



Effects of free iron oxyhydrates and soil organic matter on copper sorption-desorption behavior by size fractions of aggregates from two paddy soils

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Abstract

Effects of free iron oxyhydrates (Fe_d) and soil organic matter (SOM) on copper (Cu^{2+}) sorption-desorption behavior by size fractions of aggregates from two typical paddy soils (Ferric-Accumulic Stagnic Anthrosol (Soil H) and Gleyic Stagnic Anthrosol (Soil W)) were investigated with and without treatments of dithionite-citrate-bicarbonate and of H_2O_2 . The size fractions of aggregates were obtained from the undisturbed bulk topsoil using a low energy ultrasonic dispersion procedure. Experiments of equilibrium sorption and subsequent desorption were conducted at soil water ratio of 1:20, 25°C. For Soil H, Cu^{2+} sorption capacity of the DCB-treated size fractions was decreased by 5.9% for fine sand fraction, by 40.4% for coarse sand fraction, in comparison to 2.9% for the bulk sample. However, Cu^{2+} sorption capacities of the H_2O_2 -treated fractions were decreased by over 80% for the coarse sand fraction and by 15% for the clay-sized fraction in comparison to 88% for bulk soil. For Soil W, Cu^{2+} sorption capacity of the DCB-treated size fraction was decreased by 30% for the coarse sand fraction and by over 75% for silt sand fraction in comparison to 44.5% for the bulk sample. Cu^{2+} sorption capacities of the H_2O_2 -treated fractions were decreased by only 2.0% for the coarse sand fraction and by 15% for the fine sand fraction in comparison to by 3.4% for bulk soil. However, Cu^{2+} desorption rates were increased much in H_2O_2 -treated samples by over 80% except the clay-sized fraction (only 9.5%) for Soil H. While removal of SOM with H_2O_2 tendend to increase the desorption rate, DCB- and H_2O_2 -treatments caused decrease in Cu^{2+} retention capacity of size fractions. Particularly, there hardly remained Cu^{2+} retention capacity by size fractions from Soil H after H_2O_2 treatment except for clay-sized fraction. These findings supported again the dominance of the coarse sand fraction in sorption of metals and the preference of absorbed metals bound to SOM in differently stabilized status among the size fractions. Thus, enrichment and turnover of SOM in paddy soils may have great effects on metal retention and chemical mobility in paddy soils.

Key words: paddy soils; Cu^{2+} ; sorption-desorption; soil organic matter; free iron oxyhydrates; size fraction of aggregates

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Introduction

Soil aggregates are formed through the binding of soil minerals with organic matter and/or soil organisms under varying strengths (Monreal *et al.*, 1995) as a process of interaction of mineral, organic matter and biota in soils. They could be obtained using a low-energy ultrasonic dispersion of undisturbed bulk soils (Stemmer *et al.*, 1998). In response to soil organic matter (SOM) turnover, soil aggregates may experience the changes in both size fractions and chemical compositions. Soil aggregates of different fractions in size have been considered as the most basic and functional units of soil entity (Schulten and Leinweber, 2000). Pan (2000) argued that soil environmental processes in the filed may take place on the soil aggregate-water interface. The basic properties, retention capacity of nutrients as well as the biological functions of soil aggregates

and their variation under agricultural management have been widely addressed in the last decades (Materechera *et al.*, 1994; Kandeler *et al.*, 1999; Wilck *et al.*, 1999; Veli and Alyuz, 2007).

Paddy soils of China are considered as a unique soil type formed under hydro-agric management (Gong, 1999). Soil aggregates from paddy soils are generally considered different from those from dry croplands, especially in proportions of size fractions and composition of soil components within aggregates (Chen *et al.*, 2001). Since a decade ago, studies in soil aggregates of different size fractions from paddy soils in China have been widely reported. These studies have shown that SOM, nutrients (Li *et al.*, 2007) and heavy metals (Qian *et al.*, 1996; Li *et al.*, 2001) were preferentially distributed in size fractions of coarse sand and clay. Simultaneously, studies also indicated a high sorption-retention capacity of metals (Wang *et al.*, 2006, 2007) and organic pollutants (Li and Pan, 2005) in

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coarse sand and clay-sized fraction of aggregates. Recently, Zheng *et al.* (2007) have shown that microbial diversity and activity and, in turn, soil respiration and greenhouse gases (GHGs) production from the coarser fractions are significantly higher than that from the finer ones in a single paddy soil of Tai Lake region, China. These results indicated the different environmental functions of different size fractions soil aggregates varying in SOM quantity and quality, microbial activity and thus, the surface chemical and biological features. These differences may affect the sorption and desorption behavior of aggregates. Wang *et al.* (2006, 2007) reported that the sorption capacities of heavy metal by soil aggregates in size fractions from paddy soils varied with the contents of free iron oxyhydrates (Fe_d) and SOM. However, the relative roles of SOM and Fe_d on the sorption capacity are still unknown.

