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RESEARCH ARTICLE

Effects of long-term application of different green manures on ferric iron reduction in a red paddy soil in Southern China

GAO Song-juan[1, 2], CAO Wei-dong[1, 3], GAO Ju-sheng[1, 4], HUANG Jing[1, 4], BAI Jin-shun[1], ZENG Nao-hua[1], CHANG Dan-na[1, 2], SHIMIZU Katsuyoshi[5]

[1] *Key Laboratory of Plant Nutrition and Fertilizer, Ministry of Agriculture/Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, P.R.China*
[2] *Graduate School of Chinese Academy of Agricultural Sciences, Beijing 100081, P.R.China*
[3] *Soil and Fertilizer Institute, Qinghai Academy of Agriculture and Forestry Sciences, Qinghai University, Xining 810016, P.R.China*
[4] *Red Soil Experimental Station in Hengyang, Chinese Academy of Agricultural Sciences, Qiyang 426182, P.R.China*
[5] *Faculty of Agriculture, Kagoshima University, Kagoshima 890-0065, Japan*

Abstract

Dissimilatory Fe(III) reduction is an important process in the geochemical cycle of iron in anoxic environment. As the main products of dissimilatory iron reduction, the Fe(II) species accumulation could indicate the reduction ability. The effects of different green manures on Fe(III) reduction in paddy soil were explored based on a 31-year rice-rice-winter green manure cropping experiment. Four treatments were involved, i.e., rice-rice-milk vetch (RRV), rice-rice-rape (RRP), rice-rice-ryegrass (RRG) and rice-rice-winter fallow (RRF). Soils were sampled at flowering stage of milk vetch and rape (S1), before transplantation (S2), at tillering (S3), jointing (S4), and mature (S5) stages of the early rice, and after the harvest of the late rice (S6). The contents of TFe_{HCl} (HCl-extractable total Fe), $\text{Fe(II)}_{\text{HCl}}$ (HCl-extractable Fe(II) species) and $\text{Fe(III)}_{\text{HCl}}$ (HCl-extractable Fe(III) species) were measured. The correlations among those Fe species with selected soil environmental factors and the dynamic characteristics of $\text{Fe(II)}_{\text{HCl}}$ accumulation were investigated. The results showed that TFe_{HCl} in RRF was significantly higher than those in the green manure treatments at most of the sampling stages. $\text{Fe(II)}_{\text{HCl}}$ increased rapidly after the incorporation of green manures in all treatments and kept rising with the growth of early rice. $\text{Fe(II)}_{\text{HCl}}$ in RRG was quite different from those in other treatments, i.e., it reached the highest at the S2 stage, then increased slowly and became the lowest one at the S4 and S5 stages. $\text{Fe(III)}_{\text{HCl}}$ showed oppositely, and $\text{Fe(II)}_{\text{HCl}}/\text{Fe(III)}_{\text{HCl}}$ performed similarly to $\text{Fe(II)}_{\text{HCl}}$. The maximum accumulation potential of $\text{Fe(II)}_{\text{HCl}}$ was significantly higher in RRF, while the highest maximum reaction rate of $\text{Fe(II)}_{\text{HCl}}$ accumulation appeared in RRG. Significant correlations were found between the indexes of $\text{Fe(II)}_{\text{HCl}}$ accumulation and soil pH, oxidation-reduction potential (Eh) and total organic acids, respectively. In together, we found that long-term application of green manures decreased the TFe_{HCl} in red paddy soils, but promoted the ability of Fe(III) reduction, especially the ryegrass; $\text{Fe(II)}_{\text{HCl}}$ increased along with the growth of rice and was affected by soil conditions and

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GAO Song-juan, E-mail: gaosongjuan@caas.cn; Correspondence CAO Wei-dong, Tel: +86-10-82109622, E-mail: caoweidong@caas.cn

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environmental factors, especially the water and redox ability.

