

# Copper fertilizer effects on copper distribution and vertical transport in soils

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## Abstract

The fate of Cu fertilizer in soils is important for its plant availability and environmental significance. Little research has been done to investigate the status of Cu in soil under repeated application of Cu fertilizer. A field study was conducted to determine the distribution and transport of Cu in soil profiles after 17 years' applications of Cu fertilizer. Soil samples obtained at different application times and soil depths were analyzed for labile Cu by a diethylenetriaminepentaacetic acid (DTPA) extraction procedure. A modified sequential extraction technique was used to separate soil Cu into exchangeable (Exe), organic matter weakly bound (Wbo), carbonate bound (Carb), manganese oxides bound (MnOx), organic matter specifically bound (Sbo), and mineral bound (Min) fractions. The results showed that long-term application of Cu fertilizer caused the accumulation of Cu in the surface soil. The accumulation of soil Cu in the 0–15 cm and 0–60 cm soil layers accounted for 41.3% and 57.3% of the Cu applied over 17 years. Calculations indicated that little Cu was removed from the plots by crop harvest, which meant that about 40% of fertilizer Cu leached below the 60 cm soil depth. Additional evidence suggested that some Cu leached below 400 cm. Total labile Cu and the increase in labile Cu in the surface layer soil followed a linear relationship with the amount of Cu added and with the application time of the Cu fertilizer. Copper bound to minerals and weakly bound to organic matter accounted for 76% to 92% of the total Cu in soil. In addition, the two fractions had the same distribution trend in the soil profile. The Cu content of different fractions declined in a similar order, i.e. Min–Cu>Wbo–Cu>Exe–Cu>Sbo–Cu>Carb–Cu>MnOx–Cu, regardless of Cu treatment. Most Cu added to soil entered into Min, Exe, Wbo, and Carb fractions. The Exe–Cu, Wbo–Cu, and Carb–Cu fractions are readily mobile and can be used to predict Cu transport. The transport ability of Cu fractions followed the order of Wbo–Cu>Exe–Cu>Carb–Cu and increased with increasing soil depth. These results indicate that the accumulation of Cu in the soil resulting from the long-term application of Cu fertilizer could pose an environmental risk due to the downward mobility of Cu.

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## 1. Introduction

In the Loess Plateau of China, Cu deficiency often occurs in soils due to high carbonate content, high pH, and low total Cu content. Soil available Cu (DTPA extractable Cu) in the region varies from 0.01 mg kg<sup>-1</sup> to 4.2 mg kg<sup>-1</sup> with an average content of 0.93 mg kg<sup>-1</sup> (Yu et al., 1991). About 21% of the soils have available Cu lower than 0.5 mg kg<sup>-1</sup>, which is the critical level for the occurrence of crop nutrient deficiency in this area (Yu et al., 1991). In accordance with fertilizer recommendations, farmers have applied Cu fertilizer extensive-

ly during the past two decades and this has resulted in an increase in crop production.

However, repeated use of Cu fertilizer in agricultural production can lead to severe environmental problems. For example, studies have shown that repeated use of Cu-based chemicals in vineyards resulted in soil contamination in France (Flores-Veles et al., 1996), Australia (Pietrzak and McPhail, 2004), and India (Prasad et al., 1984). Additional studies reported Cu contamination of farmland in Sweden (Bengtsson et al., 2006), and the soil under citrus groves in the United States (Alva, 1993). Loss of Cu from agro-ecosystems may cause water contamination due to the release of accumulated Cu from sediment (Landing, 1992; Bengtsson et al., 2006), and influence human and animal health via the food chain. Therefore, understanding the effect of long-term Cu fertilizer applications

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is important not only for plant nutrition but also for environmental quality.

The fates of Cu in soils include adsorption–desorption, precipitation, complexation, and occlusion. These processes depend on factors such as the nature of mineral and organic constituents, the composition of soil solution, soil texture,  $\text{CaCO}_3$  content, and pH (Msaky and Calvert, 1990; Alva et al., 2000). On the other hand, Cu is present in different forms and associated with various soil components in different ways. These associations control Cu availability and mobility in soils (Kabata-Pendias and Pendias, 1992; Singh, 1997; Ahumada et al., 1999). Among Cu forms in soil, water soluble and exchangeable forms are considered readily available and mobile, while Cu incorporated into crystalline lattices of clays appears to be relatively immobile and unavailable. Other forms—precipitated as carbonate, occluded in Fe, Mn, and Al oxides, or complexed with organic matter—could be considered relatively active or firmly bound, depending upon the actual combination of physical and chemical properties of soil (Sposito et al., 1982; Shuman, 1985).

