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Nitrogen removal through N cycling from sediments in a constructed coastal marsh as assessed by ^{15}N–isotope dilution

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ABSTRACT

Constructed coastal marsh regulates land-born nitrogen (N) loadings through salinity-dependent microbial N transformation processes. A hypothesis that salinity predominantly controls N removal in marsh was tested through incubation in a closed system with added-$^{15}NH_4^+$ using sediments collected from five sub-marshes in Shihwa marsh, Korea. Time-course patterns of concentrations and ^{15}N–atom% of soil-N pools were analyzed. Sediments having higher salinity and lower soil organic-C and acid-extractable organic-N exhibited slower rates of N mineralization and immobilization, nitrification, and denitrification. Rates of denitrification were not predicted well by sediment salinity but by its organic-C, indicating heterotrophic denitrification. Denitrification dominated N-loss from this marsh, and nitrogen removal capacity of this marsh was estimated at 337 kg N day^{-1} (9.9% of the daily N-loadings) considering the current rooting depth of common reeds (1.0 m). We showed that sediment N removal decreases with increasing salinity and can increase with increasing organic-C for heterotrophic denitrification.

1. Introduction

Marine pollution and coastal geomorphic instability that threatens the health of marine ecosystems is a global issue caused by discharge of nonpoint pollutants from degraded inland to coastal water resources due to increasing fertilization, livestock waste production, and land reclamation and utilization (Deegan et al., 2012; Huang and Pant, 2009; Yoo et al., 2006). Public concern about the deterioration of coastal and marine water quality has also increased worldwide, as is the case in Korea. An artificial coastal marsh was constructed in the upper zone of the Shihwa lake, a 5.65×10^3-ha coastal lake, to remove nonpoint pollutants from the incoming agricultural and industrial wastewaters (Yoo et al., 2006). Removal of nitrogen (N) and phosphorus (P) from wastewater is a prerequisite to preserve coastal water quality, since excess N and P contribute to eutrophication of aquatic ecosystems.

Marsh sediments can function as transformers converting dissolved and particulate N to different forms such as gaseous N (N_2, NO or N_2O) via microbe-mediated N processes (Bellinger et al., 2014; Ji et al., 2015; Lee et al., 2014), thus protecting nearby aquatic environments from pollution (Davidsson and Ståhl, 2000). Despite their protective functions, coastal eutrophication caused by N loadings exceeding the removal capacity of salt marshes has often led to a deterioration of the health of marine ecosystem including salt marsh loss (Deegan et al., 2012; Nelson and Zavaleta, 2012). Therefore, knowledge of the N transformation processes is of particular importance in understanding N removal in the soil-water-atmosphere continuum such as fresh or brackish water marshes that lie between rivers and nearshore ocean waters. The land-born loadings of N to the nearshore ocean can be lost due to offshore discharge or to denitrification, depending on the residence time and percolation through tidal flats (Lee et al., 2014).

Denitrification in benthic sediments is the most important process for permanent N removal, despite the possible N loss due to ammonia volatilization (Zhang et al., 2016). On the other hand, N taken up by aquatic plants can serve as a temporary N sink during growing season (Lund et al., 2000). However, the assimilated N can be released into the overlying water due to the dieback of vegetation and subsequent mineralization during non-growing season (Ro et al., 2002).

Denitrification is generally favored by key environmental factors such as slightly alkaline pH, fine soil texture, high temperature, and wet soil moisture regime that enhances microbial activity and creates hypoxic or anoxic conditions of the marsh sediments (Kendall et al., 2007). Other factors affecting N removal efficiency are hydraulic residence time, floodwater depth, the quality and quantity of in-stream

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water, and vegetation in the marsh, as observed for P removal efficiency (Yoo et al., 2006). Particularly, sediment salinity is known to affect physical, chemical, and biological functions of coastal salt marshes, changing ionic strength and composition that can cause flocculation of particles, alter chemical equilibria affecting nutrient availability, and suppress microbial activity (Baldwin et al., 2006; Liang et al., 2005; Sardinha et al., 2003).

Denitrification is also controlled by the availability of NO_3^- and organic C source to denitrifying bacteria (Morley et al., 2014). Since a series of microbial transformations of N compounds in the soil regulates the availability and level of NO_3^- (a substrate for denitrification), determining the rates of N mineralization and immobilization, nitrification, and denitrification has important implications for evaluating the potential ability of a coastal marsh to remove nonpoint-source N pollutants and nutrients from fluvial discharge of agricultural and industrial wastewater, and domestic sewages.

Knowledge of N removal capacity and characteristics of sediments in a marsh should be predetermined for efficient treatment of polluted streamwater prior to entering the adjacent lake. To our knowledge, several attempts have been made to assess N dynamics mediated by sediments and discuss controlling factors for efficient removal of N through natural and constructed wetlands (Huang and Pant, 2009; Lund et al., 2000). In assessing N dynamics in the marsh, however, N originating directly from the sediments and indirectly by N-pool substitution contributed to N pools and their inter-pool processes in the soil (Jenkinson et al., 1985), and this situation has complicated any assessment of N balance among soil N pools. The use of N inputs labeled with the stable isotope, ^{15}N, has enabled to trace the ^{15}N derived from the inputs in soil N pools (Knowles and Blackburn, 1993; Ro et al., 2014).

