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## Effect of *o*-phenylenediamine on Cu adsorption and desorption in red soil and its uptake by paddy rice (*Oryza sativa*)

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### Abstract

A study was carried out of Cu adsorption and desorption processes in red soil as affected by *o*-phenylenediamine (*o*-PD) in the range 0–80 mg/l. The results indicated that the presence of *o*-PD enhanced Cu adsorption in red soil in weakly acid media, meanwhile, desorption percentage of Cu from soil, extracted by 1.0 M MgCl<sub>2</sub>, also increased when Cu adsorption in soil occurred in the presence of *o*-PD. The response of paddy rice to Cu in red soil shows that Cu toxicity was mitigated in the presence of *o*-PD and that the Cu concentration in rice straw decreased with increasing concentration of *o*-PD from 0 to 4.0 mmol/kg in soil. The fractions of background Cu in soil did not change noticeably in the presence of *o*-PD, whereas the effect of *o*-PD on the fractions of added Cu was significant. It was found that the exchangeable and carbonate bound Cu fractions decreased and the fraction of Cu bound to Fe–Mn oxides and organic matter increased with increasing *o*-PD concentration in soil when Cu was added at the same rate. Copper concentration in rice straw was significantly correlated with exchangeable Cu ( $r = 0.961$ ) and carbonate bound Cu ( $r = 0.959$ ) in soil. This result implicates that the behavior of Cu in soil is likely to be affected by organic pollutants containing amino groups.

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**Keywords:** Red soil; Cu; *o*-Phenylenediamine; Paddy rice; Interaction

### 1. Introduction

Aniline compounds often appear in industrial wastewaters, where they have a high potential toxicity to humans and other organisms; they are regarded as priority pollutants by the US Environmental Protection Agency and the Occupational Safety and Health Agency. As one of aniline compounds, *o*-phenylenediamine (*o*-PD) is widely used in pesticide and dye pro-

duction and it has been estimated that about 0.5 million tons of wastewater containing *o*-PD is produced in China each year (Sun, 1998).

Pollutants usually exist in the environment as multiple and actually or potentially interacting contaminants. Recently, much attention has been paid to the interaction of multiple pollutants although most studies have been limited to metal–metal interactions (Abdel-Sabour et al., 1988; Zheng and Chen, 1996) and organic–organic (Xing and Pignatello, 1998). Our current knowledge of the interactions between organic pollutants and metals in soil is poor (Michaud and Hoggard, 1988).

Heavy metal pollution in soil has justly been the focus of much past environmental research because of

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their high toxicities and their long-term and irreversible effects (Meima et al., 1999; Chen et al., 2000). More recently, the effects of organic acids on metal soil chemistry and metal availability to plants have been widely studied (Dramer et al., 1996; Kayser et al., 2000). Organic acids can significantly increase metal solubility in soil by forming water-soluble metal complexes (Elliot and Denny, 1982; Harter and Naidu, 1995; Schuman, 1995; Krishnamurti et al., 1997; Naidu and Harter, 1998; Florou et al., 2001). For example, it was found that lead (Blaylock et al., 1997; Huang et al., 1997; Wu et al., 1999), radiocesium (Dushenkov et al., 1999), copper (Morton et al., 2000) and nickel (Chen and Cutright, 2001) could be efficiently extracted from contaminated soil by plants in the presence of organic acids. As with organic acids, many organics including the functional groups  $-\text{NH}_2$ ,  $-\text{COOH}$  and  $-\text{OH}$  can also react with metal to form organometal complexes (Inskeep and Baham, 1983; Hass and Horowitz, 1986). Such reactions will strongly influence metal environmental behavior in soil.

This paper focuses on the interaction of *o*-PD and Cu in the soil–water–plant system. The effect of *o*-PD on Cu adsorption and desorption, plant uptake and fractions in soil were studied. It aims to explore the reaction mechanisms of *o*-PD and Cu in the environment and give some prospect of exploring the interactions between aniline compounds and metals.