Sequential extraction technique provides knowledge about Cu affinity to soil components and the strength with which it is bound to the matrix (Narwal et al., 1999). This technique also gives information about both mobile and stable fractions of Cu in soil (Nyamangara, 1998). This is important for evaluating the actual and potential transport of Cu.

Many studies have been conducted to examine the long-term effects of sewage sludge application or wastewater irrigation on the fate of Cu in soils and plants (Nyamangara and Mzezewa, 1999; Mapanda et al., 2005; Rattan et al., 2005; Muchuweti et al., 2006), but little information is available on Cu fate in relation to repeated application of Cu fertilizer in upland soils, especially with respect to the vertical movement of Cu in the soil profile. This study was therefore conducted to (i) investigate the distribution of labile Cu and chemical fractions of Cu in soil profiles after 17 years' applications of Cu fertilizer on upland soil of the Loess Plateau and (ii) assess the mobility of added Cu within soil profiles.

## 2. Materials and methods

### 2.1. Experimental site and soil characterization

The experiment was initiated in September 1984 at Changwu County, Shaanxi Province, China ( $35^{\circ}12'N$ ,  $107^{\circ}40'E$ ), which is located in the southern part of the Loess Plateau, 1200 m above sea level. Based on climate data from 1984 to 2001, average annual temperature at the site is  $9.1^{\circ}\text{C}$  and average annual precipitation is 585 mm. The soil is Hei Lu soil, which corresponds to a Calcariid Regosol according to the FAO/UNESCO classification system (FAO/Unesco, 1988). The chemical properties of the surface soil (0–20 cm) at the beginning of the experiment are presented in Table 1.

### 2.2. Experiment design

A long-term Cu fertilization experiment was conducted on three replicate plots of 5.5 m by 4.0 m. The experiment included

Table 1

Soil properties (0–20 cm) of the experiment plots at the beginning of experiment

Property	Content (Mean $\pm$ S.D.)
Organic matter ( $\text{g kg}^{-1}$ )	10.5 $\pm$ 0.8
Total nitrogen ( $\text{g kg}^{-1}$ )	0.80 $\pm$ 0.13
Available nitrogen ( $\text{mg kg}^{-1}$ )	37.0 $\pm$ 0.9
Total phosphorus ( $\text{g kg}^{-1}$ )	0.66 $\pm$ 0.05
Olsen phosphorus ( $\text{mg kg}^{-1}$ )	3.0 $\pm$ 0.4
Available potassium ( $\text{mg kg}^{-1}$ )	129 $\pm$ 4.2
Calcium carbonate ( $\text{g kg}^{-1}$ )	108 $\pm$ 4.7
pH	8.1 $\pm$ 0.13
DTPA copper ( $\text{mg kg}^{-1}$ )	1.08 $\pm$ 0.14

a control and a Cu fertilization treatment. Each plot annually received  $60 \text{ kg hm}^{-2}$  nitrogen in the form of urea and  $60 \text{ kg hm}^{-1}$  phosphorus as super-phosphate. The Cu treatment also received annually  $15 \text{ kg hm}^{-2}$   $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (net Cu concentration was 25.5%). Plots were randomly arranged and winter wheat (*Triticum aestivum* L.) was planted. Winter wheat varieties were Qinmai #4 in 1984 and 1985, Changwu #131 from 1986 to 1995 and Changwu #134 from 1996 to 2001. Wheat was sown in mid-September and harvested at the end of June in the following year. Prior to seeding, nitrogen and phosphorous fertilizers were broadcast onto the plots and incorporated to a depth of  $\sim 15$  cm. Furrows ( $\sim 10$  cm deep) were made in the soil with a small, v-shaped plow and then wheat seeds and copper fertilizer were placed on the sides of the furrows. A roller was then pulled over the soil to cover the seeds and Cu fertilizer. Field crop management practices widely adopted in this area were used for the experiment.

An average of  $8100 \text{ kg hm}^{-2}$  of winter wheat biomass containing  $16.6 \text{ mg Cu kg}^{-1}$  was harvested and removed from the Cu fertilized plots annually. In the no Cu fertilizer treatment, the amount of biomass removed averaged  $8040 \text{ kg hm}^{-2}$  and its Cu concentration was  $5.5 \text{ mg kg}^{-1}$ . The winter wheat harvest would result in the annual removal of  $134.5 \text{ g Cu hm}^{-2}$  from the Cu fertilized and  $44.2 \text{ g Cu hm}^{-2}$  from no Cu fertilizer treatments.

