

Adsorption–Desorption Behavior of Copper at Contaminated Levels in Red Soils from China

S. Yu, Z. L. He,* C. Y. Huang, G. C. Chen, and D. V. Calvert

ABSTRACT

Adsorption–desorption of copper (Cu^{2+}) at contaminated levels in two red soils was investigated. The red soil derived from the Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult) (REQ) adsorbed more Cu^{2+} than the red soil developed on the Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept) (RAR). The maximum adsorption values (M_A) that are obtained from the simple Langmuir model were 25.90 and 20.17 $\text{mmol Cu}^{2+} \text{ kg}^{-1}$ soil, respectively, for REQ and RAR. Adsorption of Cu^{2+} decreased soil pH, by 0.8 unit for the REQ soil and 0.6 unit for the RAR soil at the highest loadings. The number of protons released per Cu^{2+} adsorbed increased sigmoidally with increasing initial Cu^{2+} concentration for the RAR soil, but the relationship was almost linear for the REQ soil. The RAR soil released about 2.57 moles of proton per mole of Cu^{2+} adsorbed at the highest Cu^{2+} loading and the corresponding value for the REQ soil was 1.12. The distribution coefficient (K_d) decreased exponentially with increasing Cu^{2+} loading. Most of the adsorbed Cu^{2+} in the soils was readily desorbed in the NH_4Ac . After five successive extractions with 1 mol L^{-1} NH_4Ac (pH 5.0), 61 to 95% of the total adsorbed Cu^{2+} in the RAR soil was desorbed and the corresponding value for the REQ soil was 85 to 92%, indicating that the RAR soil had a greater affinity for Cu^{2+} than the REQ soil at low levels of adsorbed Cu^{2+} .

COPPER enters agricultural ecosystems through applications of Cu-containing fungicides, stable manures (e.g., pig slurry), and liquid or solid wastes from Cu-related mining and manufacturing. Worldwide, approximately 70 000 Mg of Cu as Bordeaux mixture [a Cu-containing fungicide: $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$] is annually sprayed on fruit orchards and other crops (Baker, 1990). The accumulated Cu concentrations in agricultural soils have reached 110 to 1500 mg kg^{-1} , compared with 20 to 30 mg kg^{-1} background levels (Baker, 1990). Copper concentrations have reached contaminating levels in soils from old vineyards in France (Delas, 1963, cited by Mocquot et al., 1996) and old citrus groves in the USA (Reuther and Smith, 1953).

Red soils are a type of highly weathered variable-charge soil with a low pH value. They are widely distributed in southern China and other subtropical regions and contain great amounts of Fe and Al oxides and kaolinite. However, these soils have a relatively low affinity and low adsorption capacity for Cu^{2+} , as compared with lateritic soils or Oxisols found in the tropical

regions, which have more crystalline Fe and Al oxides and kaolinite. In addition, the adsorbed Cu^{2+} in the red soils is more readily released, probably due to low organic matter (Yu, 1981; Wu, 1989). In recent years, Cu contamination to soils has become an increasing concern in China due to rapid development of Cu-related industries such as mines and smelters. Copper toxicity to rice (*Oryza sativa* L.) plants and other crops has been reported to occur around the mining sites and smelters in the red soil regions.

Copper, like other microelements, is essential to plants, animals, and microorganisms, but is toxic when its concentration exceeds a certain critical level (Baker, 1990). Total Cu concentration in soil solution is normally low (0.01–0.6 $\mu\text{mol L}^{-1}$), due to copper's high affinity to organic and inorganic soil colloids. Soluble copper at concentrations > 1.5 to 4.5 $\mu\text{mol L}^{-1}$ causes damage and even death to roots of growing plants (Baker, 1990). A significant decrease in root and leaf biomass of young maize (*Zea mays* L.) was observed at 10 $\mu\text{mol Cu}^{2+} \text{ L}^{-1}$ in solution culture (Mocquot et al., 1996). To control heavy metal contamination to soil and food, the USEPA and the European Union have established maximum heavy metal limits for soil and for industry by-products such as biosolids and composts to be applied to fields. The current soil cleanup criteria for Cu in the USA is 600 mg kg^{-1} (USEPA, 1999), and the upper limit of total soil Cu set by the European Union for receiving Cu-containing sewage sludge is 140 mg kg^{-1} (Department of Environment, The Ministry of Agriculture, Fisheries and Food, 1993).

There are two types of minerals that are involved in the adsorption–desorption of Cu^{2+} in soils: permanent charge and variable charge. Permanent-charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of the minerals. Variable-charge minerals such as Fe, Mn, and Al oxides carry charges varying from negative to positive, depending on pH. Adsorption and desorption of Cu^{2+} in soil are affected by the proportion of these two types of minerals. Moreover, the Fe, Al, and Mn oxides have a relatively strong affinity (pH dependent) for Cu^{2+} and other heavy metal cations and the adsorption of Cu^{2+} on these oxides is considered to be inner-sphere complex through a chemisorption process (Bertsch and Seaman, 1999). Therefore, adsorption of Cu^{2+} in the variable-charge soils is generally pH dependent (Atanassova, 1995; Atanassova and Okazaki, 1997; McBride, 1981; Wang et al., 1995). On the other hand, soil organic