## 2. Materials and methods

### 2.1. Experimental soil

A Red soil (Udic Ferrisol) was sampled from arable surface soil (0–20 cm) in Jinxian county, Jiangxi Province. The soil sample was air dried, passed through a 60 mesh screen, and stored in bottles for further use. The basic characteristics of this soil are listed in Table 1, which indicates the high concentrations of Fe and Al oxides and oxyhydroxides present in this soil, clearly identifying this as a variable charge soil.

### 2.2. Batch experimental method

One gram ( $1.000 \pm 0.002$  g) samples of red soil were weighed and put into 50 ml plastic centrifuge tubes, 5 ml

0.05 M  $\text{CaCl}_2$  was then added to each. A Cu concentration series, consisting of 0, 20, 40, 60, 80 and 100 mg/l in soil solution, was obtained by adding different volumes of 800 mg/l Cu stock solution, prepared with  $\text{CuCl}_2$ , and was made up to a total volume of 25 ml with deionized water. The effects of *o*-PD on Cu adsorption in soil were investigated by adding different volumes of 400 mg/l *o*-PD stock solution to the above adsorption solution prior to water supply and resulted in a series with concentrations of 0, 20, 40, and 80 mg/l. All soil suspensions were shaken for 2 h in a horizontal direction shaker. This soil suspensions were then centrifuged at 4000 r/min for 10 min and filtered through a 0.45  $\mu\text{m}$  filter membrane.

The procedures described above were used to examine the effect of pH on Cu adsorption. Firstly, 1.000 ( $\pm 0.002$ ) g of red soil were weighed and put into 50 ml plastic centrifuge tubes. Five milliliters of 25 mg/l Cu stock solution and 5.0 ml of 0.05 M  $\text{CaCl}_2$  were added. The pH of the soil solution was adjusted using 0.001 M HCl and NaOH and made up to a total volume of 25 ml with deionized water. The final concentration of  $\text{CaCl}_2$  was 0.01 M and the Cu concentration was 5.0 mg/l.

*o*-PD stock solution (400 mg/l) were added to the above Cu adsorption solution at rates of 0, 1.25 and 5.0 ml giving final *o*-PD concentrations of 0, 20 and 80 mg/l. These were used to investigate the effects of *o*-PD on Cu adsorption in soil at different pH values. All soil solutions were shaken for 2 h in a horizontal shaker and then centrifuged at 4000 r/min for 10 min. The centrifuged solution was filtered through a 0.45  $\mu\text{m}$  microporous filter membrane.

Copper desorption was assessed by adding 25 ml 1.0 M  $\text{MgCl}_2$  to the above centrifuged residues. The soil solution was then shaken for 2 h, following centrifugation. Copper concentrations and pH values in the resulting centrifuged solutions were determined by atomic absorption spectrometer (AAS) and pH meter, respectively.

### 2.3. Paddy rice response to Cu toxicity in the absence and presence of *o*-PD

Pot experiments were conducted with the 20 treatments and four replicates shown in Table 2; 200 g red soil was used in all pots, and Cu was added as  $\text{CuCl}_2$ . According to Table 2, different volumes of Cu (62.5 mM)

Table 1  
Characteristics of red soil

pH (1:2.5)	OM (g/kg)	CEC (mmol/kg)	$\text{Fe}_2\text{O}_3$ (%)	$\text{SiO}_2$ (%)	$\text{Al}_2\text{O}_3$ (%)	MnO (%)	Cu (mg/kg)
4.95	7.60	140.6	6.57	64.22	17.37	0.52	27.4

OM: organic matter, CEC: cation exchange capacity.

Table 2  
Treatment levels of Cu and *o*-PD for pot experiments

	Treatment no.																			
	s1	s2	s3	s4	s5	s6	s7	s8	s9	s10	s11	s12	s13	s14	s15	s16	s17	s18	s19	s20
Cu (mg/kg)	0	0	0	0	10	10	10	10	25	25	25	25	50	50	50	50	100	100	100	100
<i>o</i> -PD (mmol/kg)	0	1	2	4	0	1	2	4	0	1	2	4	0	1	2	4	0	1	2	4

*o*-PD: *o*-phenylenediamine.

and *o*-PD (160 mM) stock solution were mixed with soil thoroughly and equilibrated for one week prior to planting.