### 2.3. Soil sampling

Surface soil (0–20 cm) was collected from each plot in 1984, 1987, 1990, 1991, 1992, 1993, 1995, 1996, and 2001 for the determination of labile Cu. Soil samples were also collected from 0–20, 20–50, 50–80 cm layers in September 1996, 0–400 cm layer at intervals of 20 cm in March 2001, and 0–15, 15–30, 30–45, 45–60, 60–80, 80–100 cm layers in September 2001. These samples, which were collected near the center of each plot, were used for the determination of labile Cu. Additional samples collected in September 2001 from 0–15, 15–30, 30–45 and 45–60 cm soil layers were prepared for sequential extraction. Five random cores were taken from each plot with a 5-cm diameter tube auger. Large pieces of undecomposed organic material were removed by hand, and subsamples of the moist field soil were then brought to the laboratory, air dried and ground to pass through 1 mm and 0.25 mm nylon screens prior to laboratory analysis.

#### 2.4. Chemical analysis

Soil pH and organic matter were analyzed according to standard methods described by Page et al. (1982). Soil pH was determined using an electrode pH-meter in a 1:2 soil/water suspension. Cation exchange capacity was determined by replacement of exchangeable cations by ammonium acetate. Organic matter was determined using the Walkley–Black method.

Labile Cu was extracted by the DTPA procedure which was designed for calcareous soils (Lindsay and Norvell, 1978). 20 mL of 0.005 mol L<sup>-1</sup> DTPA (diethylenetriaminepentaacetic acid)+0.1 mol L<sup>-1</sup> TEA (trietanolamine)+0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> (pH 7.30) were added to 10 g soil (<1.0 mm), and the suspensions were shaken for 2 h at 25 °C and then filtered through Whatman no. 5 filter paper.

Total Cu content was measured by a tri-acid digestion method (Shuman, 1985). Soil (0.5000 g, <0.25 mm) was placed into a Teflon beaker on a hot plate, and digested with a mixture of HNO<sub>3</sub>–HClO<sub>4</sub>–HF. After complete digestion, the digest was transferred into a 100 mL flask.

The modified sequential extraction scheme used in the study was based on that of Tessier et al. (1979) and Jiang et al. (1990), as it defined a wide variety of chemical fractions including the manganese oxides bound fraction. This sequential extraction system also divided organic bound fractions into organic matter weakly bound and specifically bound fractions. Five grams of sieved soil were extracted in 80 mL polypropylene centrifuge tubes to minimize the loss of solid material. Each of the chemical fractions was handled as follows.

- (1) Exchangeable (Exe): Soil samples were shaken at 25 °C with 50 mL of 1 mol L<sup>-1</sup> Mg(NO<sub>3</sub>)<sub>2</sub> at pH 7.0 for 2 h and centrifuged at 4000 rpm for 10 min. The supernatant was filtered with Whatman no.5 filter paper.
- (2) Weakly Bound to Organic Matter (Wbo): The residue from (1) was shaken at 25 °C for 2 h with 50 mL of 1 mol L<sup>-1</sup> Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> adjusted to pH 9.5, and the suspension was then centrifuged and filtered as in step (1).
- (3) Bound to Carbonates (Carb): The residue from (2) was shaken at 25 °C for 5 h with 50 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>COONa adjusted to pH 5.0 with CH<sub>3</sub>COOH. The suspension was then centrifuged and filtered as in step (1).
- (4) Bound to Manganese Oxides (MnOx): 50 mL of 0.04 mol L<sup>-1</sup> NH<sub>2</sub>OHHCl were added to the residue from (3), shaken for 0.5 h, and the suspension was then centrifuged and filtered as in step (1).
- (5). Specifically Bound to Organic Matter (Sbo): 3 mL of 0.02 mol L<sup>-1</sup> HNO<sub>3</sub> and 5 mL of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2.0 with HNO<sub>3</sub> were added to the residue from (4) and the mixture was placed in a water bath at 85±2 °C for 2 h with intermittent agitation. An additional 5 mL of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2.0 with HNO<sub>3</sub> were then added and the mixture was kept in the water bath at 85±2 °C for another 3 h with intermittent agitation. After cooling,

50 mL of 1 mol L<sup>-1</sup> Mg(NO<sub>3</sub>)<sub>2</sub> at pH 7.0 was added, and the suspension was shaken for 2 h, centrifuged and filtered as in step (1).