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Abbreviations: C, equilibrium concentration of dissolved ion; K_d , distribution coefficient; M_A , maximum adsorption level; q, adsorbed concentration; RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

matter has a strong affinity for Cu^{2+} at low levels of Cu^{2+} (Buffle, 1988). Recently, Alcacio et al. (2001) provided spectroscopic evidence for the hypothesis proposed by McBride (1994) for possible binding configurations of Cu^{2+} on complexes of oxide minerals and organic matter: (i) Cu^{2+} is bonded to the mineral surfaces only (inner-sphere complex); (ii) Cu^{2+} is bonded to the organic matter that is adsorbed by the oxides at high levels (Type B ternary complex); and (iii) Cu^{2+} acts as a bridge cation between the oxides and the organic matter that is adsorbed at low levels (Type A ternary complex). Therefore, Fe, Al, and Mn oxides and organic matter are considered to play a very important role in the adsorption–desorption of Cu^{2+} in the variable-charge soils.

For most agricultural soils, bioavailability of Cu^{2+} is controlled by adsorption–desorption process (Xie, 1996). Remediation of Cu-contaminated soils requires an understanding of Cu^{2+} adsorption–desorption behavior and the major factors. Adsorption of Cu^{2+} in soils is often coupled with proton release (Padmanabham, 1983; Wang et al., 1995; Wu, 1989; Wu and Chen, 1983). A significant drop of solution pH has been reported to accompany Cu^{2+} adsorption, H^+ being replaced by Cu^{2+} (Aoyama et al., 1993; Aoyama and Itaya, 1995; Speir et al., 1999). Soil components vary greatly in their adsorption capacity for Cu^{2+} . Adsorption capacity decreases in the order: organic matter > Fe, Al, and Mn oxides >>> clay minerals (Adediran and Kramer, 1987, cited by Baker, 1990).

Adsorption of Cu^{2+} on soil and soil components can be described by a linear (McLaren et al., 1990), a Langmuir, or a Freundlich adsorption model (Wu, 1989; Atanassova, 1995; Atanassova and Okazaki, 1997). Although there are some different opinions regarding the use of Freundlich and Langmuir models for interpreting the adsorption of metal cations in soils (Sparks, 1995), some parameters from these models, such as maximum adsorption (M_A) and the distribution coefficient ($K_d = q/C$, where q is the amount of the adsorbed Cu^{2+} and C is the equilibrium Cu^{2+} concentration in solution), are useful in characterizing Cu^{2+} adsorption in soils (Atanassova, 1995; Wang et al., 1995; Basta and Tabatabai, 1992). However, most of the previous studies were conducted on other types of soils or pure oxide minerals using low concentrations of Cu^{2+} or a single rate of Cu^{2+} , and the obtained information may not be transferable to variable-charge soils, particularly those at high levels of Cu contamination.

A number of extractants including 0.1 mol HCl L^{-1} , 0.01 mol CaCl_2 L^{-1} (Sauve et al., 1997), Mehlich 3 reagent (Mehlich, 1984; Grazebisz et al., 1997), 1 mol NH_4Ac L^{-1} (pH 4.8) (Sakal et al., 1984; Brun et al., 2001), DTPA (Bertoni et al., 2000; Brun et al., 2001), and EDTA (Schramel et al., 2000; Brun et al., 2001) have been proposed for use in estimating the relationships between plant uptake of Cu and the extractable amount of soil Cu. Among frequently used extractants, 1 mol NH_4Ac L^{-1} is most widely used for measuring soil Cu availability due to its extractable Cu being closely correlated with plant uptake of Cu. However, 0.01 mol CaCl_2

L^{-1} is often employed for characterizing desorption of Cu^{2+} in soils (McLaren and Crawford, 1974; Cavallaro and McBride, 1984; Atanassova, 1995). Information is lacking on the relationship between the bioavailability of Cu to plants and the adsorption–desorption characteristics of Cu^{2+} in soils.

The overall objective of this study is to quantify Cu^{2+} adsorption–desorption behavior and soil pH change in two acidic soils at contaminated levels of Cu^{2+} . Adsorption isotherms were measured and modeled at relatively high Cu concentrations. Proton release and pH changes during Cu^{2+} adsorption were determined to understand adsorption–desorption mechanisms, including H^+ – Cu^{2+} exchange stoichiometry. A 1 mol NH_4Ac L^{-1} (pH 5.0) solution was used to extract a portion of the adsorbed Cu in an attempt to evaluate the relationship between the potential Cu^{2+} availability and the adsorbed Cu.

MATERIALS AND METHODS

Soils

Two red acidic soils were used in this study: the RAR soil (clayey, mixed siliceous thermic typic Dystrochrept), derived from Arenaceous rock, and the REQ soil (clayey, kaolinitic thermic plinthite Aquult), developed on Quaternary red earths. Soil samples were collected at 0 to 20 cm from Longyou County (119°02'~120°20' E, 28°44'~29°17' N), Zhejiang Province, southeastern China. Composite samples of the soils were air-dried, ground, and passed through a 60-mesh sieve prior to use. Some basic physicochemical properties of the soils are given in Table 1. Based on X-ray diffraction analysis of powder samples, the dominant clay minerals in both soils were kaolinite, iron and aluminum oxides, and quartz. However, the RAR soil contained also small amounts of chlorite and illite. Both soils contained considerable amounts of crystalline and non-crystalline Fe and Al oxides (Table 1). The RAR soil had significantly greater amounts of exchangeable H^+ and Al^{3+} , consistent with its lower pH, but the REQ soil had a greater cation exchange capacity (CEC) (Table 1).