Therefore, the purpose of this study is to characterize the relative roles of SOM and Fe_d on the metal sorption and desorption by size fractions of aggregates from paddy soils through the chemical treatments and to discuss the differences between soil types.

1 Materials and methods

1.1 Studied paddy soils

Two paddy soils with contrasting chemical properties were used in this study. Soil H is a Ferric-Accumulic Stagnic Anthrosol with slightly acid reaction, was collected from Jinjiaba Township ($31^{\circ}5'N$, $120^{\circ}46'E$), Wujiang Municipality, Suzhou, China. Soil W is a Gleyic Stagnic Anthrosol with neutral reaction, and was collected from Xinzhuang Township ($31^{\circ}33'N$, $123^{\circ}38'E$), Changshu Municipality, Suzhou. Topsoil samples at the depth of 0–15 cm were collected in triplicates in May, 2005 before rice planting. After shipping to laboratory, one portion of samples was stored in refrigerator prior to the separation of size fractions, while another portion as bulk soil was air-dried, ground to pass a 0.25-mm sieve.

1.2 Separation of size fractions

Following the procedure described by Stemmer *et al.* (1998), 4 fractions in size of the diameter (coarse sand of 2.00–0.25 mm, fine sand of 0.25–0.02 mm, silt of 0.02–0.002 mm and clay of < 0.002 mm) were separated. Field moist soil (35 g equivalent dry weight) was placed into a 150-mL glass beaker and dispersed in 100 mL distilled water, standing over night. Then, the beaker was subject to a probe-type ultrasonic disaggregator (JYD-650, Zhisun Instrument Co., Ltd., Shanghai) under output energy of 50 J/s for 120 s. Coarse sand fraction was obtained by wet sieving through a 0.25-mm nylon sieve. In addition, fine and silt sand fractions were obtained by sedimentation using Stock's Law and clay-sized fraction by centrifugation. All samples were dried with a freezing-drier (Thermo Savant 100 Colin Drive, Holbrook, NY) and were ground to pass a 0.25-mm sieve before analysis.

1.3 Analytical methods

Determination of basic soil properties was done

following the conventional laboratory methods described by Lu (2000). Soil pH was measured using a Mettler-Toledo pH meter with water:soil ratio of 2.5:1 (V/V). Cation exchange capacity (CEC) was measured with 1 mol/L ammonium acetate (pH 7). The content of SOC was determined by wet digestion with $\text{K}_2\text{Cr}_2\text{O}_7$ and Fe_d by dithionite-citrate-bicarbonate (DCB) extraction. The properties of bulk sample are shown in Table 1.

Table 1 Properties of bulk topsoil of two paddy soils (0–15 cm)

| Soil | pH (H_2O) | SOC (g/kg) | N_t (g/kg) | Clay (g/kg) | CEC (cmol/kg) | Fe_d (g/kg) |
|--------|--------------------------------|---------------|------------------------|----------------|------------------|-------------------------|
| Soil H | 5.6 | 15.8 | 1.6 | 303.5 | 19.8 | 24.0 |
| Soil W | 7.0 | 21.4 | 1.8 | 230.6 | 20.4 | 11.9 |

SOC: soil organic carbon; CEC: cation exchange capacity; Fe_d : free iron oxyhydrates; N_t : soil total nitrogen.

