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Vertical distribution of denitrification end-products in paddy soils

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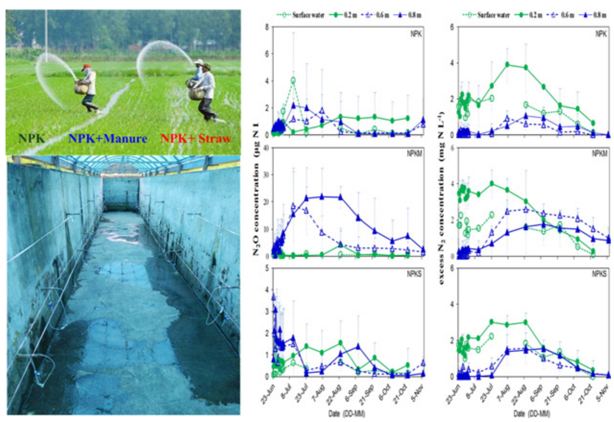
HIGHLIGHTS

- Indirect N_2O emission via leachate was comparable to the IPCC default value.
- The loss of N through denitrification can be underestimated if research is focused only on the surface paddy soil and the extent to which denitrification is underestimated may be affected by the application of organic carbon.

GRAPHICAL ABSTRACT



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ABSTRACT

Knowledge of denitrification process and its end-product at various depths of paddy soil is very important for our understanding of its role in mitigating reactive N and indirect nitrous oxide (N_2O) emission. In this study, the end-products of denitrification were determined at four depths in a long-term field lysimeter experiment in southeast China over a rice season. Three treatments were included: (1) chemical fertilizer (NPK); (2) NPK plus pig manure (NPKM); and (3) NPK plus straw (NPKS). The concentration of dissolved N_2O increased with soil depth across all treatments and the highest concentration of excess dinitrogen (N_2) was observed at 0.2 m depth, as was the highest dissolved organic carbon (DOC) content. Denitrification reduced the amount of nitrate by 48–54% in the paddy soil profile, especially at 0.2 m depth (68–88%), whereas the lower reduction of NO_3^- (17–44%) in the subsoil (at 0.6 and 0.8 m depth) was accompanied by a higher concentration of NO_3^-. Our results demonstrated that DOC was the major limiting factor of denitrification in the subsoil. The application of pig manure markedly increased the amount of DOC in the surface soil, resulting in a high rate of denitrification, whereas the addition of straw had no effect on denitrification. The indirect emission factors for N_2O (EF5-g, 0.001–0.006) were comparable with the default value (0.0025) reported by the Intergovernmental Panel on Climate Change. The low N_2O production was probably caused by the complete reduction of N_2O to N_2, as reflected by the lower $N_2O/(N_2O + N_2)$ ratios in the paddy soil profile. Although the surface soil was identified as a hotspot for denitrification, a considerable amount of excess N_2 was observed in the subsoil for all three treatments. We therefore conclude that the loss of N through denitrification may be significantly underestimated if only the surface soil is considered.

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1. Introduction

The contamination of groundwater by nitrate (NO_3^-) is of global concern as a result of its impact on both the environment and human health (Galloway et al., 2008). High concentrations of NO_3^- in streams, lakes, and rivers increase the risk of eutrophication in surface waters (Stark and Richards, 2008). The contamination of surface water and groundwater with NO_3^- is common in watersheds dominated by agricultural activities, mainly as a result of diffuse pollution from intensive farming (Foster and Young, 1980; Townsend et al., 2003). The leaching of NO_3^- to groundwater below arable land in rice–wheat rotation systems has been reported in China (Zhu and Wen, 1992; Zhu and Chen, 2002). It has been recognized that a variety of processes such as denitrification and nitrate reduction to ammonium (DNRA) are involved in the nitrate dynamics, however the mitigation of excess NO_3^- in paddy soil generally relies on denitrification (Jarvis, 2000; Bernard et al., 2015; Shan et al., 2016).

Denitrification is a multistep biological process producing nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2) from NO_3^- and mainly occurs in the anaerobic zone (Jahangir et al., 2013). Four requirements must be met to trigger denitrification. In addition to the presence of NO_3^- as the substrate, there needs to be an anaerobic environment, an electron donor, and microbes capable of denitrification. As NO_3^- and suitable microbes are ubiquitous in arable land, denitrification thus mainly depends on the existence of anaerobic conditions and the availability of electron donors (Seitzinger et al., 2006). Denitrification in the soil profile has been widely studied in wetland, grassland, and upland soils. The soil redox conditions and the presence of dissolved organic carbon (DOC) are the major controlling factors of denitrification in upland soil profiles (Sotomayor and Rice, 1996; Elmi et al., 2003; Elmi et al., 2005; Mathieu et al., 2006). For example, a high accumulation of NO_3^- in the soil profile has been reported in Chinese semi-humid croplands, where NO_3^- cannot be denitrified due to the presence of oxygen and a lack of carbon sources (Zhou et al., 2016a). However, in flooded environments, such as wetland soils and in groundwater, the rate of denitrification is mainly related to the amount of DOC (Hill and Cardaci, 2004; Xiong et al., 2006; Rivett et al., 2008; Minamikawa et al., 2010; Khalil and Richards, 2011). Many studies have observed the highest rates of denitrification in the upper soil horizon (0–0.2 m), the extent of which depends on the moisture content (Küstermann et al., 2010; Clément et al., 2002; Friedl et al., 2016). However, higher rates of denitrification in the subsoil (0.15–0.3 m) than in the surface soil (0–0.15 m) have also been reported (McCarty and Bremner, 1992; Paul and Zebarth, 1997). There is now increasing evidence of significant denitrification activity in subsoils (Hill and Cardaci, 2004; Khalil and Richards, 2011; Dixon et al., 2010) and subsoil denitrification has been suggested as an important mechanism for the removal of excess NO_3^- before it is leached to groundwater or discharged to the surface aquifer (Sotomayor and Rice, 1996; Fenton et al., 2009; Bernard-Jannin et al., 2016).