Soil pH was measured using a pH meter (Mettler Toledo [Columbus, OH] MP120) at a soil to solution ratio of 1:2.5 in both deionized water and 1 mol KCl L^{-1} . Soil organic carbon was determined by the modified Tinsley method (Tinsley, 1950). Total exchangeable acidity and exchangeable Al^{3+} and H^+ were determined by the 1 mol KCl L^{-1} extraction–titration method (Liu et al., 1996). Particle size distribution was measured by the hydrometer method (Liu et al., 1996). The CEC and exchangeable bases were determined using 1 mol NH_4Cl L^{-1} (pH 7.0) following the procedure described by Lu (2000). Exchangeable Cu was extracted by 0.1 mol HCl L^{-1} at a soil to solution ratio of 1:5 (Lu, 2000) and total Cu in the soil sample was determined by HF– HClO_4 digestion method (Tessier et al., 1979). The concentrations of Cu in the extract or digest were measured using atomic absorption spectrometry (AAS) in an acetylene–air flame (Shimadzu [Kyoto, Japan] AA6800). Contents of free Fe and Al oxides in the soils were measured by the citrate–bicarbonate–dithionite method, and amorphous Fe and Al oxides by the ammonium oxalate method (pH 3.2) (Lu, 2000). The concentrations of Fe and Al in the extracts were simultaneously determined by the colorimetric method proposed by Xu and Chen (1980). The specific surface areas (internal, external, and total) were estimated by the method of Lu (2000), which involves measuring

glycerol adsorption on soil samples heated to 110°C (total surface area) or 600°C (external surface area).

Adsorption of Copper Ion and Proton Release

Portions of 2.0 g air-dried soil were placed into 100-mL polypropylene centrifuge tubes, and 50 mL of 0.01 mol NaNO₃ L⁻¹ (pH 5.0) solution containing 0, 15.75, 31.50, 78.74, 157.48, 314.96, 629.92, and 1259.84 μmol Cu²⁺ L⁻¹ (equal to 0, 25, 50, 125, 250, 500, 1000, and 2000 mg Cu²⁺ kg⁻¹soil) [as Cu(NO₃)₂] were added to each tube. The suspensions were shaken at 200 rpm for 2 h at 25°C and then equilibrated in a dark incubator for an additional 22 h. No pH control was imposed. At the end of the designated time, the suspensions were centrifuged at 2500 × g relative centrifugal force for 10 min and filtered through 0.45-μm filter paper (Fisherbrand, Pittsburgh, PA). Ten milliliters of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Cu²⁺ concentration using atomic absorption spectrometry. Total amounts of adsorbed Cu²⁺ (*q*) were calculated by the difference between the total applied Cu²⁺ and the soluble Cu²⁺ in the equilibrium solution.

The amounts of protons released during Cu²⁺ adsorption were quantified by titrating another 10 mL of the filtrate with standardized NaOH solution (0.004 mol NaOH L⁻¹, diluted from 0.02 mol NaOH L⁻¹ freshly prepared and standardized before use). The remaining solution was used for measuring pH.

Desorption of Adsorbed Copper Ion by 1 mol NH₄Ac L⁻¹ (pH 5.0)

The residue of Cu²⁺-enriched soil separated from the supernatant solution by centrifugation, from the above adsorption experiment, was rinsed several times with 95% ethanol (vortexing and shaking at 200 rpm for 15 min and centrifuging for 10 min at 2500 × g relative centrifugal force) to remove Cu²⁺ in the entrapped solution until no Cu²⁺ was detected. The

Table 1. Basic properties of the tested soils.†

Item	RAR soil	REQ soil
pH (H ₂ O)/(1 mol L ⁻¹ KCl)	4.86/3.96	5.39/4.33
Total organic carbon, g C kg ⁻¹	6.65	9.03
Exchangeable acidity, mmol H ⁺ kg ⁻¹		
Total	41.09	15.20
H ⁺	4.15	0.95
1/3 Al ³⁺	36.93	14.25
Cation exchange capacity _{pH7.0} , cmol kg ⁻¹	12.12	15.99
Exchangeable bases, mmol kg ⁻¹		
Total	77.31	120.04
1/2 Ca ²⁺	67.88	101.96
1/2 Mg ²⁺	6.79	15.44
K ⁺	2.64	2.64
Na ⁺	ND‡	ND‡
Background levels of Cu, mg kg ⁻¹		
Total Cu	28.56	85.51
Exchangeable Cu (0.1 mol L ⁻¹ HCl, 1:5)	1.83	32.34
Particulate components, g kg ⁻¹		
Clay (<0.002 mm)	421.0	483.4
Silt (>0.002 and <0.05 mm)	350.1	261.9
Sand (>0.05 mm)	228.8	254.7
Oxides of Fe and Al, g kg ⁻¹		
Free Fe oxide (Fe ₂ O ₃)	60.36	52.45
Free Al oxide (Al ₂ O ₃)	24.64	35.57
Amorphous Fe oxide (Fe ₂ O ₃)	0.99	1.47
Amorphous Al oxide (Al ₂ O ₃)	1.19	1.53
Specific surface area, m ² kg ⁻¹		
Internal	17 294	11 521
External	3 390	5 959
Total	20 684	17 480