1.4 Fe_d and SOM removal

Both bulk soil and size fractions of aggregates were used in this study. Samples were divided into three portions for the different treatments respectively: one portion was treated with DCB to remove Fe_d , a second portion was treated with 30% H_2O_2 to remove SOM, and a third portion was without any treatment as control. The detailed procedures for these treatments were as follows (Xiong, 1985): for Fe_d removing, 1.0 g sample was placed in a 50-mL centrifuge tube, adding 20 mL of 0.3 mol/L citrate and 2.5 mL of 1 mol/L bicarbonate; after heating in water bath up to 80°C , 0.5 g dithionite was added and stirred for 15 min; the tube was centrifuged after cooling; repeat this process 2 or 3 times. Finally, the residue was washed with distilled water for 2 or 3 times using 1 mol/L NaCl as a Fe_d -removed fraction. For SOM removing, 30 g size fraction was placed in a glass beaker, and 5 mL of 30% H_2O_2 was added. Then the suspension was stirred at room temperature before put into a water bath at 70 – 80°C . When frothing had completely subsided, repeated the treatment until no reaction was observed upon further addition of H_2O_2 . Excess H_2O_2 was expelled via heating. Finally, the H_2O_2 -treated size fraction was obtained after centrifuging and washing with distilled water. The properties of size fractions are shown in Table 2. The recovery from the size fractions to the bulk total was in range of 91.4%–110.0%.

1.5 Sorption-desorption experiment

Sorption experiment of Cu^{2+} by both the treated and untreated samples was conducted using the batch isothermal equilibrium sorption method as described by Wu *et al.* (1999). A 1.00-g sample was placed in a 100-mL centrifuge tube containing 20 mL of 40 mol/L CuCl_2 and 0.01 mol/L CaCl_2 solution (as a background electrolyte, pH 6.0). Then the tube was shaken in a rotatory shaker (ZD-88-B, Bolaite Instrument Company, China) at 180 r/min, 25°C for 24 h. The suspension was centrifuged at 3600 r/min for 10 min and filtered through a 0.45- μm filter paper. Finally, Cu^{2+} in solution was determined and the amount of absorbed Cu^{2+} was calculated by the difference between the amount added and remained in solution.

Table 2 Properties of size fractions comparing with bulk soil samples

| Property | Soil | Bulk soil | Coarse sand fraction | Fine sand fraction | Silt sand fraction | Clay-sized fraction |
|------------------------|------|-----------------|----------------------|--------------------|--------------------|---------------------|
| Mass (%) | H | NA | 19.06 ± 1.49 c | 43.56 ± 3.90 a | 28.73 ± 2.70 b | 8.28 ± 1.80 d |
| | W | NA | 23.55 ± 2.73 b | 43.22 ± 0.32 a | 23.62 ± 0.79 b | 8.36 ± 0.23 c |
| SOC (g/kg) | H | 15.81 ± 0.65 b | 20.57 ± 1.12 a | 14.20 ± 0.19 b | 10.13 ± 0.17 c | 21.69 ± 0.39 a |
| | W | 21.35 ± 0.35 c | 28.75 ± 0.44 a | 17.76 ± 0.34 d | 18.16 ± 0.26 d | 25.61 ± 1.01 b |
| Fe _d (g/kg) | H | 23.96 ± 0.33 c | 28.14 ± 0.61 b | 20.81 ± 0.32 d | 14.62 ± 0.21 e | 39.07 ± 1.23 a |
| | W | 11.86 ± 0.11 c | 15.29 ± 0.28 b | 9.06 ± 0.16 d | 12.19 ± 0.22 c | 22.42 ± 0.42 a |
| CEC (cmol/kg) | H | 19.82 ± 0.53 bc | 21.88 ± 1.79 b | 18.87 ± 1.06 c | 21.20 ± 1.05 b | 39.69 ± 0.54 a |
| | W | 20.42 ± 0.42 c | 24.80 ± 1.15 b | 15.44 ± 0.29 d | 19.20 ± 0.13 c | 40.66 ± 1.64 a |

Comparison between means was made with the LSD test. Different letters in a same row indicated a significant difference between the fractions of a single soil at $p < 0.05$. NA: not applicable.

Desorption experiment of the absorbed Cu²⁺ on the residues was performed immediately after sorption experiment was completed. The procedures were as follows: weigh the residue with tube from the sorption experiment, add 20 mL of 0.01 mol/L CaCl₂ (pH 6.0) solution in the residue tube, and shake the suspension at 180 r/min, 25°C for 24 h according to the method by Singh *et al.* (2001) and Wu *et al.* (1999). Then, the suspension was centrifuged at 3600 r/min for 10 min and filter through a 0.45- μ m filter paper. A blank tube with 20 mL of 0.01 mol/L CaCl₂ (pH 6.0) desorption solution was included in the experiment.

The performance of both sorption and desorption experiment was conducted in duplicates.