Paddy soils are widely distributed across south and northeast China. Rice requires a 0.03–0.07 m deep layer of water during most of its growing season, which results in the development of a reducing layer under the root zone. The low, flat landform, loamy to clayey parent materials, and a long cultivation history of rice have led to the development of a unique soil profile in paddy soils that is conducive to denitrification (Li et al., 2014; Xing et al., 2002). Thus the denitrification process is different in paddy soil profiles from that in upland soils, where denitrification is limited due to the presence of oxygen. Complete denitrification in paddy soil profiles has been reported based on the observation of very low concentrations of N_2O in leachates or the attenuation of nitrate during infiltration (Zhu et al., 2003; Xiong et al., 2006; Choi et al., 2013; Majumdar, 2013), though the evidence was insufficient because the concentration of N_2 was not determined. As serious environmental problems are caused by high inputs of reactive N to agricultural land in China, a knowledge of the factors controlling the denitrification process and the $N_2O/(N_2 + N_2O)$ ratio are crucial to our understanding of the extent of mitigation of NO_3^- via denitrification in paddy soil profiles (Zhu and Chen, 2002; Ju et al., 2009; Xia and Yan, 2012). Few studies have focused on denitrification in paddy soil profiles as a result of the methodological difficulties in the direct quantification of the end-products of denitrification.

There are two known difficulties in the quantification of denitrification in soil profiles. First, the high background levels of atmospheric N_2 make it difficult to determine the end-product of denitrification. Second, under field conditions, O_2, NO_3^-, and DOC, factors that control denitrification in the deep soil layers, are diffused or leached from the upper soil layers. This differs from the results obtained by the incubation of soil cores, especially for paddy soils. Therefore it is unsuitable to investigate soil profile denitrification by soil core incubation of different layers. The lack of information about specific areas in paddy soil profiles with high or low rates of denitrification hinders the accurate quantification of the loss of N during the process as a whole (Groffman et al., 2006; Davidson and Seitzinger, 2006).

N_2O is an obligate intermediate in the denitrification process and N_2 is the final product in this process. Thus the quantification of dissolved N_2O and excess N_2 can be used as a tool to investigate denitrification (Kana et al., 1994; Böhlke, 2002; Weymann et al., 2008). Membrane inlet mass spectrometry (MIMS) can be used to measure a large number of dissolved gases by auto-degassing water samples with almost no interference from the high background levels of atmospheric N_2. It can thus be used to quantify denitrification in situ at low cost and has been used to study denitrification in water bodies, including groundwater and sediments (Weymann et al., 2008; Jahangir et al., 2014; Chen et al., 2014).

In this study, MIMS was used to determine the N_2 produced in profile from a flooded paddy soil. Although variety processes such as anaerobic oxidation of ammonia (Aanammox), chemodenitrification and Feammox (ammonium oxidation coupled to iron reduction) can contributed to N_2 formation, denitrification was recognized as the major process to produce N_2 in paddy soil (Hou et al., 2015; Zhu et al., 2011; Shan et al., 2016). As it is impossible to separate and to quantify the contribution of the N_2 production from different processes in this study. Thus N_2 production was not distinguished from denitrification and other processes in present study; instead, the net production of N_2 was referred to as “denitrification” for simplicity (Li et al., 2014; Jahangir et al., 2014; Chen et al., 2014). We hypothesized that denitrification in the paddy soil profile might significantly reduce NO_3^- before it was leached to the groundwater or discharged into surface water bodies and that the $N_2O/(N_2O + N_2)$ ratios in the deeper layers would be affected by the availability of NO_3^- and DOC leached from the upper layers. The objectives of this study were (1) to investigate the distribution of denitrification in a paddy soil profile by measuring the concentrations of N_2O and excess N_2 at various vertical depths and (2) to link the denitrification end-product with biogeochemical parameters.

2. Materials and methods

2.1. Study sites

The experiments were conducted from June 23 to October 23, 2015 in the long-term field lysimeter experiment at the Changshu Agroecological Experimental Station (31° 32′ N, 120° 41′ E) of the Chinese Academy of Sciences in Jiangsu Province. The soil is classified as a hydromorphic paddy soil; the surface soil (0–20 cm) of the experimental plots was sampled on June 1, 2015 for the determination of physical and chemical properties and the results are listed in Table 1. The annual mean air temperature in this region is 25.6 °C and the annual mean precipitation is 1054 mm. The average groundwater table is below 0.5 m during the summer and below 0.8 m during the winter.