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Nitrogen fate in a subtropical mangrove swamp: Potential association with seawater-groundwater exchange

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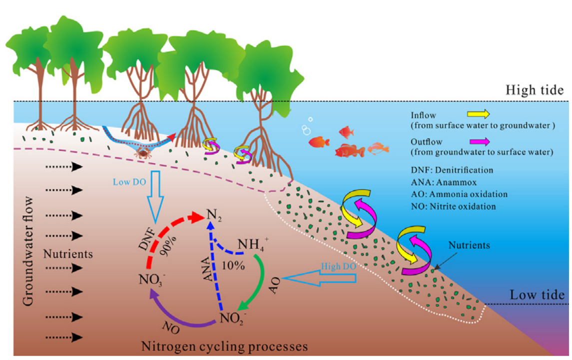
HIGHLIGHTS

- A multidisciplinary study of hydrology, geochemistry and microbiology was conducted in mangrove swamps.
- The intertidal zone of mangrove swamps should be divided into different hydrodynamic subzones.
- A positive correlation between seawater-groundwater exchange rate and nutrient concentrations was found.
- Denitrification was the main contribution to nitrogen removal in the mangrove swamp.

GRAPHICAL ABSTRACT



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ABSTRACT

Coastal mangrove swamps play an important role in nutrient cycling at the land-ocean boundary. However, little is known about the role of periodic seawater-groundwater exchange in the nitrogen cycling processes. Seawater-groundwater exchange rates and inorganic nitrogen concentrations were investigated along a shore-perpendicular intertidal transect in Daya Bay, China. The intertidal transect comprises three hydrologic subzones (tidal creek, mangrove and bare mudflat zones), each with different physicochemical characteristics. Salinity and hydraulic head measurements taken along the transect were used to estimate the exchange rates between seawater and groundwater over a spring-neap tidal cycle. Results showed that the maximum seawater-groundwater exchange occurred within the tidal creek zone, which facilitated high-oxygen seawater infiltration and subsequent nitrification. In contrast, the lowest exchange rate found in the mangrove zone caused over-loading of organic matter and longer groundwater residence times. This created an anoxic environment conducive to nitrogen loss through the anammox and denitrification processes. Potential oxidation rates of ammonia and nitrite were measured by the rapid and high-throughput method and rates of denitrification and anammox were measured by the modified membrane inlet mass spectrometry (MIMS) with isotope pairing, respectively. In the whole transect, denitrification accounted for 90% of the total nitrogen loss, and anammox accounted for the remaining 10%. The average nitrogen removal rate was about 2.07 g per day per cubic meter of mangrove sediments.

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1. Introduction

Mangrove swamps, which are highly productive ecosystems at the land-sea margin, can perform a variety of ecological functions, such as maintaining biodiversity and providing habitats for fish and crustaceans (Atwood et al., 2017; Luther and Greenberg, 2009; Mumby et al., 2004; Nagelkerken et al., 2001). Particularly, they can play an important role as a biogeochemical reactor, transforming and removing nutrient compounds (Alongi, 1996; Bouillon et al., 2008; Pennings, 2012).

Hydrological dynamics in the intertidal zone are very complex, involving periodic seawater submergence and groundwater discharge (Deitchman and Loheide II, 2009; Schwendenmann et al., 2006; Tait et al., 2016). Previous studies have reported that seawater-groundwater exchange can play a potentially key role in controlling large imbalances in coastal biogeochemical budgets (Kroeger and Charette, 2008; Mazda et al., 1990; Slomp and Cappellen, 2004; Spiteri et al., 2008; Santos et al., 2014). The concept of the "mangrove pump" caused by tidal flushing of crab burrows was recently proposed to highlight the significance of water exchange on soluble organic and inorganic matter in mangrove swamps (Stieglitz et al., 2013).

Assessing seawater-groundwater exchange rates is challenging due to the complex and heterogeneous nature of the sediments in mangrove swamps. Common methods used in previous studies include numerical simulations (e.g., Akamatsu et al., 2009; Heron and Ridd, 2008; Wolanski, 1992; Xia and Li, 2012) and natural geochemical tracers (e.g., Gleeson et al., 2013; Stieglitz et al., 2010; Santos et al., 2014; Tait et al., 2016). In general, accurate numerical estimation requires multiple model parameter inputs in coastal wetland models (Moffett et al., 2012; Xiao et al., 2017), and geochemical isotope-based estimation is usually of large uncertainty of groundwater endmember (Burnett et al., 2006; Moore, 2008; Peterson et al., 2008). Recently, the generalized Darcy's law was also used to calculate the seawater-groundwater exchange rate in coastal wetlands (Hou et al., 2016; Ma et al., 2014; Qu et al., 2017; Wilson et al., 2015). This method was the most straightforward, only involving the product of hydraulic conductivity and vertical hydraulic gradient, both of which can be measured in-situ.