Rice seeds were immersed in cold water for 24 h, and then soaked in warm water of 40–45 °C for 5 min and then at 52 °C for 10 min. The seeds were then transferred on gauze in a tray and kept moist. When the seeds had grown to 3 cm in height, 10 similar sized plants were transferred to pots and cultivated for one month.

The paddy above ground was harvested using stainless scissors, weighed and then washed with deionized water. The plant was dried in a baking oven at 75 °C and then crushed to pass through a 100 mesh screen. Copper concentrations in the plant materials were determined as follows: Firstly, about 0.7 g plant samples were weighed and digested with 10 volumes conc. HNO<sub>3</sub> and 1 volume conc. HClO<sub>4</sub>. During the digestion, conc. HNO<sub>3</sub> was supplied once the solution was heated to dryness. The digestion was finished when no plant tissues remained in digestion tube. The digestion solution was then transferred into a flask, and made up to a fixed volume for further metal determination by AAS. One reference rice straw from Institute of Soil Science, Chinese Academy of Sciences was used to verify the accuracy of the metal determinations. The recovery rate for Cu was within 105 ± 2.42% (*n* = 6).

#### 2.4. Cu fractions in red soil

After the pot experiments were completed, the air dried soils were passed through a 60 mesh screen. Copper fractions in soil were analyzed by sequential extraction using procedures similar to those of Lakes (1984); 2.000 (±0.001) g soil was weighed and put in a 100 ml centrifuge tube, and then 20 ml of different extractant was added sequentially to extract Cu from soil.

Soils were firstly extracted using 0.5 M Mg(NO<sub>3</sub>)<sub>2</sub> (pH 7.0) and shaken continuously at 25 °C for 2 h, the resulting concentrations of heavy metals in the supernatant were determined and defined as water-soluble plus exchangeable (SE) fraction. Secondly, the residues were extracted with 0.5 M NaOAc–HOAc (pH 5.0) at 25 °C and shaken for 2 h, heavy metals in the supernatant were considered to be the weakly specifically adsorbed

fraction. Thirdly, sequential extraction with 0.175 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 85 °C and UV irradiation for 2 h gave the Fe and Mn oxide bound fraction. Finally, organic bound (ORG) fraction was obtained by extracting the resulting residues with 5 ml 30% H<sub>2</sub>O<sub>2</sub> and 3 ml of 0.02 M HNO<sub>3</sub> in hot water bath at 85 °C for 2 h. Heavy metals left in the soil and obtained by digestion with HCl–HNO<sub>3</sub>, were regarded as the residual fraction.

#### 2.5. Statistical analysis

The data were analyzed using Microsoft Excel software and Sigmapstat 3.0 (SPSS Science). One-way analysis of variance was carried out to compare the treatments at the same Cu loading rate in soil but with different *o*-PD concentration. Differences between individual means were tested using least significant difference tests at a 0.05 significance level.

### 3. Results and discussion

#### 3.1. Cu adsorption in red soil as affected by pH and *o*-PD

Fig. 1 shows the Cu adsorption isotherms in red soil in the absence and presence of *o*-PD. It can be observed

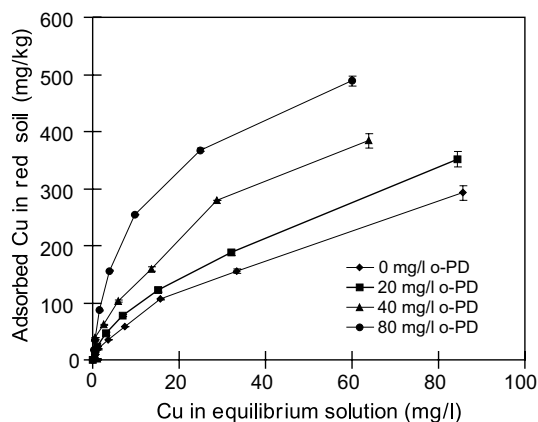


Fig. 1. Cu adsorption isotherms in red soil in the absence and presence of 20, 40 and 80 mg/l *o*-PD.

that the quantity of Cu adsorbed in soil increased with increasing Cu concentration in the equilibrium solution. The presence of *o*-PD enhanced Cu adsorption in soil, which suggests that Cu adsorption was directly affected by *o*-PD.

