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Does sulfur fertilizer influence Cu migration and transformation in colloids of soil pore water from the rice (*Oryza sativa* L.) rhizosphere?[☆]

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ABSTRACT

Colloids are ubiquitous in soils, and it has been reported that colloids can act as carriers to increase the mobility of poorly soluble contaminants in subsurface environments. Addition of sulfur (S) fertilizer greatly influences on heavy metal behavior in paddy soil, while the influence of S fertilizer on Cu migration and transformation in colloids of soil pore water has not yet been studied. The influence of S fertilizer (S^0 and Na_2SO_4) applied in paddy soils on Cu migration and transformation in colloids of soil pore water from the rice rhizosphere region was explored in this study. The speciation of Cu in colloids of soil pore water from the rice rhizosphere region was explored by advanced synchrotron-based X-ray absorption near-edge spectroscopy (XANES) techniques. The morphology of colloids was characterized by field emission scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDX). At a depth of 20 cm, the concentration of Cu in colloids of the rhizosphere soil pore water in the control was 2.4- and 6.5- fold higher than that in treatments of S^0 and Na_2SO_4, respectively. The colloids in soil pore water were all positively charged, ranging from 2.4 to 7.8 mV, and the size of colloids was 440–740 nm. The proportion of Fe in colloids in the rhizosphere region decreased with S fertilizer application, while the proportions of C and O increased. Sulfur fertilizer application, increased the proportion of Cu-Cysteine, while the proportion of Cu_2S decreased in soil colloids. In conclusion, application of sulfur fertilizer in paddy soil decreased the Cu concentration in soil pore water and colloids of the rhizosphere region, thereby decreasing the vertical migration of Cu in soil pore water.

1. Introduction

Excessive copper (Cu) is considered toxic to organisms due to the production of reactive oxygen species by autoxidation and Fenton reaction or altering target protein functions by binding to proteins or other targets through -SH, $-COO^-$ or imidazole (Schutzendubel and Polle, 2002). The release, transformation and transport of Cu in a soil system largely determine the environmental risk of Cu. Soil colloids are suspended particles with sizes that are between 1 nm and 10 μm. The two main types of colloids in the soil system are abiotic colloids (e.g., clay, metal oxides and humic substances) and biocolloids (i.e., viruses, bacteria, and protozoa). Colloids are ubiquitous in soils and are important carriers that increase the mobility of poorly soluble contaminants in subsurface environment (McCarthy and Zachara, 1989; Ouyang et al., 1996; Kretzschmar et al., 1999). Sulfide particles, which usually form in a reduced environment, are suggested to cause the vertical transport of heavy metals in the water system (Jacobs et al., 1985). Under sulfate-reducing conditions, the sequestration of metal sulfide into precipitates immobilizes chalcophile metal contaminants such as Cd, Cu and mercury (Hg) (Kirk, 2004). However, the metal sulfide precipitation is proposed to generate contaminant-bearing sulfide colloids in sulfate-reducing soils and sediments, which could transport contaminants traditionally thought to be immobilized by metal sulfide formation (Weber et al., 2009). Thus, the transport of soil colloids plays an important role in the environmental behavior of chalcophile metals.

The rice rhizosphere is the "bio-influenced zone" surrounding rice roots, which is thought to be the critical zone for the

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assessment of metal bioavailability in paddy soils (Harmsen, 2007; Bravin et al., 2011). The chemical changes induced by rice roots and the resulting gradients of physicochemical properties can undoubtedly influence the availability of heavy metals in the rice rhizosphere (Hinsinger and Courchesne, 2007). Bravin et al. (2011) found that rhizosphere alkalization of durum wheat (*Triticum turgidum durum* L.) significantly decreased the uptake of Cu by wheat plants, confirming that chemical changes induced by roots in the rhizosphere should be better accounted for in the assessment of heavy metal bioavailability to plants. Wetland plants with large amounts of radial oxygen loss from roots decrease the pH and concentration of Fe(II) but increase the Eh in rhizosphere soils, which leads to the transformation of Pb and Zn from unstable fractions to more stable fractions in rhizosphere soils, thereby decreasing their potential metal mobility factors (Yang et al., 2012). However, the mobilization and speciation transformation of Cu in colloids of the rice rhizosphere have not yet been extensively studied. Exploring the transport and transformation of Cu in colloids of the rice rhizosphere region will help better understand the environmental behavior of Cu.