1.6 Cu²⁺ determination

The concentration of Cu²⁺ in solution was determined using Atomic Adsorption Spectroscopy (AAS, TAS-986, Puxi General Instruments Co., Ltd., Beijing). To guarantee the accuracy of analysis, background sorption subtraction was conducted with the recommended approaches according to the users' manual. A standard Cu²⁺ solution with a concentration of 1000 μ g/mL (GSB G62024-90/2902) purchased from National Standard Material Center was used as internal standard. All chemical reagents used were in GR grade. All the experiments were carried out in triplicates and the average values were reported. The Cu²⁺ recovery was in a range of 97.5%–102.3% and the relatively error of the replicates was less than 10%.

1.7 Statistical analysis

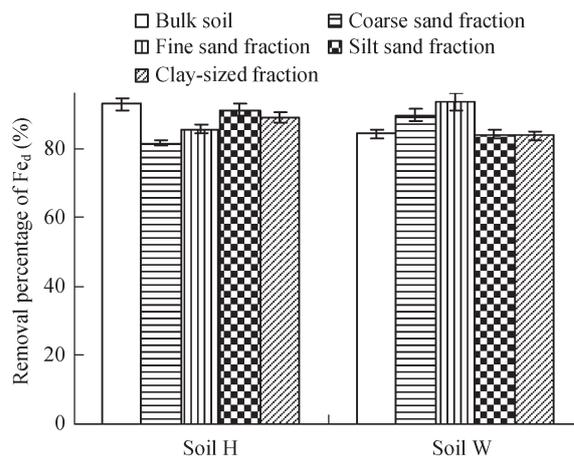
All data were processed using Microsoft Excel 2000 and statistical analyses were conducted using the programs of SAS 8.2. Significance of the differences among the size fractions or treatments was defined at $p < 0.05$.

2 Results and discussion

2.1 Removal of Fe_d and SOM

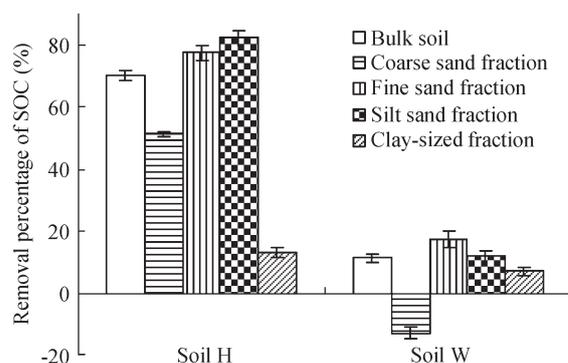
2.2 Fe_d removal with DCB treatment

As shown in Fig. 1, Fe_d was mostly removed with DCB treatment. The removal percentage ranged from 81.4% to 93.6% for bulk soils and size fraction samples. Because Fe_d content of the residual was so small, the Cu²⁺ sorption and desorption on it could be neglected.

**Fig. 1** Quantity of Fe_d removed with DCB treatment.

2.2.1 SOM removal with H₂O₂ treatment

The removal of SOM measured as SOC varied with soil types and size fractions. The SOM removed by H₂O₂ was generally considered as labile pool of SOM. As shown in Fig. 2, the percentage of SOM removal with H₂O₂ treatment ranged from < 15% (clay-sized fraction) to over 80% (silt sand fraction), and about 70.3% removal in bulk soil sample for Soil H. However, for Soil W, H₂O₂ treatment removes SOM hardly from both bulk soil and size fractions. The removal percentage ranged from 7.0% for clay-sized fraction to 17.3% for fine sand size fraction, and 11.3% from bulk soil sample. It indicated a relatively stable nature of SOM in these size fractions, which could be characterized by its chemical stabilization (Zhou *et al.*, 2008).