We hypothesized that sediment salinity affects N cycling through a set of interlinked microbial N processes, thus causing a difference in the fate and removal of land-born N loadings in marsh sediments. Here, we tested this hyphotesis by measuring the time-course patterns of the concentrations and corresponding ^{15}N atom% of inorganic (NH_4^+ and NO_3^-) and organic N during incubation with sub-marsh sediments enriched with $(^{15}NH_4)_2SO_4$ to calculate the potential rates of N processes including N removal of the sediments by ^{15}N isotope dilution (Bellinger et al., 2014; Ji et al., 2015; Ro et al., 2014). The constructed marsh chosen for this study has five sub-marshes differing in salinity of sediments and is of great concern, since it receives fluvial discharge of livestock wastewater and domestic sewage loadings from three (Banweol, Donghwa, and Samhwa) streams.

2. Materials and methods

2.1. Site description and sediment sampling

A 75-ha Shihwa marsh was constructed on a tideland located in Ansan (126°50′N, 37°17′E), Gyeonggi, Korea, between 1997 and 2001. The texture of the basin is silt clay loam (SiCL), and common reed (*Phragmites australis* (Cav.) Trin. Ex Steudel) was planted for water purification. The marsh mainly comprises three parts [islands, open water (pond), and closed water planted with *P. australis*], and is an overland-flow system that receives waters mainly from three streams: the Banweol, Donghwa, and Samhwa. For the Banweol and Donghwa stream areas, these marshes are divided into high and low marshes based on the height difference (2.0 m) above sea level. Accordingly, Shihwa marsh consists of five sub-marshes: Banweol high (B_H, 19.0 ha) and low (B_L, 22.6 ha), Donghwa high (D_H, 15.2 ha) and low (D_L, 11.3 ha), and Samhwa (S, 6.9 ha) marshes (KWRC, 2002). The map of the Shihwa marsh and location of sampling stations was described as Fig. 1.

High marsh areas receive waters by using a pump and low marsh areas receive waters by hydraulic gradient. The hydraulic retention time of the marshes ranges from 6.4 to 7.9 days for the high marsh and 2.4 to 4.7 days for the low marsh, and is 1.9 days for the Samhwa marsh, and the flow rate ranges from 1.0 to 2.0 $m^3 s^{-1}$. During the study period, the floodwater level was highest (over 0.6 m) in the wet season (April–September) and lowest (below 0.2 m) in the dry season (October–March) (KWRC, 2002). Sediment sampling sites at each sub-marsh were spaced at least 20 m apart from each other in a direction of water flow: 4 sites each for B_H, B_L, D_H and D_L, and 2 sites for S sub-marsh (Fig. 1). Surface sediments (0–15 cm) were collected using a soil auger in early spring (10 March), and composited for the batch incubation experiments. The soil samples were air-dried at room temperature to minimize unexpected solute loss while handling and maintain a relatively constant pore-water salinity after rewetting. The air-dried soil samples were passed through a 2-mm sieve to remove gravel and undecomposed coarse plant debris and homogenize the soil sample, and used for physicochemical analyses (Table 1) and batch incubation experiment.

2.2. Characteristics and analyses of sediments

Some physicochemical properties of the sediments from each sub-marsh were shown in Table 1. The pH was measured potentiometrically in 1:1 (w/v) soil/water suspensions with a pH meter (DMP2000, DMS, Korea), and the electrical conductivity of a saturated soil extract (ECe) was measured with a digital conductivity meter (PW9509/20, Philips, UK). Organic carbon was determined by the Walkley-Black method (Nelson and Sommers, 1982), and the texture of sediments was determined by pipette method according to the USDA classification scheme (Gee and Bauder, 1986). Inorganic N (2 M KCl-extractable NH_4^+ and NO_3^-) were determined by steam distillation using MgO and Devarda's alloy (Keeney and Nelson, 1982). Water-extractable organic N and acid-extractable organic N were determined in filtrates of 1:2 (w/v) soil/water suspensions and 1:5 (w/v) soil/1 M HCl suspensions, respectively. The ECe values of sediment samples collected from the B_H, B_L, D_H, D_L, and S sub-marshes were 2.7, 2.3, 3.6, 1.5, and 9.2 dS m^{-1}, respectively (Table 1). The ECe values of sub-marsh sediments measured in this marsh were not different from those obtained for 2 years in our previous investigation (Ro et al., 2002), if the $EC_{1:5}$ (electrical conductivity of 1:5 soil-to-water extract) values were converted (He et al., 2013).

2.3. A batch incubation experiment

Twenty-five grams (dry basis) of each triplicate sub-sample from each composite soil sample representing each sub-marsh were placed into a 100 mL flask. Twenty-five milliliters of distilled water were added into each flask to replenish the air-dried samples and give a ponding depth of 5 mm. However, compared with in-situ salinity, the salinity of the sediment sample after air-drying may differ slightly, since we did not measure a loss of pore-water (sediment water content at sampling) from each sub-marsh sediment during air-drying. Subsequently, the flasks were individually sealed with perforated cap to ensure gas exchange, and then pre-incubated at 25 ± 0.5 °C for 7 days under 5 mm overlying water to recover microbial activity of previously dried sediments. After pre-incubation, 5 mL of 400 mg N L^{-1} $(^{15}NH_4)_2SO_4$ solution at 5.0 ^{15}N atom% was added cautiously into each flask without mixing, and then incubated at 25 ± 0.5 °C for 28 days under hypoxic conditions (a ponding depth of 5 mm). The redox potential of the sediments was maintained under hypoxic conditions throughout the incubation. The amount of NH_4^+-N added was set to about 20% of the daily N loadings (3400 kg N day^{-1}) entering the Shihwa marsh (KEI, 2007) on the basis of the surface area. At the desired time (0, 3, 7, 14, and 28 days), each soil sample was analyzed for concentrations and corresponding ^{15}N atom% of inorganic (NH_4^+ and NO_3^-) and organic N.