

# UNIVERSITY of **FLORIDA**

# Mn Oxide affects nitrification and N<sub>2</sub>O emissions in a subtropical rice soil with variable water regimes

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# **High lights**

- 1. Manganese oxide retarded nitrification rate in aerobic conditions
- 2. Manganese oxide increased nitrification rate in anaerobic conditions
- 3. Manganese oxide decreased  $N_2O$  emission rate in anaerobic conditions

# Introduction

Approximately 155 million ha of land are used for rice cropping, and more than 50% of the world's population feeds on rice, while nitrogen fertilizer-use efficiency in rice-based ecosystems is usually less than half of the efficiency found in other agricultural systems (Roy et al. 2003). The periodic short-term redox cycles induced by paddy management affects soil redox potential, leading to the formation of distinct layers characterizing Fe/Mn distribution /redistribution (Roy et al. 2003) and nutrient transformations influence soil microorganisms and soil nitrogen cycling (Kikuchi et al. 2007; Xin et al. 2014). Manganese toxicity to microorganisms has been proposed (He et al. 2005; Xin et al. 2015), and MnO<sub>2</sub> may also act as electron acceptor, oxidizing  $NH_3/NH_4^+$  to N<sub>2</sub> directly under anaerobic conditions, which is thermodynamically favorable, especially in acid soils (Luther et al. 1997). Therefore, we hypothesized that MnO<sub>2</sub> may play an important role in nitrification and denitrification in rice-based ecosystems with variable water management, since it has both environmental and economic concerns.

Soil species	Moisture content (WHC)	Model	Np (mg N kg-1)	K <sub>0</sub> (mg N kg <sup>-1</sup> day <sup>-1</sup> or K <sub>1</sub> (day <sup>-1</sup> )	R <sub>2</sub>	Vp (mg N kg <sup>-1</sup> day	Va
Control	50%	First-order	17.9	0.57	0.99	10.2	1.87
	100%	Zero-order		2.06	0.99		2.19
	200%	First-order	0.22	14.0	0.99	3.09	1.11
+ 3% Mn	50%	Zero-order		1.62	0.99		1.67
	100%	Zero-order		1.86	0.99		1.89
	200%	Zero-order		2.02	0.98		1.80

**Materials and Methods** 

Paddy soils were collected from Purple Soil Ecology Experimental Station of Southwest University, Chongqing, China (30° 26' N, 106° 26' E). Subsamples were prepared by amendment with 0% (unamended control) or 3% birnessite by weight. Soil moisture content of each sample was adjusted with deionized water to form three treatments: 50%, 100%, and 200% Water-holding capacity (WHC) moisture contents. After pre-incubation for 7 days, each spiked with 120 mg N kg<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and At the intervals of 0, 1, 3, 7, and 10 days, subsamples were taken and analyzed for NH<sub>4</sub>-N, NO<sub>3</sub>-N, pH, Eh and N<sub>2</sub>O fluxes. NO<sub>3</sub><sup>-</sup>-N concentration were modeled with a first-order reaction kinetic model. Data were subjected to one-way ANOVA and mean values were separated using Tukey's test and Duncan's multiple range test at *P*<0.05. All statistical analyses were performed by SPSS statistical package.

Table 1. Parameters of zero or first-order kinetics fitting  $NO_3^{-}-N$  accumulation during the 10 days' incubation in a subtropical rice soil with variable water regimes. Np was potential nitrification; k0 or k1 was the rate constant of zero or first–order kinetics model; Vp was potential nitrification rate calculated from first-order kinetics as  $Vp = k1^* Np$ ; Va was average net nitrification rate.



#### Results

mg

Ζ





 $(NH_4)_2SO_4$ ). Error bars represent standard deviation, n=3.

## Discussion

- > Simulated results from nitrification dynamics indicated that Mn addition changed the pattern of nitrification from first-order to zeroorder model (Table 1). This indicated that the substrate for nitrification (NH<sub>3</sub>) was sufficient relative to the oxidizing capacity of the ammonia oxidizers, and nitrification rates were limited by ammonia oxidizers rather than the substrate (NH<sub>3</sub>) supply. Possible mechanisms may include Mn toxicity to nitrifying microorganisms, such as AOB and AOA (Xin et al. 2015).
- $\geq$  Nitrification was retarded by MnO<sub>2</sub> under aerobic condition while significantly increased in the anaerobic treatment. The stimulation of nitrification by  $MnO_2$  in the anaerobic condition may imply that  $MnO_2$  plays an essential role as electron acceptor when  $O_2$  is depleted.  $\succ$  The N<sub>2</sub>O emission rate decreased while NO<sub>3</sub>-N accumulation increased significantly after MnO<sub>2</sub> addition at 200% WHC (Figures 1 and 2), indicating that denitrification was depressed or inhibited by Mn oxide under anaerobic conditions. Possible mechanisms involved

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Manganese oxide affects nitrification and N<sub>2</sub>O emissions in a subtropical

rice soil with variable water regimes, implying that manganese oxides may

play an important role in the variation of nitrification in acidic soils.