In contrast to this result from *o*-PD, many organic acids have been found to reduce metal adsorption in soil (Hass and Horowitz, 1986; Stadler and Schindler, 1993; Harter and Naidu, 1995). The reason is that organic acids complex with metal and form water-soluble organic complexes in the soil solution. So, increased Cu adsorption in soil with *o*-PD was postulated due to Cu–*o*-PD complex formed in the soil solution and that this complex was more readily adsorbed from soil solution than Cu itself (Diallo et al., 1999).

The effect of pH on Cu adsorption in red soil was studied and the results are presented in Fig. 2. The quantity of Cu adsorbed increased with increasing pH, and the adsorption percentage reached nearly 100% at pH > 6.0; this can be ascribed to the high negative surface charge of red soil appearing at high pH (Naidu et al., 1997). Further, the quantity of Cu adsorbed increased with increasing *o*-PD concentration in acid media.

According to the results from solution chemistry of Cu and *o*-PD using ion selective electrode, Cu reacted with *o*-PD and formed a Cu complex only when solution pH is greater than 5. This means that no Cu complex was formed in the soil solution at pH < 5.0. From this, increasing Cu adsorption in soil in the presence of *o*-PD may be attributed to the reaction of the *o*-PD, adsorbed onto the red soil, with Cu to form Cu complexes on soil surfaces through catalysis. In an earlier study, Davis and Leckie (1978) also examined similar Cu and glutamic acid complexes formed on soil surfaces.

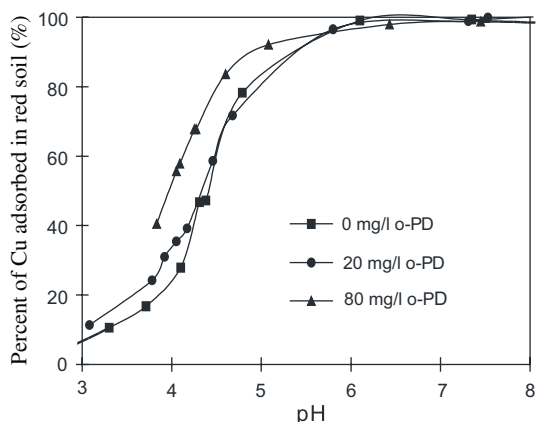


Fig. 2. Dependence of adsorption percentage of 5.0 mg/l Cu in red soil on pH in the absence and presence of 20 and 80 mg/l *o*-PD.

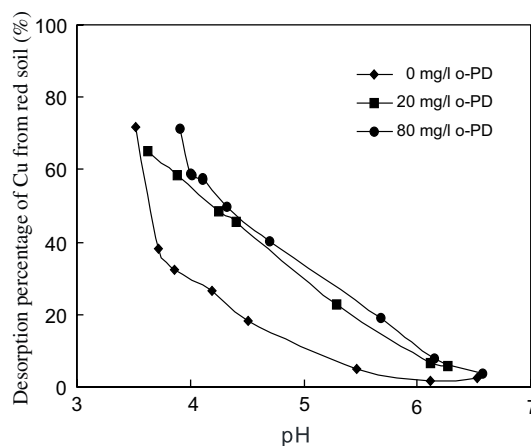


Fig. 3. Dependence of desorption percentage of Cu in red soil on pH when 5.0 mg/l Cu adsorption was performed in the absence and presence of 20 and 80 mg/l *o*-PD.

The dependence of Cu desorption from red soil on pH is shown in Fig. 3. The percentage of Cu desorption from red soil decreased with increasing pH. It is known that Cu was adsorbed in an ion exchangeable form and through specific adsorption in red soil at low and high pH values, respectively. The ion exchangeable form can be readily desorbed from soil with 1.0 M MgCl<sub>2</sub>, although the specifically adsorbed form is difficult to desorb. When Cu was adsorbed onto soil in the presence of *o*-PD, its desorption was increased compared with that in the absence of *o*-PD, which suggests that the complex of Cu and *o*-PD, formed under soil catalysis, was easily destroyed by high concentration of salt. Fabrega et al. (2001) studied the competitive adsorption of aromatic amines and metal cations on soil surface and also found that a model based on ion exchange could predict their amine adsorption in soil. Low pH favors adsorption of aromatic amines on soil surface.

