrate reduction to ammonium [DNRA]) were investigated at two sampling sites with different tree ages in the mangrove region of the Jiulong River Estuary, China. The results show that sediments at mangrove flat area have relatively strong capability to reduce NO_3^- , in which the DNRA rate is relatively high ($204.53 \pm 48.32 \mu\text{mol N m}^{-2} \text{h}^{-1}$), which is approximately 75.7–85.9% of the total NO_3^- reduction, while the denitrification and anammox rates are relatively low – only approximately 5.6–9.5% and 8.5–14.8% of the total NO_3^- reduction, respectively. Thus, in the nitrogen-enriched subtropical mangrove system, DNRA is the main pathway to reduce NO_3^- , and most of the input nitrogen is conserved as NH_4^+ in the system, which assures high productivity of the mangrove system.

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1. Introduction

The mangrove system is an open ecosystem of the intertidal zone that is distributed in tropical and subtropical coasts and estuaries (Kathiresan and Bingham, 2001; Li and Lee, 1997). Mangrove habitat – coastal tidal wetland – is an important component of the estuarine sedimentary area, which behaves as an important source/sink pool, and convertor for global carbon, nitrogen, and phosphors (Armentano, 1980; Seitzinger et al., 2005; Zhou et al., 2007). In recent years, because of frequent human activities, a large amount of NO_3^- has been released to coastal ecosystems (Galloway et al., 2004; Schlesinger et al., 2006; Vitousek et al., 1997), resulting in increasingly nitrogen-saturated marine water bodies (Aber et al., 1998; Mulholland et al., 2008). Increased NO_3^- concentration contaminates underground drinking water resources, which subsequently threatens human health (Burgin and Hamilton, 2007; Burow et al., 2010). Increased dissolved N release to downstream water bodies might lead to increments in harmful algal blooms (HABs), anoxia, and emission of greenhouse gas (N_2O , Burgin and Hamilton, 2007; Codispoti, 2010; Mccarthy et al., 2007; Rabalais, 2002), resulting in ecological disruption (Burow et al., 2010). Thus, as an important ecological barrier, mangroves play an increasingly critical

role in digesting the increased nitrogen input from continents along the marine continental boundary.

In the mangrove system, the degree of nitrogen conservation depends on NO_3^- reduction processes, including denitrification, anaerobic ammonium oxidation (anammox), and dissimilatory nitrate reduction to ammonium (DNRA, Bernard et al., 2015). Available nitrogen forms include nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), and organic nitrogen (ON) (Brandes et al., 2007). The mangrove system can convert inorganic nitrogen to gaseous N_2 by nitrogen burial, physical transport, denitrification, anammox, and microbial activities (Vitousek et al., 1997) and conserve nitrogen through the DNRA process (Bernard et al., 2015; Fernandes et al., 2012). The denitrification process reduces NO_3^- and NO_2^- to N_2 and N_2O , respectively; therefore, it removes nitrogen that was originally stabilized in mangroves. Because the products (N_2 and N_2O) cannot be easily used by living organisms compared with NH_4^+ and NO_3^- (Howarth et al., 1988), denitrification compensates increased input of nitrogen to mangroves. Anammox ($\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2$) also removes bioavailable nitrogen, and this process widely exists in coastal basins as well as pelagic oceans (including water bodies, sediments, mangrove sediments, and even Arctic ice sheets) (Brandes et al., 2007). Moreover, DNRA converts NO_3^- to NH_4^+ , which is more bioavailable; thus, it conserves nitrogen in the ecosystem (Bernard et al., 2015; Fernandes et al., 2012; Giblin et al., 2013). Thus, DNRA reduces the loss of nutrients caused by denitrification through this nitrogen recycling process and is an important mechanism to produce reusable nitrogen,

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which assures high productivity of the mangrove system (Fernandes et al., 2012).

However, in different ecosystems, denitrification, anammox, and DNRA all have different rates of reducing the overall NO_3^- . Previous studies showed that denitrification is dominant (Hou et al., 2012). However, recent studies have found that in certain environments, DNRA has higher capability for reducing nitrogen than denitrification and can even completely reduce all the NO_3^- in the system (Giblin et al., 2013; Trimmer and Nicholls, 2009). For example, comparing the rates of DNRA and denitrification at 55 coastal stations, Giblin et al. (2013) found that more than half of those stations had a ratio of DNRA NO_3^- reduction to the total NO_3^- reduction $>30\%$ and that the DNRA rate even exceeded the denitrification rate at certain times or places in approximately 30% of the stations. Even in the mangrove system with limited nitrogen, DNRA is still the main mechanism to remove NO_3^- (Fernandes et al., 2012).

We aim to identify nitrogen input and output conditions in the nitrogen-enriched mangrove system by studying sediments and nutrient fluxes of overlying water and to identify N cycling rates in the mangrove system using the isotope pairing technique (IPT) or isotope dilution technique (IDT), which can reveal the DNRA rate in the nitrogen-enriched subtropical mangrove system.