In recent decades, sulfur (S) fertilization in agricultural soil has received much attention due to the frequent sulfur deficiency in soil systems (Luo et al., 2014; Yang et al., 2015). Sulfur is a typical redox active element, with different oxidation states. The speciation transformation of S in soil system is closely related to the biogeochemical processes of many nutrients and toxic elements (Luo et al., 2014). Studies have focused on the influence of different amounts of S in soil on the speciation transformation of Cu under flooding conditions. Weber et al. (2009) reported that S was capable of reducing the availability of Cu in floodplain soil by forming barely dissolved CuS_x under reducing conditions. Yang et al. (2015) found that S fertilizers could significantly affect the release and transformation of Cu in pore -water in a Cu contaminated paddy soil under flooding conditions. Lin et al. (2010) found that both the transformation of S and organic compounds contributed to an increase in the amount of soluble and exchangeable Cu in the rice rhizosphere. However, the influence of S fertilizer application in paddy soil on Cu transformation in colloids of soil pore water from the rice rhizosphere region has not been extensively studied, which is of critical importance for both agricultural production and contaminant management.

Elemental S and sulfate are two typical S species in S fertilizers (Chien et al., 2011). In this study, we explored the influence of the two typical forms of S fertilizer (S^0 and Na_2SO_4) on Cu transport and speciation transformation in colloids of soil pore water by conducting a soil column experiment. The main aims of this study were to 1) explore the effect of sulfur fertilizer on Cu concentration in colloids of rice rhizosphere soil and 2) reveal the influence of sulfur fertilizer on Cu speciation transformation in colloids of rice rhizosphere soil.

2. Materials and methods

2.1. Soil samples and experimental treatments

Paddy soil samples were collected from the top layer (0–20 cm) of an agricultural field located in Fuyang City of Zhejiang Province, China (119°55′29.7″E, 29°56′22.6″N). Rice growth in this field was forbidden due to contamination of heavy metal caused by smeltering activities nearby. The experimental soil was air-dried and sieved to less than 2 mm after collection from the paddy field. The basic properties of the experimental soil were measured following the standard procedures and listed in Table S1. Three basic fertilizers (phosphorous, potassium and nitrogen) were mixed thoroughly with the soil at the beginning of the experiment to ensure adequate mineral nutrition for the growth of rice seedlings (Liu et al., 2006). The amount and forms of the three fertilizers applied are referred to our previous studies (Sun et al., 2018). Two forms of S fertilizer (S^0 and Na_2SO_4) were applied at two doses (0 mg/kg, 100 mg/kg), and four replicates were set in each treatment.

A soil column experiment was conducted in a greenhouse under controlled conditions. Perspex columns (ø 80 × 300) were specially designed for soil pore water collection. Three sample outlets were on the column at depths of 5, 15 and 25 cm, representing soil depths of at 0, 10 and 20 cm. Each sample outlet was a small column (ø 8 × 40), and a small piece of nylon mesh was mounted on the end of the small column to prevent soil entering in the sample outlet (Fig. S1A). A total of 1250 g of dry soil (200–2000 μm) was placed into each soil column. To maintain a 5 cm water layer above the soil surface, distilled water was added daily. After two weeks to reach equilibrium, a rice seedling was transplanted into the central part of the column (Fig. S1B).

2.2. Rice cultivation

Cultivar NO. 39 Zhongzao, which was widely grown in Zhejiang Province, China, was chosen as our study material. The cultivating methods are described in our previous study (Sun et al., 2017). Briefly, seeds were washed thoroughly with deionized water after sterilization for 15 min in 30% H_2O_2 solution. All the rice seeds were germinated on a nylon screen (with 8 meshes per inch) and immersed in deionized water. Rice seedlings were transplanted into nutrient solution two weeks later. After growing for another week, one rice seedling (three-weeks old) was transplanted into the soil in the central part of the specially designed column. All the columns were set randomly in a greenhouse. The greenhouse conditions were humidity of 60–70% and a temperature of 25 °C during the day (16 h) and 20 °C at night (8 h). Columns without cultivation of rice plants but with the same treatments were set as the nonrhizosphere region.

2.3. Sampling

To study the influence of the specific oxidation environment of the rice rhizosphere on heavy metal behavior, soil pore water was collected from the three sample outlets using a peristaltic pumb with water flow of 30 mL/min in the tillering stage of rice plants. The water samples were collected from the top to the bottom to prevent the mixture of water samples from different depths. The sample from a depth of 20 cm was chosen as the main object of our study because it was influenced by both rice roots and vertical movement. The pore water colloidal particles separation was followed the methods reported by Liang et al. (2010), and details can be referred to the supporting information. The four replications were blended together in the process of colloid separation to collect sufficient colloid particles for further analysis. The dissolved phase referred to the supernatant of soil water after ultracentrifugation. After removal of the supernatant, colloidal particles were quickly transferred into a chamber for freeze-drying for 72 h and then quickly sealed in a sample holder filled with N_2. The soil pore water properties pH, redox potential (Eh), and electrical conductivity (EC) were measured in situ by using an ion analyzer (Thermo-Orion, Beverly, MA) equipped with a pH electrode, an oxidation-reduction potential electrode and a conductivity meter.

2.4. Element concentration and morphology determination of colloids

Total contents of Cu, Fe, and S in the filtered dissolved phase