Keywords: green manure, red paddy soil, ferric iron reduction, rice-rice-winter green manure cropping system

1. Introduction

Green manures play important roles in supplying nutrients for crops, improving ecological environments of agricultural fields, reducing soil erosion and pollution (Becker *et al.* 1995), restraining global warming potentials (Robertson 2000), and contributes to higher crop yields (Tejada *et al.* 2008). Green manures can be fitted into rice farming systems in either the pre-rice or post rice phase (Garrity and Flinn 1988). In Southern China, planting of winter green manures after the late rice has been proved to be an effective rotation pattern in improving soil conditions, soil fertility and rice yields (Gao *et al.* 2011, 2013). Many studies reported that the application of green manures changed the chemical and biological characteristics of soils (Elfstrand *et al.* 2007; Bernard *et al.* 2012). Milk vetch (*Astragalus sinicus* L.), one kind of winter-growing legumes, has been widely used as green manure in rice fields to fertilize the soils in Japan and China (Samarajeewa *et al.* 2005), and as an alternative N source for chemical fertilizer in double-rice cropping systems in Southern China (Zhu *et al.* 2014). Rape and ryegrass are also commonly used as green manures in Southern China (Cai *et al.* 2001), and have the potential to improve sustainable production of double cropping rice (Tang *et al.* 2015).

Dissimilatory Fe(III) reduction mainly occurs in anoxic soils and sediments, and is an important process in the geochemical cycle of iron in anoxic environment (Takai and Kamura 1966; Lovley *et al.* 2004; Roden 2006). Total Fe, Fe(III) species and Fe(II) species are three forms of Fe studied as the indexes of Fe(III) reduction. Total Fe is mainly consisted of Fe(II) species and Fe(III) species. Variations of Fe(III) are normally affected by total Fe content and the situation of Fe(III) reduction. As the electron acceptor and substrate of ferric iron reduction, Fe(III) is an important index of Fe(III) reduction in paddy soils (Roden 2006). The reduction ability of different Fe(III) forms is interdependent with the accumulation of Fe(II) species. Fe(II) species, including water soluble (ionic and complex states), absorbed, structural, and sedimental status, etc. (Fredrickson *et al.* 1998; Van Bodegom and Van Reeven 2003), are produced by the reductive dissolving actions of ferric iron oxides under the combined effects of chemistry and microbes (Lovley *et al.* 2004), hence their accumulation can indicate the Fe(III) reduction ability well (Lovley 2006). Studies had proved that $Fe(II)_{HCl}$ (HCl-extractable Fe(II) species) could represent most biological and chemical sources of Fe(II) species produced by ferric iron reduction, and could keep their concentration and valence state stable during the extraction (Lovley and Phillips 1986; Roden and Wetzel 2002; Chacon *et al.* 2006). Importantly, $Fe(II)_{HCl}$ is biologically available for microorganisms and crops, therefore, its content can suggest the status of soil iron nutrition (Van Bodegom and Van Reeven 2003).

The iron cycling has close relationships with the cycles of carbon, nitrogen, sulphur, and oxygen, and is one of the most important ways of energy and electron transportations (Stumm and Sulzberger 1991; Otoidobiga *et al.* 2015). The Fe(III) reduction process was affected by soil moisture, organic matter, oxidation-reduction potential (Eh), pH, and temperature, etc. (Takai and Kamura 1966; Ponnamperuma 1972). The change of ferric iron reduction process in paddy soils can influence the redox status, inhibit the production of CH_4, and play important roles in the restriction of global warming (Jackel and Schnell 2000; Liesack *et al.* 2000). By now, there were no reports about the long-term effects of green manures on ferric iron reduction in paddy soil in Southern China. Most studies about ferric iron reduction were conducted under control conditions (Yu *et al.* 2014; Jia *et al.* 2015; Li *et al.* 2016), and few were done on fields *in situ*. Fe(III) reduction as well as iron availability in paddy soils after green manures being input into the double-rice system are still unclear. In this study, based on a 31-year long-term experiment in a rice field from Southern China, reduction ability of Fe(III) was investigated at different stages of the rice field with the purpose to understand the effects of winter green manures on Fe(III) reduction in red paddy soil.

2. Materials and methods

2.1. Studied field

The field experiment are located at Hengyang Red Soil Experimental Station of Chinese Academy of Agricultural Sciences (latitude 26.45°N, longitude 111.52°E and altitude 150 m above sea level) in Qiyang County, Hunan Province, which is a typical double-rice area in Southern China. Average annual temperature is 18.3°C, accumulated temperature above 10°C is 5 600°C, the frost-free period is 300 days, average annual precipitation is 1 250 mm. The soil is developed from quaternary red clay, the soil texture is loamy clay, and the main