2. Materials and methods

2.1. Research location

Fugong mangroves are in the Zhangzhou mangrove natural reserve, which is located at the Jiulong River Estuary in Fujian (Fig. 1) with an area of 15.0 ha. This place is affected by the south Asian tropical marine climate, and hence it is warm and has abundant precipitation. The annual average temperature is 21.5 °C, with low temperature of 13.5 °C in January and high temperature of 28.9 °C in July. The annual average precipitation lasts for 134 days at 1365 mm. The precipitation usually spans from March to September. According to the characteristics of

precipitation seasons at this location, its four seasons can be divided as follows: spring from March to June, summer from July to September, fall from October to November, and winter from December to February. Two sites in *Kandelia obovata* (Rhizophoraceae) forest with different forest ages were chosen as sampling sites in the mangrove reserve, which were planted at S1 (24°23'37"N, 117°54'18"E) in 1986 and S2 (24°23'41"N, 117°54'38"E) in 1962. There are three sampling spots at each sampling site along the vertical direction of coastal line, representing mudflats (S1-1 and S2-1), the near-water side (S1-2 and S2-2), and the near-shore side (S1-3 and S2-3) of the mangrove flat area. From March to December 2011, samples were taken monthly and then measured using IDP in August 2011 and IPT from June to December 2011.

2.2. Water sampling

In order to accurately reflect the effect of tidal water on mangrove sediments, tidal water was sampled after the mudflat was flooded. Water samples were filtered using 0.45- μm filter membranes in situ, and chloroform was added for stabilization. The samples were then refrigerated at 4 °C and taken back to the laboratory for measurements.

The NH_4^+ concentration in water bodies was measured using a three-nutrient simultaneous measurement system (Tri-223 auto-analyser), and NO_2^- and NO_3^- concentrations were measured using a continuous-flow autoanalyzer (AA3 auto-analyser, BRAN-LUEBBE Co., Germany).

2.3. Sediment sampling

Undisturbed sediment core samples from bare mudflat and mangrove beach sediments were collected in each S1 and S2 sampling site. Because the sampling time is constrained by tidal water, summer sampling at S2-1 and winter sampling at S2-1 and S2-3 were not conducted. Surface sediments were sampled by taking 0–20-cm mixed surface sediments, which were stored in valve bags and refrigerated for later measurements in the laboratory. The core samples were extracted from the

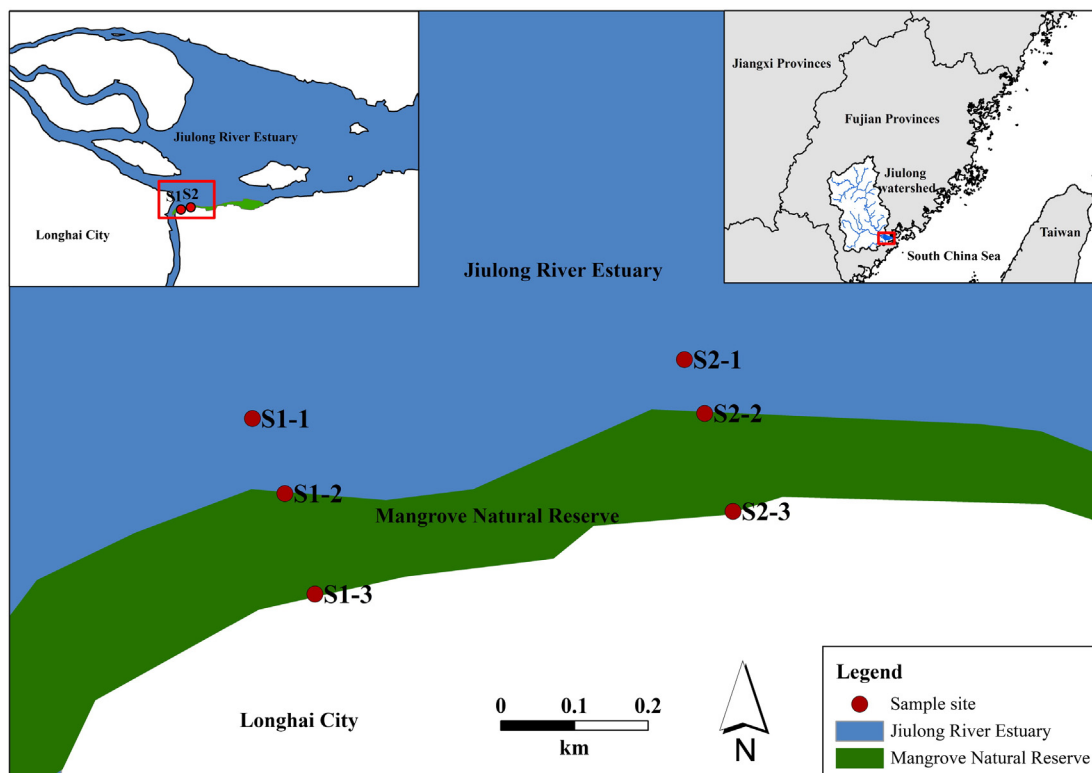


Fig. 1. Locations of sampling sites.

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