† RAR soil = red soil developed on Arenaceous rock (clayey, mixed, siliceous thermic typic Dystrachrept), REQ soil = red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

‡ Not detected.

mass balance was performed for each tube and the lost weight was recorded. Fifty milliliters of 1 mol NH₄Ac L⁻¹ (pH 5.0) were added to each tube containing the Cu-enriched soil residue. The suspensions were shaken at 200 rpm for 2 h at 25°C and equilibrated for an additional 10 h. The equilibrated suspensions were then centrifuged at 2500 × g relative centrifugal force for 10 min and then filtered. Ten milliliters of the filtrate were pipetted into a 10-mL polypropylene centrifuge tube for measuring Cu²⁺ concentration. In order to estimate the affinity of Cu in soils, the desorption process was repeated five times (D1 to D5). The non-extractable fraction of the adsorbed Cu²⁺ in soils was obtained by the difference between the total adsorbed Cu²⁺ and the total recovered Cu²⁺ by five successive extractions with the NH₄Ac solution (pH 5.00 ± 0.02).

Statistical Analysis

All data were processed by Microsoft Excel (Microsoft, 2000), and the regression of linear and nonlinear and other statistical analyses were conducted using the programs of SAS Release 6.12 (SAS Institute, 1996).

RESULTS AND DISCUSSION

Adsorption Isotherms of Copper and its Effect on Soil pH and Proton Release

Adsorption of Cu²⁺ increased steeply with Cu²⁺ concentration in the equilibrium solution at the low concentration range (0–10 mg L⁻¹), then the slope of the isotherm decreased at equilibrium Cu²⁺ concentrations > 10 mg L⁻¹ (Fig. 1 and Table 2), possibly because Cu²⁺ adsorption in soils involves multiple adsorbing sites (McBride, 1995; Alcacio et al., 2001). The REQ soil adsorbed more Cu²⁺ than the RAR soil at the same Cu²⁺ equilibrium concentrations. At the highest level of added Cu²⁺ (2000 mg Cu²⁺ kg⁻¹ soil), the RAR soil adsorbed approximately 50% of the applied Cu²⁺ and the REQ soil adsorbed more than 68% of the applied Cu²⁺ (Table 2), suggesting that the REQ soil might not reach its maximum adsorption even at the designed highest Cu²⁺ loading. The difference in Cu²⁺ adsorption between the two soils may be attributed to the higher concentrations of organic matter (approximately 50% higher), clay, and exchangeable bases, and higher CEC

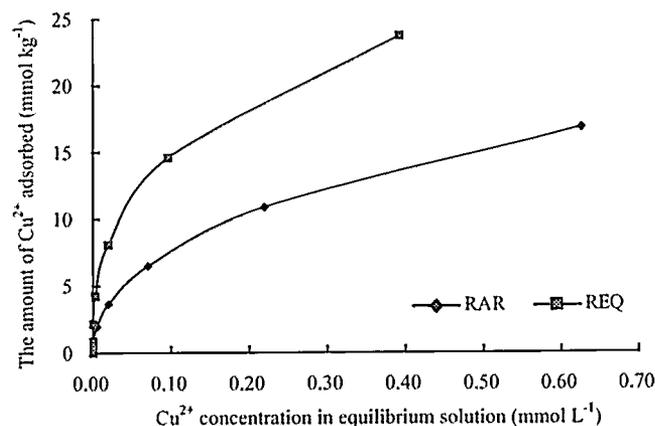


Fig. 1. Isotherms of Cu²⁺ adsorption in the two red soils. RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrachrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

Table 2. Characteristics of Cu²⁺ adsorption and desorption with 1 mol NH₄Ac L⁻¹ (pH 5.0) in two red acidic soils.†

Cu ²⁺ added mg kg ⁻¹ soil	Cu ²⁺ adsorbed‡	Cu ²⁺ desorbed with 1 mol NH ₄ Ac L ⁻¹ (pH 5.0)	
		Total§	First extraction¶
RAR soil			
25	100	61.00	82.91
50	99.69	73.05	83.46
125	93.34	87.94	84.56
250	87.08	89.98	86.15
500	77.55	90.96	87.57
1000	65.05	94.55	89.18
2000	50.27	93.47	90.88
REQ soil			
25	100	85.42	75.56
50	100	86.58	75.64
125	100	89.05	78.26
250	98.00	89.14	79.60
500	93.78	91.18	81.64
1000	84.65	92.41	83.88
2000	68.80	92.49	86.00

† RAR soil = red soil developed on Arenaceous rock (clayey, mixed, siliceous thermic typic Dystrochrept), REQ soil = red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).
 ‡ Percentage of the adsorbed Cu²⁺ in the total applied Cu²⁺.
 § Percentage of the desorbed Cu²⁺ by five successive extractions in the total adsorbed Cu²⁺.
 ¶ Percentage of the desorbed Cu²⁺ by the first extraction in the total desorbed Cu²⁺.

and soil pH of the REQ soil, as compared with the RAR soil (Table 1). These results were in agreement with previous reports (Padmanabham, 1983; Wu, 1989; Atanassova, 1995; Wang et al., 1995; Atanassova and Okazaki, 1997).

