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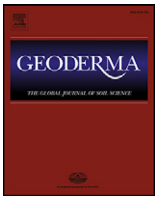

Iron oxidation affects nitrous oxide emissions via donating electrons to denitrification in paddy soils

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ABSTRACT

Paddy soils are important source of nitrous oxide (N_2O), which production is mainly regulated through redox processes and electron transfer. Ferrous iron [Fe(II)] oxidation coupled to denitrification is ubiquitous in paddy soils, which could affect N_2O production via donating electrons to denitrification. To clarify the effects of Fe(II) oxidation on denitrification and N_2O emissions, a flooding experiment was conducted in two paddy soils with contrasting Fe(II) levels. The soil with high Fe(II) concentration emitted less N_2O than did the other soil with low Fe(II) concentration. Nitrate addition decreased Fe(II) concentration and stimulated N_2O production in both soils, suggesting that Fe(II) oxidation is coupled to denitrification. The stoichiometry of electron transfer between nitrate reduction and Fe(II) oxidation demonstrated that the percentage of electrons contributed by Fe(II) to denitrification accounted for 16.2% and 32.9%, and the ratios of the electrons donated by Fe(II) to the electrons accepted by nitrate for N_2O production were 43.7% and 130.7% in the two soils with low and high Fe(II) concentration, respectively. The ratio beyond 100% implies that the electrons donated by high Fe(II) concentration exceed the electron demand for N_2O production, which lead to the further reduction of N_2O to N_2. In conclusion, Fe(II) oxidation coupled to denitrification affects N_2O emissions via electron donation, and Fe(II) in a high concentration bears great potential for efficient denitrification and low N_2O emissions from paddy soils.

1. Introduction

Atmospheric nitrous oxide (N_2O) contributes to global warming and stratospheric ozone depletion (Wuebbles, 2009). As a long-lived trace gas in the atmosphere (Butterbach-Bahl et al., 2013), N_2O is the third most important greenhouse gas next to carbon dioxide (CO_2) and methane (CH_4), and it is also recognized as the dominant ozone-depleting substance emitted in the 21st century (Ravishankara et al., 2009). The threat of N_2O emission to the environment motivates the managements of N_2O production and emission (Kanter et al., 2013).

Agricultural soils are major N_2O sources because of intensive nitrogen (N) fertilization (Hoben et al., 2011; Shcherbak et al., 2014). Irrigation management is also an important factor in N_2O emissions from agricultural soils (Liu et al., 2011), especially the flooding and drainage regime in paddy soils with specific redoximorphic features (Kögel-Knabner et al., 2010). The total annual N_2O emissions from paddy soils in China were determined to be about 29.0 Gg N_2O-N (Zou et al., 2007). Hence, the studies of N_2O emissions from paddy soils are particularly important.

N_2O is a byproduct of nitrification and an obligate intermediate of denitrification processes (Canfield et al., 2010), but N_2O emissions from paddy soils mainly derive from denitrification (Liu et al., 2012). In flooded paddy soils, redox processes strongly affect denitrification and electron transfer. Organic carbon frequently serves as the dominant electron donor to denitrification under anoxic conditions (Burford and Bremner, 1975; Cayuela et al., 2014; Melton et al., 2014). In addition, ferrous iron [(Fe(II)] also donates electrons to denitrification through oxidation reaction. Previous research demonstrated that Fe(II) oxidation coupled to denitrification was energetically viable at neutral pH (Klueglein and Kappler, 2013; Melton et al., 2014; Weber et al., 2006b), which suggested that Fe(II) could affect N_2O emissions.

Iron (Fe) is the fourth most abundant element in the Earth's crust, and the redox transition between ferrous and ferric valences plays a fundamental role in modern environmental biogeochemistry (Melton et al., 2014; Weber et al., 2006a). With the periodic drying–wetting alternation in paddy soils, Fe is subjected to various oxidation state changes and interacts with the dynamics of N through redox reactions (Kögel-Knabner et al., 2010), such as nitrate-dependent Fe(II) oxidation (NDFO) (Ratering and Schnell, 2001; Weber et al., 2001). Mixotrophic

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nitrate-dependent Fe(II) oxidation is restricted to anoxic conditions and regulates the oxidation of Fe(II) to Fe(III) in the upper few millimeters of sediments (Melton et al., 2012). Most nitrate-reducing Fe(II)-oxidizing bacteria can reduce NO_3^- to NO_2^- and further denitrification intermediates and products, including the gaseous species NO, N_2O and N_2 (Chakraborty and Picardal, 2013; Melton et al., 2014; Muehe et al., 2009). As NO_2^- is an intermediate of denitrification and also a strong chemical oxidant for Fe(II), Fe(II) oxidation by the reactive NO_2^- intermediate can be a significant indirect abiotic process which is involved in NDFO (Melton et al., 2014). Thus, both biotic and abiotic NDFO processes play an important role in global Fe cycles, and also regulate denitrification in soils (Canfield et al., 2006; Melton et al., 2014; Weber et al., 2006a). As an intermediate of denitrification and a potential chemical oxidant of Fe(II), N_2O can be further reduced to N_2 by Fe(II) in the NDFO processes. This implies that, in paddy soils, N_2O emissions from denitrification are related to Fe(II). However, the effect of Fe(II) on N_2O emissions from soils has not been completely uncovered. The elucidation of the relevance of Fe(II) with denitrification and N_2O emissions is beneficial to take measures to mitigate the threat of N_2O emission to global climate change.

In this study, we hypothesized that Fe(II) regulated N_2O emissions by donating electrons to denitrification in paddy soils and a high Fe(II) concentration could decrease N_2O emissions through the further reduction of N_2O to N_2. In order to assess the effects of Fe(II) on denitrification and N_2O emissions, we focused on the interactions between nitrate and Fe(II) in two paddy soils with contrasting Fe(II) concentrations under flooding conditions by a nitrate addition experiment.