Periodic hydrological dynamics in the intertidal zones of coastal wetlands form unique phases of coupling aerobic and anaerobic sedimentary microenvironments, which can affect nitrogen cycling processes in the intertidal zone (Hirsch et al., 2011; Kristensen et al., 1998; Liu and Lee, 2006; Spiteri et al., 2008; Santoro, 2010; Wolanski, 1992). Microbe-mediated activities, such as transformations of nitrogen, are the key processes contributing to the dissolved inorganic nitrogen (DIN) budget of "subterranean estuaries" with steep gradients in salinity and oxygen (Santoro et al., 2008; Santoro, 2010). Significant nitrogen cycling processes include nitrification, denitrification, anaerobic ammonium oxidation (anammox) and dissimilatory nitrate reduction to ammonium (DNRA) (see supplementary information (SI)).

Recent studies have revealed the potential effect of water exchange on the abundance, diversity and structure of N-transferred microbes by studying molecular ecology in the intertidal zone (e.g., Santoro et al., 2008; Sáenz et al., 2012; Smith et al., 2015; Wang et al., 2012). However, quantitative studies on the coupling of complex seawater-groundwater exchange and microbial activity are limited, and the coupling mechanisms in intertidal mangrove swamps are still not well understood. Furthermore, investigating nitrogen budget processes is critical to improve understanding of the ecological function of mangrove swamps. This is particularly important, as the total mangrove area is declining by 1% to 2% per year, and is predicted to disappear in the next 100 years if the present rate of decline continues (Duke et al., 2007; Giri et al., 2011).

In order to fill these gaps, we present a case study coupling seawater-groundwater exchange, N-cycling and microbial activity in a typical subtropical mangrove swamp in China. The aim of this study is to (1) quantify spatial variations of nitrogen transformation rates and functional microbial activity in different hydrologic subzones using molecular and ^{15}N isotopic tracing technologies and (2) reveal the potential effects of seawater-groundwater exchange on nitrogen transformation and subsequent nitrogen removal.

2. Materials and methods

2.1. Field sites

Field investigations were performed in a mangrove swamp (N 22.826°, E 114.774°) in the northeast bay of Daya Bay, China (Fig. 1a). Daya Bay is a semi-enclosed bay of the northern South China Sea. Tidal current in Daya Bay belongs to a semidiurnal irregular tide with a mean and maximum tidal range of 1.03 m and 2.60 m, respectively (Wang et al., 2017). The region belongs to a subtropical monsoonal climate with an annual average temperature of 22 °C and an average precipitation of 1700 mm (Wang et al., 2018).

The northeast bay is a small, semi-enclosed water body, with a maximum width of 2 km. There are two small seasonal rivers flowing in the northeast bay, the Guijing River in the north and the Huang Suzhou River in the south. A typical shore-perpendicular intertidal transect, with an average slope of 0.15%, was selected for field hydrological observations near the estuary of the Huang Suzhou River. Lush mangrove trees, including *kenaelia candel*, *aegiceras corniculatum* and *pagatpat*, thrived there, with heights ranging from 1.2 m to ~5.0 m (Fig. 1b and c).

2.2. Field measurements and sampling

The intertidal transect consisted of three subzones: a tidal creek zone with a maximum depth of 0.55 m (-12 m ≤ x ≤ 44 m), a mangrove zone (44 m < x ≤ 132 m), and a bare mudflat zone (132 m < x ≤ 203 m). Here, we hypothesized that among different subzones there may be a steep gradient in water exchange capability, salinity, temperature and DO, which may affect N-cycling process and abundances of microbial organisms. To verify this hypothesis, we monitored groundwater hydraulic head, temperature, and salinity and sampled intertidal groundwater and seawater along the transect during a spring-neap tidal period.

Seawater-groundwater exchange monitoring systems, consisting of six pair-wells (numbered W1 to W6), were deployed along the intertidal transect. The so-called pair-wells are a pair of wells equipped with two transducers (CTD-Diver, *Schlumberger*), which were installed at two different depths (Fig. 1d). In order to minimize the effects of backfilled sediment, the transducers were set to work ten days after installation. The installations of pair-wells were the same as those described by Hou et al. (2016) and Qu et al. (2017).

The monitoring period started on 15 Dec 2015, 00:00 a.m. and lasted for 366 h (i.e., 15 days, a spring-neap cycle). One single-well (W0) was added later near the sea embankment. The monitoring period of the single-well started on 25 Dec 2015, 02:30 p.m. and lasted for 112 h (about 5 days). The monitoring interval of all transducers was 30 min. During low tides, the surface elevations and relative distance of each monitoring well from W1 (which was set to be the origin of the *x*-axis) were surveyed by an electronic total station (TS-800, Johanna). Along the landward direction of ~400 m, an artificial unconfined well with a depth of 20 m in the paddy field was used to sample inland groundwater (Fig. 1b).

Vertical hydraulic conductivities (K_v) of sediments at the six pair-wells were estimated using the in-situ falling head method (Chen, 2000; Li et al., 2010; Wang et al., 2014). A PVC tube (Fig. 1 in Wang et al., 2014) was inserted into sediments at locations 1–2 m away from the well sites to ensure that the test was done in undisturbed soil. Test sites for measuring falling head were chosen carefully to avoid crab burrows and plant roots, so that the estimated K_v only represented the bulk soil (not the soil with preferential migration passages created by crab burrows or plant roots). A seepage meter was installed later to estimate the contribution of crab burrows in seawater-groundwater exchange near W5 in the bare mudflat zone (Fig. 1d).