However, there were no apparent differences in the percentage of Cu desorbed from red soil when Cu adsorption occurred in the presence of different concentrations of *o*-PD. This result suggests that Cu is adsorbed in soil mainly as Cu–*o*-PD complex in the presence of *o*-PD.

### 3.2. Paddy rice response to Cu in red soil

Fig. 4 shows the wet weight of the above ground parts of paddy rice plants with different treatments. When only Cu existed in red soil, the wet weight of paddy rice obviously decreased with increasing Cu concentration, indicating strong toxicity of Cu to paddy. When external Cu concentrations in soil were 10, 25, 50 and 100 mg/kg, the biomasses of paddy were 80%, 58%, 24% and 15%, respectively, of that for the control sl.

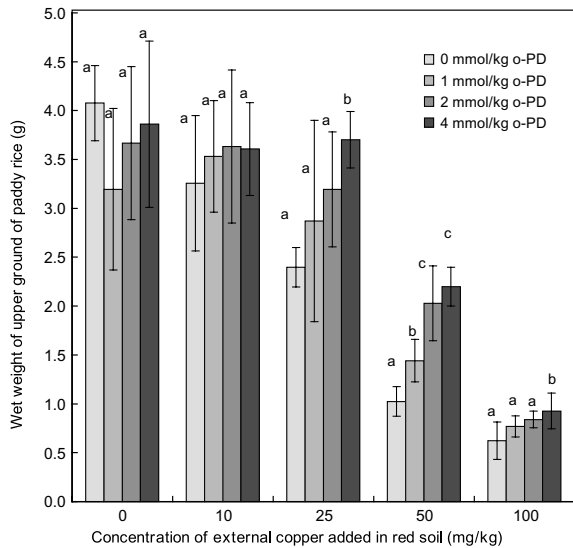


Fig. 4. Wet weight of above-ground parts of paddy rice with different treatments. Different letters at the same copper concentration but with different *o*-PD loading rate indicate a significant difference at  $p \leq 0.05$  according to the SPSS analysis.

In addition, it was found that the paddy rice appeared chlorotic, and root growth was retarded seriously with decreasing numbers of main and side roots. Some paddy rice plants exposed to the higher concentrations of Cu began to die after one-month's growth.

The presence of *o*-PD ameliorated metal toxicity to paddy rice and improved plant biomass, especially for the treatments with high Cu concentrations. When the external Cu concentration in the red soil was 50 mg/kg, the biomass of paddy rice increased by 40.7%, 98%, and 114.7% in the presence of 1.0, 2.0, and 4.0 mmol/kg *o*-PD, respectively, compared with that obtained in the absence of *o*-PD (s13). However, when the external Cu concentration in red soil was 100 mg/kg, only treatment s20 with the highest concentration of *o*-PD increased the biomass of the paddy rice plants significantly.

Chen and Cutright (2001) found that adding HEDTA and EDTA led to a severe yield reduction in the biomass across the treatments. The levels of HEDTA above 0.5 g/kg added or the metal-HEDTA compounds formed in soil were already high and therefore toxic to the plants, because organic acids and their metal complexes were less adsorbed in soil. In this study, *o*-PD reacted with Cu to form a complex in soils that decreased metal availability to paddy rice and lead to the maintenance of a satisfactory plant biomass.

Fig. 5 shows Cu concentration in the above ground parts of paddy rice under different treatments. It is clear that Cu concentration in paddy rice increased with increasing Cu loading rate in red soil. When *o*-PD and Cu

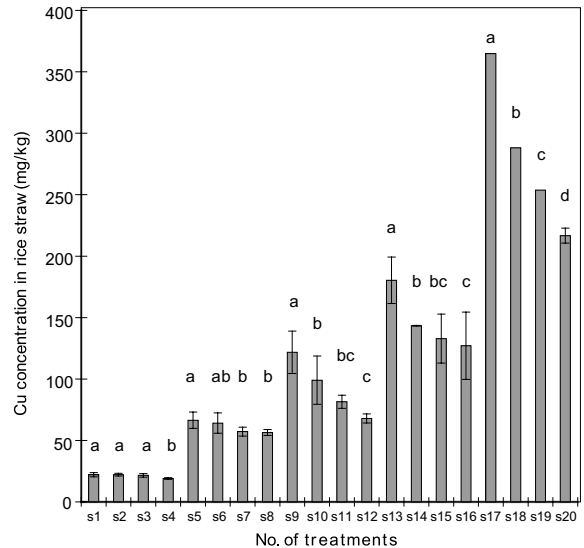


Fig. 5. Copper concentration in upper ground of paddy under different treatment. Different letters at the same copper concentration but with different *o*-PD loading rate indicate a significant difference at  $p \leq 0.05$ , according to the SPSS analysis.