**Fig. 2** Percentage of SOC removal with H₂O₂ treatment.

2.2.2 Effects of Fe_d and SOM on Cu²⁺ sorption

As shown in Fig. 3, the amounts of Cu²⁺ sorption by both untreated bulk soils and size fraction samples were similar for two studied soils. For Soil H, total adsorbed Cu²⁺ for fractions ranged from 720 mg/kg (silt sand fraction) to 816 mg/kg (clay-sized fraction) and was 810 mg/kg for the bulk soil. For Soil W, total adsorbed Cu²⁺ ranged from 819 mg/kg (fine sand fraction) to 831 mg/kg (clay-sized fraction), and was 821 mg/kg for the bulk soil. Different responses on Cu²⁺ sorption behavior of size fractions could be mainly attributed to the differences in composition (Oades *et al.*, 1991), surface area (Dong *et al.*, 2006) and contents of SOM and Fe_d. Dong *et al.* (2006) reported that the surface areas of size fractions for Soil H followed the general trend: clay-sized fraction (374.3 m²/g) > silt fraction (362.3 m²/g) > fine sand fraction (346.3 m²/g) > coarse sand fraction (250.6 m²/g), and was 352.2 m²/g for bulk soil; the variable negative charge density ranged from 1.63 cmol/kg for fine sand fraction to 4.47 cmol/kg for clay-sized fraction with 2.65 cmol/kg for bulk soil. Thus, the Cu²⁺ sorption capacity of size fractions followed the general trend of the surface charge among the fractions.

Sorption capacity by the fractions was significantly decreased under treatments of DCB and H₂O₂ for both soils. For Soil H, despite the insignificant decrease for bulk soil, decreasing in Cu²⁺ sorption capacity was detected for all size fractions (as high as 40.4% to control for coarse sand fraction) (Fig. 3a). However, H₂O₂ treatment caused that the sorption capacity decreased to about 100 mg/kg for size fractions, except clay-sized fraction. Particularly, decrease in sorption capacity by the coarse sand fraction under H₂O₂ treatment was 88.4% to control. For Soil W, sorption capacities of DCB-treated samples ranged from 192 mg/kg (silt fraction) to 581 mg/kg (coarse sand fraction) (Fig. 3b). However, for H₂O₂-treated samples, the sorption capacities ranged from 695 mg/kg (fine sand fraction) to 813 mg/kg (coarse sand fraction). The DCB treatment caused decrease in sorption capacity over 75% by the silt sand fraction and 30% by coarse sand fraction, while H₂O₂ treatment resulted in a decrease at 15% for the fine sand fraction and only 2% for coarse sand fraction as SOM was hardly removed from Soil W. These

findings supported the conclusion again that the coarse sand fraction was a dominant fraction from paddy soils with enrichments of relatively fresh and labile SOM (Li *et al.*, 2007) and metals were preferably associated with SOM in soil aggregates (Ducarouir and Lamy, 1995; Wang *et al.*, 2006, 2007). The decrease in Cu²⁺ sorption capacities for DCB treated and H₂O₂ treated samples varied with soil types and size fractions of aggregates. For Soil W, greater decrease in sorption capacity was found in DCB treated than that in H₂O₂ treated samples as the sorption capacity of DCB-treated samples was lower than that of H₂O₂-treated ones. This could be explained by the low percentage of SOM removal (Fig. 2) and the exposure of more reactive sites of SOM, which were originally associated with free oxyhydrates.

Wang *et al.* (2007) reported that Cu²⁺ sorption capacities were significantly correlated with either the SOC or Fe_d of size fractions for untreated samples. Whereas, such correlation was not observed for the samples with DCB and H₂O₂ treatments, indicating the effect of binding forms of SOC or Fe_d in size fractions on the sorption capacities. Cu²⁺ sorption by bulk soil and by size fractions could be affected highly by SOM than by Fe_d. For Soil H, decrease in sorption capacity for coarse sand fraction, a dominant fraction for SOM and Cu²⁺ sorption (Wang *et al.*, 2007), was much higher (over 80%) under H₂O₂ treatment than under DCB treatment (ca. 40%). For Soil W, SOM was removed hardly by H₂O₂ treatment and thus the capacity was slightly decreased in H₂O₂ treated samples, while the capacity decreased greatly in DCB treated samples. This phenomena could be attributed to the reduction of negative charges associated with the relatively recalcitrant SOM bound with oxyhydrates, which has been demonstrated by Ducarouir and Lamy (1995) and Lin *et al.* (2007). Presumably, the total negative charge reacted with Fe_d occurring in the soil particles could be reduced because of the SOM removal with H₂O₂ treatment (Yu *et al.*, 1996). However, little influence was detected in Cu²⁺ sorption and fixation ability of the clay-sized fraction after SOM removed from an acid soil from New York, USA (Cavallaro and McBride, 1984), which also indicated that the effect of SOM and Fe_d on metal sorption could vary with soil types. In soils with acidic reaction and poor in SOM positive, charges associated with free oxyhydrates