Copper adsorption in both soils was well described by the Freundlich ($q = k_f C^b$) and Langmuir ($q = k_L M_A C / (1 + k_L C)$) adsorption models. The correlation coefficients (r^2) were 0.98 for the RAR soil and 0.96 for the REQ soil with the Langmuir model, but were 0.99 for both soils with the Freundlich model. The Freundlich model gave a better fit with the adsorption data than the Langmuir model. This result was consistent with the conclusion of Barrow (1987) that in variable-charge soils the Freundlich model better describes the adsorption behavior of heavy metals than the Langmuir model. The physical meaning of k_f and b parameters from the Freundlich and k_L from the Langmuir equation is not well defined. However, the monolayer maximum adsorption (M_A) from the Langmuir equation seems useful for comparing potential adsorption capacity of different soils and soil components (Sparke, 1995). The M_A value (mmol Cu²⁺ kg⁻¹ soil) was 25.90 for the REQ and 20.17 for the RAR soil. The difference in M_A values is consistent with the difference in Cu²⁺ adsorption between the two soils.

Adsorption of Cu²⁺ significantly decreased soil pH (Fig. 2). Greater decrease in pH was observed in the RAR soil than the REQ soil at low to medium adsorbed Cu²⁺ levels (<10.9 mmol Cu kg⁻¹), but the reverse was true at high levels of adsorbed Cu²⁺ (Fig. 2). This indicates that different mechanisms may be involved in Cu²⁺ adsorption at different levels of Cu²⁺ loading and between the two soils. The maximum decrease in pH was about 0.8 unit in the REQ soil and 0.6 unit in the RAR soil. The decrease in soil pH (Δ pH) was linearly related

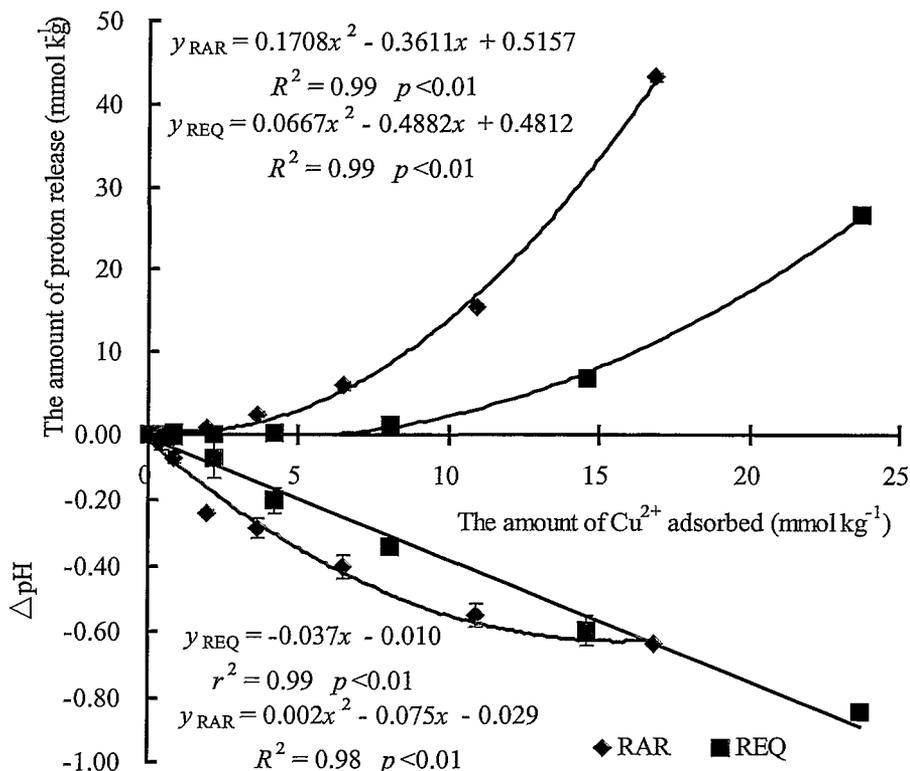


Fig. 2. The pH changes and proton release in relation to Cu²⁺ adsorption in the two red soils. RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

with the amounts of Cu^{2+} adsorbed for the REQ soil ($r^2 = 0.99$, $P < 0.01$), but this relationship was curvilinear for the RAR soil ($R^2 = 0.98$, $P < 0.01$) (Fig. 2). At high levels of adsorbed Cu^{2+} , pH decrease became less in the RAR soil, probably because of approaching maximum adsorption and limited availability of H^+ (Table 2). The pH-Cu adsorption relationship from this study is consistent with previous findings by Atanassova and Okazaki (1997) and Speir et al. (1999). However, the REQ soil did not seem to reach the maximum Cu^{2+} adsorption even at the highest levels of added Cu^{2+} ($2000 \text{ mg Cu}^{2+} \text{ kg}^{-1} \text{ soil}$) (Fig. 1 and Table 2). If higher amounts of Cu^{2+} had been applied, the same curvilinear response might have occurred in the REQ soil, too.