2. Materials and methods

2.1. Soil

Two paddy soils were taken from the top layer (0–20 cm) at Xianning, Hubei Province, China (30°1.1′ N, 114°22.1′ E, called S1) and Yueyang, Hunan Province, China (28°42.9′ N, 112°55.6′ E, called S2). Both soils develop from the quaternary red earth. Soil samples were air-dried and then ground to pass through a 20-mesh sieve for the incubation experiment. The geochemical properties of the soils are presented in Table 1.

2.2. Experimental design and treatments

In this study, the variations of Fe(II) concentration, nitrate content, and N_2O emission were detected after nitrate addition in the flooded soils. Fe(II) oxidation and nitrate reduction were described by the decrease of Fe(II) concentration and nitrate content, respectively. The electron transfer between Fe(II) oxidation and nitrate reduction was calculated to clarify the contribution of electrons donated by Fe(II) to denitrification and N_2O production. The experiment was conducted as follows.

Air-dried soil samples (S1 and S2) were activated at 20% soil moisture content at 25 °C for 3 days. Subsequently, aliquots (18.75 g) of the activated soils corresponding to 15 g dry soil were respectively loaded into 132 bottles with the capacity of 145 mL each. All soil samples in the bottles were preincubated under submerged conditions (dry soil: water = 1:1.25 (*w*/*v*)) at 25 °C for 7 days to create a stable soil environment.

Two treatments were established: (i) nitrate treatment performed by adding KNO_3 solution to the preincubated soils with the N fertilizer rate of 100 mg N kg^{-1} dry soil (corresponding to 225 kg N ha^{-1} $year^{-1}$); (ii) control treatment performed by adding deionized water to the soils. The final ratio of soil to water was 1:1.5 (*w*/*v*). Each treatment was conducted with three replications. The soils then were incubated in the dark at 25 °C for 40 days. Soil and water were stratified without disturbance during the incubation, and so O_2 diffusion was limited. The soil layer was about 8 mm and the water layer was 10 mm.

The headspace gases in the bottles were sampled every day for the analysis of N_2O concentration. N_2O fluxes were determined as the changes of N_2O concentration in the headspace gases within 1 h. Soil pH and redox potential (Eh) were detected in situ without stirring the soil layer and water layer. After the gas sampling and soil pH and Eh measurements, the flooded soils were mixed homogeneously to obtain slurries for the other property analyses. The destructive sampling was carried out to determine dissolved organic carbon (DOC), ammonium, nitrate, nitrite, Fe(II), and Fe(III) on day 0, 1, 3, 6, 10, 14, 18, 22, 27, 32, and 40, respectively. Each time the destructive sampling consumed 12 bottles (3 for the nitrate treatments and 3 for the controls in the two soils).

2.3. Analytical methods

N_2O concentrations of the gas samples were analyzed by GC (Agilent 7890A, Agilent Technologies Inc., Santa Clara, CA, USA) with an electron capture detector (ECD). Soil Eh was measured with an oxidation-reduction potentiometer (Nanjing Jaoyuan Analytical Instrument Company Limited, China) by using a platinum composite electrode. The pH was determined with a pH meter (Sartorius, Basic pH Meter PB-10, Germany). DOC was extracted with water from soil slurry samples and analyzed by a TOC analyzer (vario TOC cube, Elementar, Germany). Soil total N was determined by an elemental analyzer (vario MAX CN, Elementar, Germany), and soil organic N was calculated as the difference between total N and inorganic N. Inorganic N was extracted with 1 M KCl from soil slurry, ammonium was analyzed by the phenol hypochlorite method (Scheiner, 1976), and nitrite was analyzed by the modified Griess-llosvay method (Moorcroft et al., 2001).

Nitrate was analyzed by the ultraviolet spectrophotometry method (Cawse, 1967). To remove the interference of dissolved organic matter (DOM) and Fe(III) on soil nitrate analysis, 5 ml aliquots of soil extracts were mixed with 20 ml of alumina suspension and spinned in a centrifuge. Alumina suspension was prepared as the following procedure: (i) 30 g of potassium aluminum sulfate was dissolved in 1 L of deionized water, and then the suspension was filtered; (ii) the filtrate was added to a mixture of 225 ml of deionized water and 25 ml of ammonia solution to promote aluminum hydroxide free precipitating from sulfate; and (iii) finally the suspension of the precipitate was diluted to 1 L for nitrate analysis (Cawse, 1967). The final pH of alumina suspension was about 6.8, and alumina suspension was well agitated during use. In addition, 100 μL of 1 M Na_2HPO_4 solution was added to 5 mL of soil

Table 1
The geochemical properties of the two paddy soils.

Sample sites	pH (H_2O)	Organic C (g C kg^{-1})	Total N (g N kg^{-1})	NH_4^+ (mg N kg^{-1})	NO_3^- (mg N kg^{-1})	Total Fe (g kg^{-1})	0.5 M HCl-extracted Fe (g kg^{-1})	Texture		
								Slit (%)	Clay (%)	Sand (%)
Xianning (S1)	5.3 (0.00)	10.5 (0.05)	1.3 (0.02)	46.5 (0.76)	15.9 (0.83)	22.5 (0.25)	1.8 (0.07)	69.6 (0.74)	28.1 (1.08)	2.3 (0.42)
Yueyang (S2)	5.2 (0.00)	19.2 (0.09)	2.3 (0.11)	82.0 (0.63)	8.7 (0.55)	24.6 (0.81)	3.1 (0.03)	60.1 (1.92)	34.5 (1.28)	5.4 (0.82)

Standard errors (n = 3 replicate samples) are shown in parentheses.