were added in red soil simultaneously, Cu concentration in the paddy rice decreased with increasing *o*-PD loading rate. For example, when Cu was added to red soil at 50 mg/kg level and the *o*-PD concentration in red soil was 1.0, 2.0, and 4.0 mmol/kg, the concentration of Cu in paddy rice, compared with the control at 0 mmol/kg *o*-PD loading rate (s13), decreased 21.4%, 31.35% and 42.5%, respectively. In addition, when the external Cu concentration in red soil was 100 mg/kg, copper concentration in paddy rice for treatment s20 decreased 49.1% compared with the control s17. The decreased Cu uptake by the rice plant is consistent with increased Cu adsorption in soil in the presence of *o*-PD.

When Cu concentrations in the paddy rice plants was correlated with the external rate of Cu added to the red soil at the same *o*-PD concentration, the results are listed as follows:

$$0 \text{ mmol/kg } o\text{-PD: } C_{\text{Cu in paddy rice}} = 3.32C_{\text{external-Cu}} + 30.25 \quad R^2 = 0.991 \quad (1)$$

$$1.0 \text{ mmol/kg } o\text{-PD: } C_{\text{Cu in paddy rice}} = 2.56C_{\text{external-Cu}} + 28.13 \quad R^2 = 0.992 \quad (2)$$

$$2.0 \text{ mmol/kg } o\text{-PD: } C_{\text{Cu in paddy rice}} = 2.24C_{\text{external-Cu}} + 24.78 \quad R^2 = 0.991 \quad (3)$$

$$4.0 \text{ mmol/kg } o\text{-PD: } C_{\text{Cu in paddy rice}} = 2.56C_{\text{external-Cu}} + 23.42 \quad R^2 = 0.981 \quad (4)$$

It is clear that excellent correlations were obtained between Cu concentration in soil and its uptake by paddy rice plants.

### 3.3. Copper fractions in red soil in the absence and presence of *o*-PD

Table 3 shows the fractions of Cu in red soil after one-month's growth with paddy rice. The results clearly indicate that *o*-PD, added to soil, affected Cu fractions in red soil. When no external Cu was added to the soil, the SE Cu fractions increased with increasing *o*-PD concentration. Other Cu fractions did not change obviously. However, when external Cu was added to red soil, Cu fractions in soil were different. The SE and carbonate bound Cu fractions decreased with increasing *o*-PD spike rate in soil. In contrast to above two fractions, Fe and Mn oxide bound and organically bound fractions in soil increased with an increasing rate of *o*-PD addition. This result supports the conclusion that Cu and *o*-PD complex was formed on soil surfaces.

SE Cu was reasonably regarded as the fraction available for plant uptake. The decrease of SE Cu in the presence of *o*-PD reduced the availability of Cu to paddy rice correspondingly. Although many authors have recognised that metal uptake by plants is enhanced in the presence of organic acid because plants can efficiently uptake such metal complexes, Robinson et al. (1999) recently reported that in their study, neither calcium and

magnesium carbonates, nor the addition of synthetic chelating agents were effective in increasing metal uptake by *Berkheya coddii* (Family Compositae) on serpentine soils. It implied that metal uptake by plants was complex, strongly related with soil properties, metal and organic kinds as well as plant species.

## 4. Conclusions

Under soil catalysis, Cu complexed with *o*-PD on the colloid surfaces of the red soil although such complexes cannot be formed at same solution pH (<5.0) without soil. The desorption percentage of Cu, adsorbed in soil in the presence of *o*-PD, also increased compared with the control and this suggests that Cu is adsorbed in soil in the absence of *o*-PD mainly through specific adsorption, even in weakly acid media. The Cu–*o*-PD complex, formed through soil catalysis, was desorbed more readily than the specifically adsorbed form.