There was a quadratic relationship between proton release and Cu^{2+} adsorption (Fig. 2). Minimal amounts of protons were released at low Cu^{2+} adsorption ($< 8.08 \text{ mmol kg}^{-1}$ for the REQ soil and $1.95 \text{ mmol kg}^{-1}$ for the RAR soil), but the release of protons exponentially increased with increasing amount of Cu^{2+} adsorbed, especially in the RAR soil, which contained more exchangeable H^+ and Al^{3+} (Fig. 2). These results indicate that both cation exchange and inner-sphere surface complexation reactions might have been involved in Cu^{2+} adsorption and other exchangeable cations such as K^+ , Ca^{2+} , and Mg^{2+} were probably replaced by Cu^{2+} earlier than H^+ and Al^{3+} . It is interesting to note that the RAR soil that adsorbed less Cu^{2+} released more protons than the REQ soil for the same amount of Cu^{2+} adsorbed, especially at high Cu^{2+} adsorption saturation (Fig. 2). This could be attributed to the greater amounts of Fe oxides and exchangeable Al and lower pH in the RAR soil. As a result, the RAR soil has more hydroxylated surfaces, which are highly protonated at low pH (< 4.5) than the REQ soil. Therefore, more protons were released in the RAR soil because of more Cu^{2+} being specifically adsorbed onto positively charged sites (M-OH_2^+), as compared with the REQ soil. Basta and Tabatabai (1992) also inferred in their paper that at low heavy metal loadings, heavy metals might replace adsorbed Ca^{2+} and Mg^{2+} because they have less affinity to soil constituents than Al^{3+} . However, at higher heavy metal loadings, exchange reactions between heavy metals and Al^{3+} might happen, followed by hydrolysis of Al^{3+} and a decrease in solution pH, especially in soils that have significant amounts of exchangeable acidity and exchangeable Al^{3+} .

The number of protons released per Cu^{2+} adsorbed increased with increasing initial Cu^{2+} concentrations and more protons per Cu^{2+} adsorbed were released in the RAR soil than the REQ soil (Fig. 3). The relationship between H^+ to Cu^{2+} ratio and initial Cu^{2+} concentration was sigmoidal for the RAR soil, but was quadratic for the REQ soil (Fig. 3). At the highest Cu^{2+} level, the H^+ to Cu^{2+} ratio reached up to 2.57 for the RAR soil and 1.12 for the REQ soil. Basta and Tabatabai (1992) did not have the same observation for the two permanent-charge soils with four cropping systems in their study. They obtained an H^+ to Cu^{2+} ratio of < 1.0 from the slope of $\log_{10} K_d$ vs. pH of the equilibrium solution at the rate of $2000 \mu\text{M Cu}^{2+}$ (equal to 3175 mg

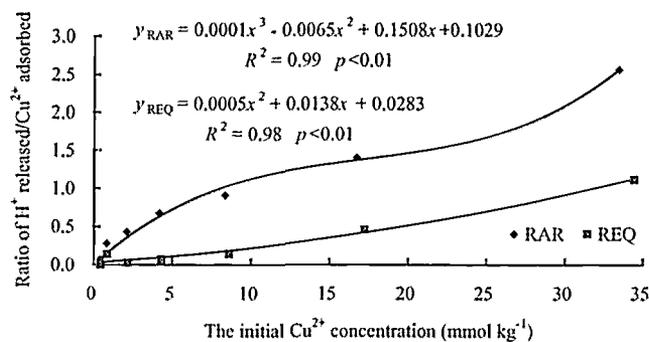


Fig. 3. Effect of initial Cu^{2+} concentration on proton release per Cu^{2+} adsorbed (H^+ to Cu^{2+} ratio) in the two red soils. RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typic Dystrachrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

$\text{Cu}^{2+} \text{ kg}^{-1} \text{ soil}$). Wang et al. (1995) obtained similar findings with the clay fraction from a red soil, the ratio close to 1.0 at $6270 \text{ mg Cu}^{2+} \text{ kg}^{-1} \text{ soil}$ clay. The difference in H^+ to Cu^{2+} ratio between the reported value by Wang et al. (1995) and our results may be caused by the difference between pure clay and whole soil and different calculation approaches used.