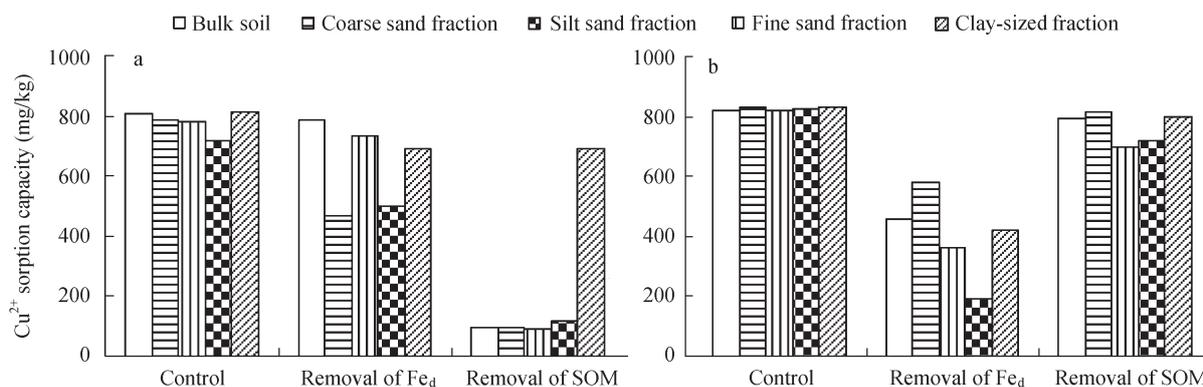


Fig. 3 Cu²⁺ sorption capacities of size fractions for DCB-treated (removal of Fe_d), H₂O₂-treated (removal of SOM), and untreated (control) samples. (a) Soil H; (b) Soil W.

were common and removal of Fe_d could exert greater reduction in the sorption capacity than that of SOM.

2.3 Effects of Fe_d and SOM on Cu²⁺ desorption by size fractions

As shown in Table 3, for untreated samples, the percentage of desorbed Cu²⁺ to the adsorbed ranged from 0.1% (clay-sized fraction) to 16.4% (silt sand fraction) for Soil H. In contrast, desorption percentage ranged from 0.1% (coarse sand fraction) to 1.0% (fine sand fraction) for Soil W. This was in consistence to the difference in sorption capacity between two soils without any treatment.

As shown in Table 3, small changes in desorption rates of size fractions existed with DCB treatment for both soils. However, under DCB treatment, the desorption percentage increased greatly for Soil H and slightly for Soil W. This was coincident with the extent of SOM removal from both soils with H₂O₂ treatment as SOM was hardly removed from Soil W (Fig. 2). The Cu²⁺ desorption rates were increased much in the H₂O₂-treated samples as high as over 80% except clay-sized fraction (9.5%) for Soil H. Thus, removal of SOM greatly decreased the binding of metal and solid phase, and Cu²⁺ could be desorbed easily and released from Soil H. High desorption rates of size fractions with H₂O₂-treatment suggested that the specific sorption of Cu²⁺ was dominantly associated with SOM. However, for Soil W, H₂O₂ treatment tended to slightly increase the desorption rate with the biggest value 5.2% for the silt-sized fraction.

Low Cu²⁺ desorption percentage demonstrated that Cu²⁺ sorbed on agricultural soil could be hardly desorbed by CaCl₂ (Yu and Zhou, 2004; Shan *et al.*, 2007), because the specific sorption was supposed to be the major sorption in soil surface (Xu, 1997). Thus, the relative low desorption rate by CaCl₂ indicated a preference of specific sorption of metals associated with SOM in these samples (Dong *et al.*,

2006).

According to Table 3, the desorption percentage decreased with DCB treatment while increased with H₂O₂ treatment comparing to control. High increase in Cu²⁺ desorption percentage from H₂O₂-treated samples suggested a preference of specific adsorption sites with SOM. This was in disagreement with Zou *et al.* (2004), who argued that iron hydrates could act as the major agent for specific sorption of four variable charged soils from South China using bulk samples. Therefore, SOM but not Fe_d was the dominant agent for Cu²⁺ specific sorption by size fractions from the paddy soils.