Paddy rice is susceptible to Cu toxicity in red soils. The presence of *o*-PD obviously modified Cu toxicity to paddy rice and to Cu fractions in red soil. The SE Cu and carbonate bound fractions decreased and the Fe and Mn oxide bound and organically bound Cu increased with increasing concentrations of added *o*-PD. Furthermore, plant Cu uptake decreased in the presence of *o*-PD and this is ascribed to decreasing SE Cu fractions in soil.

Table 3  
Concentration of different copper fractions in soil

Treatment no.	Cu spiked rate (mg/kg)	Exchangeable (mg/kg)	Carbonate bound (mg/kg)	Fe–Mn oxide bound (mg/kg)	ORG (mg/kg)
s1	0	0.91 ± 0.06 a	0.98 ± 0.13 a	7.90 ± 0.99 a	1.64 ± 0.13 a
s2	0	0.65 ± 0.06 b	1.06 ± 0.19 ab	7.21 ± 0.36 a	1.55 ± 0.09 a
s3	0	0.44 ± 0.08 c	1.17 ± 0.13 ab	7.18 ± 0.60 a	1.61 ± 0.10 a
s4	0	0.51 ± 0.06 d	0.8 ± 0.24 c	7.50 ± 0.31 a	1.63 ± 0.17 a
s5	10	1.88 ± 0.07 a	2.47 ± 0.14 a	12.33 ± 0.30 a	2.13 ± 0.07 a
s6	10	1.81 ± 0.2 a	2.39 ± 0.13 a	12.82 ± 0.72 ab	2.19 ± 0.36 a
s7	10	1.73 ± 0.15 a	2.17 ± 0.08 b	12.46 ± 0.20 ab	2.03 ± 0.10 a
s8	10	1.43 ± 0.15 b	2.06 ± 0.14 bc	13.24 ± 0.40 c	2.16 ± 0.36 a
s9	25	4.64 ± 0.19 a	5.42 ± 0.08 a	18.84 ± 0.98 a	2.83 ± 0.14 a
s10	25	4.42 ± 0.43 a	4.99 ± 0.47 b	18.38 ± 0.64 ab	2.64 ± 0.12 a
s11	25	3.76 ± 0.28 a	4.91 ± 0.28 b	19.55 ± 0.50 ab	3.08 ± 0.30 b
s12	25	3.71 ± 0.16 b	4.62 ± 0.07 b	20.12 ± 1.11 c	2.93 ± 0.13 b
s13	50	11.24 ± 0.14 ab	10.30 ± 0.05 a	27.57 ± 0.75 a	3.58 ± 0.08 a
s14	50	10.92 ± 0.09 b	10.19 ± 0.09 a	27.80 ± 0.60 ab	3.65 ± 0.21 a
s15	50	10.20 ± 0.22 c	9.81 ± 0.18 b	28.60 ± 0.73 bc	4.26 ± 0.19 b
s16	50	9.06 ± 0.37 c	9.33 ± 0.21 c	29.58 ± 0.52 c	4.59 ± 0.13 c
s17	100	30.35 ± 0.60 a	19.86 ± 0.22 a	40.78 ± 0.61 a	5.25 ± 0.18 a
s18	100	28.52 ± 0.49 b	19.59 ± 0.09 b	41.53 ± 0.33 a	5.25 ± 0.22 a
s19	100	26.86 ± 0.36 c	19.30 ± 0.25 b	41.58 ± 0.61 a	5.68 ± 0.26 b
s20	100	24.16 ± 0.26 d	17.76 ± 0.25 c	42.99 ± 1.11 b	6.57 ± 0.13 c

Different letters as a, b, c and d at the same Cu concentration but with different *o*-PD loading rate indicate a significant difference at  $p \leq 0.05$  according to the SPSS analysis.

The results of this study imply that metal behavior in the soil–water–plant system is likely to be modified by organic aniline compounds. It would be desirable to find or design similar new compounds, which are readily degraded in soil, to assist in future remediation of Cu contaminated soil.

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