Theoretically, 1 mole of Cu^{2+} adsorbed can release 1 mole of protons if only a mono-dentate adsorption mechanism is involved, 2 moles of protons if a bidentate adsorption occurs on hydroxylated surfaces or through cation exchange reaction (one Cu^{2+} replacing two H^+) on exchange complex (Padmanabham, 1983), and three moles of protons if a concurrent reaction of Cu^{2+} hydrolysis and a bidentate adsorption of Cu^{2+} and/or hydroxyl Cu happens on the hydroxylated surfaces of oxides (Sumner, 1998). Adsorption of Cu^{2+} in the REQ soil agreed with the bidentate adsorption or cation exchange mechanism. However, in the RAR soil more than 2 moles of protons were released per mole of Cu^{2+} adsorbed at $2000 \text{ mg Cu}^{2+} \text{ kg}^{-1} \text{ soil}$ added. A number of factors might contribute to the increased proton release. First of all, copper ion can form a stable complex with more than two acidic functional groups of humus, such as $-\text{COO}^-$ (Stevenson and Fitch, 1981), especially at low pH (< 5.0) (Schnitzer and Khan, 1978). In those cases, one Cu^{2+} may replace more than two H^+ . However, in our case, since the RAR soil contains less organic matter than the REQ soil, the chelation of Cu^{2+} with soil organic matter may not explain more H^+ release per Cu^{2+} adsorbed in the RAR soil. Secondly, for many heavy metals such as Zn, their concurrent hydrolysis and a bidentate adsorption on oxides or hydroxides can release three H^+ into solution (Kinniburgh, 1983). Copper may undergo similar reactions. The RAR soil contained greater amounts of Fe and Al oxides and had lower pH, and consequently, more Cu^{2+} might be adsorbed onto surfaces of Fe and Al oxides through the above-stated mechanisms, thereby releasing more protons per Cu^{2+} adsorbed, as compared with the REQ soil at the highest level of Cu^{2+} added. In addition, hydrolysis of aluminum ions (mono or polymerized forms) after Cu^{2+} replaced them might provide additional protons. Molecular studies will be needed to identify the mechanisms of H^+ - Cu^{2+} exchange stoichiometry.

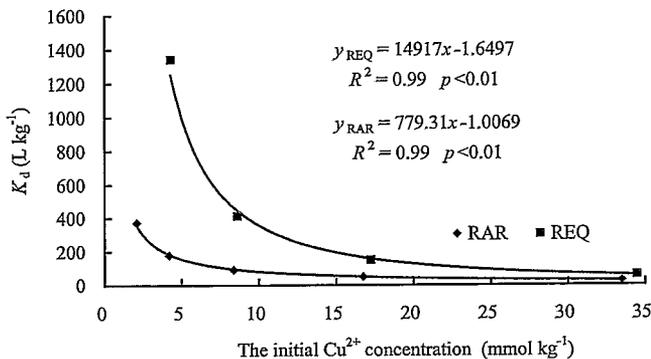


Fig. 4. Effect of initial Cu^{2+} concentration on Cu^{2+} distribution coefficient (K_d) in the two red soils. RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typical Dystrochrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

Distribution Coefficient of Copper

The distribution coefficient (K_d) is defined as the ratio of adsorbed Cu^{2+} to dissolved Cu^{2+} . This parameter reflects the overall copper-surface affinity (Atanassova, 1995; Wang et al., 1995). The REQ soil had slightly higher K_d than the RAR soil (Fig. 4). The K_d values at very low levels of added Cu^{2+} ($< 125 \text{ mg Cu}^{2+} \text{ kg}^{-1}$ soil) were not measured because the added Cu^{2+} was almost completely adsorbed (Table 2) and Cu^{2+} concentrations in the equilibrium solution were below detection limits. The K_d values decreased exponentially with increasing initial Cu^{2+} concentrations in both soils (Fig. 4). This can be attributed to the high affinity of Cu^{2+} for those highly selective sites (specific adsorption) at low Cu^{2+} concentrations, followed by adsorption of Cu onto those less-selective sites at high Cu^{2+} loadings (nonspecific adsorption) (Basta and Tabatabai, 1992). Lehmann and Harter (1984) reported that Cu^{2+} was mainly adsorbed onto low binding energy sites at Cu^{2+} rates exceeding $100 \text{ mg Cu kg}^{-1}$ soil in a comparable soil. These sites can adsorb Cu^{2+} through electrostatic forces or by forming Type A or Type B ternary surface complexes (Alcacio et al., 2001). In this study, added Cu^{2+} levels (0, 25, 50, 125, 250, 500, 1000, or 2000 $\text{mg Cu}^{2+} \text{ kg}^{-1}$ soil) were

mostly above this level and therefore, adsorption of Cu^{2+} in the two red soils was mainly involved with the low binding energy adsorbing sites. The REQ soil had a greater concentration of organic matter, larger external surface, and higher pH and CEC (Table 1), and thus adsorbed more Cu^{2+} than the RAR soil.

Desorption of Adsorbed Copper

In this study, $1 \text{ mol L}^{-1} \text{NH}_4\text{Ac}$ (pH 5.0) was used for desorption of the adsorbed Cu^{2+} in the two soils based on the assumption that the amount of Cu desorbed in the NH_4Ac may be more closely related to Cu uptake of plants than in the CaCl_2 solution (Sakal et al., 1984). In addition, the acetate anion has the $-\text{COO}^-$ functional group, which has a strong affinity for Cu^{2+} (Stevenson and Fitch, 1981). This functional group can form soluble organic- Cu^{2+} complexes to enhance desorption of adsorbed Cu^{2+} in soils with low organic matter contents and prevent re-adsorption of released Cu^{2+} (Schramel et al., 2000).