The differences in Cu²⁺ retention capacity (calculated as the difference between Cu²⁺ sorption capacity and desorption amount) among size fractions with DCB- and H₂O₂-treated are listed in Table 4. The Cu²⁺ retention capacities lowered with DCB- and H₂O₂- treatment. For Soil H, there hardly remained Cu²⁺ retention capacity by size fractions after H₂O₂ treatment except for clay-sized fraction. However, high Cu²⁺ retention capacity by the size fractions from Soil W remained after H₂O₂-treatment. Differences in Cu²⁺ retention capacities between two paddy soils could be accounted for the difference in nature of SOM. SOM was relatively stable and hardly removed by H₂O₂ in Soil W, which was a low-lying paddy soil formed on paleo-marsh sediments with higher pH (Xu, 1980). Fu *et al.* (2006) and Alva *et al.* (2004) have demonstrated that high Cu²⁺ sorption capacities were observed in soils with high pH, SOM content, and clay-sized fraction.

3 Conclusions

Removal of Fe_d and SOM had a significant effect on the sorption and desorption of Cu²⁺ by size fractions. Both treatments with DCB and H₂O₂ caused decreased in Cu²⁺ sorption capacity and varied with soil types. Par-

Table 3 Percentage of Cu²⁺ desorbed from bulk soil and size fractions to absorbed (%)

| Soil | Treatment | Bulk soil | Coarse sand fraction | Fine sand fraction | Silt sand fraction | Clay-sized fraction |
|--------|-------------------------------|----------------|----------------------|--------------------|--------------------|---------------------|
| Soil H | Control | 2.2 b | 5.9 b | 6.4 b | 16.4 b | 0.1 b |
| | DCB | 0.0 (-2.2) c | 0.0 (-5.9) c | 1.2 (-5.2) c | 0.7 (-15.7) c | 0.0 (-0.1) b |
| | H ₂ O ₂ | 95.1 (+92.9) a | 95.3 (+89.4) a | 91.0 (+84.6) a | 81.3 (+64.9) a | 9.5 (+9.4) a |
| Soil W | Control | 0.6 b | 0.1 a | 1.0 b | 0.7 b | 0.2 b |
| | DCB | 0.0 (-0.6) b | 0.0 (-0.1) a | 0.0 (-1.0) b | 0.0 (-0.7) b | 0.0 (-0.2) b |
| | H ₂ O ₂ | 2.0 (+1.4) a | 0.6 (+0.5) a | 5.8 (+4.8) a | 5.9 (+5.2) a | 1.6 (+1.4) a |

Values in the parenthesis indicated the changes compared to desorption of control. Different letters in the same column indicated significant difference between different treatments at $p < 0.05$.

Table 4 Cu²⁺ retention capacities of bulk soil and size fractions (mg/kg)

| Soil | Treatment | Bulk soil | Coarse sand fraction | Fine sand fraction | Silt sand fraction | Clay-sized fraction |
|--------|-------------------------------|--------------|----------------------|--------------------|--------------------|---------------------|
| Soil H | Control | 792 a | 741 a | 730 a | 602 a | 815 a |
| | DCB | 786 (99.2) a | 469 (63.3) b | 725 (99.4) a | 494 (82.1) b | 691 (84.8) b |
| | H ₂ O ₂ | 5 (0.6) b | 5 (0.6) c | 8 (1.1) b | 22 (3.7) c | 626 (76.8) c |
| Soil W | Control | 816 a | 829 a | 811 a | 816 a | 830 a |
| | DCB | 455 (55.8) c | 581 (70.1) c | 363 (44.7) c | 192 (23.5) c | 421 (50.7) c |
| | H ₂ O ₂ | 777 (95.2) b | 808 (97.5) b | 654 (80.7) b | 677 (82.9) b | 784 (94.5) b |

Values in the parenthesis indicated the Cu²⁺ retention capacity to untreated (%). Different letters in the same column indicate significant difference at $p < 0.05$.

ticularly for Soil H, the Cu^{2+} sorption capacity decreased dramatically with H_2O_2 treatment for size fractions except clay-sized fraction. Desorption rates of size fractions were affected little by DCB treatment for both soils, however, it was increased much for Soil H and little for Soil W under H_2O_2 -treatment. Simultaneously treatments of DCB and H_2O_2 decreased the Cu^{2+} retention capacity for all size fractions. These findings supported again the dominance of the coarse sand fraction in sorption of metals and the preference of absorbed metals bound to SOM in differently stabilized status. Thus, enrichment and turnover of SOM in paddy soils may have great effects on metal retention and chemical mobility.

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