Most of the adsorbed Cu^{2+} in the soils was readily desorbed by the NH_4Ac . After five successive extractions, 61 to 95% of the total adsorbed Cu^{2+} in the RAR soil was desorbed. The corresponding values for the REQ soil were 85 to 92% of the total adsorbed Cu^{2+} (Fig. 5 and Table 2). From 8 to 39% of the adsorbed Cu^{2+} in both soils was not recovered by the NH_4Ac extraction. The proportion of the adsorbed Cu^{2+} that was not desorbed (as percent residual Cu^{2+}) increased with decreasing concentration of adsorbed Cu^{2+} (Fig. 5), implying that a portion of the Cu^{2+} was adsorbed with a high binding energy, and may not be available to plants. The proportion of the tightly bonded Cu^{2+} was significantly higher in the RAR soil than in the REQ soil at low Cu^{2+} loadings. At application rates $\leq 125 \text{ mg Cu}^{2+} \text{ kg}^{-1}$ soil, the residual fraction accounted for 12 to 39% and 11 to 15% of adsorbed Cu^{2+} , respectively, in the RAR and the REQ soil. At application rates $> 125 \text{ mg Cu}^{2+} \text{ kg}^{-1}$ soil, neither the RAR nor the REQ soil could retain more than 10% of the adsorbed Cu^{2+} after five successive extractions with 1 mol

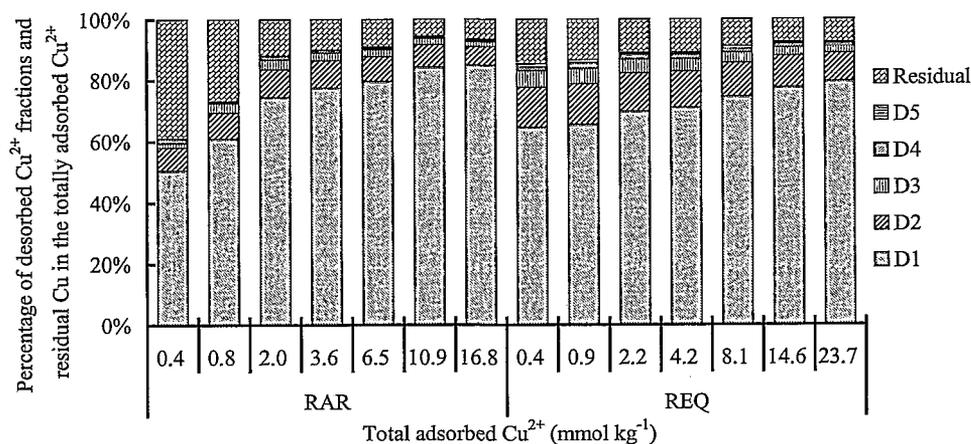


Fig. 5. Fractions of five successive extractions and residual Cu^{2+} in the total adsorbed Cu^{2+} . The terms D1 to D5 represent the fraction of desorbed Cu^{2+} from each of the five successive extractions and the residual Cu^{2+} represents the fraction of adsorbed Cu^{2+} that is not recovered by the five successive extractions with $1 \text{ mol L}^{-1} \text{NH}_4\text{Ac}$ (pH 5.0). RAR, red soil developed on Arenaceous rock (clayey, mixed siliceous thermic typical Dystrochrept); REQ, red soil developed on Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult).

$\text{NH}_4\text{Ac L}^{-1}$ (pH 5.0) (Table 2). These findings agreed with the results of Lehmann and Harter (1984) that Cu^{2+} was adsorbed onto high binding energy sites only at the added Cu^{2+} levels < 100 or $125 \text{ mg Cu}^{2+} \text{ kg}^{-1}$ soil.

CONCLUSIONS

Adsorption of Cu^{2+} near the native pH in two acidic soils dominated by oxide minerals was well described by both the Freundlich and the Langmuir models with correlation coefficients ranging from 0.96 to 0.99 ($P < 0.01$). Behavior of Cu^{2+} adsorption-desorption was related to soil properties. Under acidic conditions (pH 4 to 5.5), the RAR soil, which contains greater amounts of exchangeable Al and Fe oxides and has a lower pH, had a lower adsorption capacity but a higher affinity for Cu^{2+} than the REQ soil. Adsorption of Cu^{2+} resulted in significant decrease in pH. The pH decrease caused by Cu^{2+} adsorption was more apparent in the RAR soil than in the REQ soil at low to medium adsorption saturation. The reverse was true at higher levels of added Cu^{2+} . More protons per Cu^{2+} adsorbed were released in the RAR soil than the REQ soil. The RAR soil released 2.57 moles of protons for adsorption of 1 mole of Cu^{2+} , as compared with 1.12 in the REQ soil at the highest level of Cu^{2+} loading. The 1 mol L^{-1} NH_4Ac (pH 5.0) could release 61 to 95% and 85 to 92% of adsorbed Cu^{2+} from the RAR soil and the REQ soil, respectively. At low levels of adsorbed Cu^{2+} ($\leq 125 \text{ mg Cu}^{2+} \text{ kg}^{-1}$ soil), the RAR soil could retain more adsorbed Cu^{2+} than the REQ soil, which were not desorbed by five successive extractions with $1 \text{ mol NH}_4\text{Ac L}^{-1}$.

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