- (6). Bound to Minerals (Min): The residue from Step (5) was heated to dryness at 180 °C, then 0.5000 g residue (<0.25 mm) was placed in a Teflon beaker on a hot plate, and digested with a mixture of HNO<sub>3</sub>–HClO<sub>4</sub>–HF. The digest was transferred into a 100 mL flask.

Between each successive extraction, the supernatant solution was removed and stored in a polyethylene bottle at 4 °C prior to analysis. The residue was washed once with 10 mL of deionized water before proceeding to the next step in the extraction procedure. For each sample, sequential extraction and extraction with DTPA were conducted in three replications. All glassware was soaked in 14% HNO<sub>3</sub> (v/v) and rinsed with deionized water prior to use. Reagents were analytical grade.

All soil extracts and digests were analyzed for Cu using atomic absorption spectrometry (SpectrAA-220 Zeeman, Varian Inc., Palo Alto, CA). For each Cu fraction, a standard solution with the same matrix as the extraction solution or digest was prepared.

#### 2.5. Statistical analysis

Analysis of variation and correlation analysis were conducted using SAS software (SAS Institute, 1989).

### 3. Results and discussion

#### 3.1. Total Cu content in soil profile

Differences in the total Cu content in these soil profiles are due to the effects of long-term application of Cu fertilizers. Total Cu contents were highest in the surface layer (0–15 cm) and declined with depth in both Cu fertilizer and no Cu fertilizer treatments (Table 2). This agrees with the finding of Yu et al. (1991) who reported that in the Loess Plateau area, even with illuvial transport, total Cu content in soil was larger in the surface and shallow subsurface soil than in the deeper soil layers. The largest increase in total Cu due to fertilization occurred in the 0–15 cm soil depth which contained 74% more Cu than in the no Cu fertilizer treatment. Total Cu contents were 7% to 15% higher in the 15–30, 30–45, and 45–60 cm soil depths of the Cu fertilized treatment compared to the control, though the differences were not significant. The relatively large accumulation of Cu in the surface soil is probably due to the

Table 2  
Total Cu content in soil profile (mg kg<sup>-1</sup>)

Treatments	Soil depths			
	0–15 cm	15–30 cm	30–45 cm	45–60 cm
Cu fertilizer	27.6	16.1	14.9	11.7
No Cu fertilizer	15.9	15.0	12.9	10.3
% Change	73.7	7.0	15.2	13.9

LSD<sub>0.05 treatment</sub> = 8.14; LSD<sub>0.05 profile</sub> = 11.51.

adsorption and fixation of the Cu after it was added to the soil. The application of phosphorus fertilizer could also contribute to the accumulation of fertilizer Cu in surface soil since  $\text{Cu}^{2+}$  can form an insoluble salt,  $\text{CuHPO}_4$ , with  $\text{HPO}_4^{2-}$  (Shuman, 1988).

Application of Cu fertilizer for 17 years at the rate of  $15 \text{ kg CuSO}_4 \text{ hm}^{-2}$  would increase total Cu content of the soil by  $57.4 \text{ kg hm}^{-2}$ . We observed that Cu fertilization increased total Cu in the 0–60 cm soil depth by  $32.8 \text{ kg Cu hm}^{-2}$  compared to the no Cu fertilized treatment, which corresponds to 57.3% of the fertilizer Cu applied to the soil (assuming a bulk density of  $1.35 \text{ g cm}^{-3}$ ). Of the total fertilizer Cu applied to the plots, approximately 41.3% was accounted for in the 0–15 cm depth, 3.9% in the 15–30 cm, 7.1% in the 30–45 cm depth, and 4.9% in the 45–60 cm depth. Calculations presented in an earlier section showed that less than 2.7% of the fertilizer Cu was removed by crop harvest. Furthermore, there was little or no erosion on these plots that would have resulted in the loss of fertilizer Cu. This means that approximately 40% of the applied Cu was leached below the 60 cm soil depth. Additional evidence for this is provided below in our discussion regarding the distribution of labile Cu in the soil profile.

### 3.2. Labile Cu distribution in soil profile

After 17 years of Cu fertilizer applications, labile Cu in the 0–60 cm and 120–400 cm soil layers of the Cu fertilized treatment was significantly higher than in the no Cu fertilizer treatment (Fig. 1). Labile Cu in the 60–120 cm soil layer was also higher in the fertilized treatment compared to the control, but the difference was not significant. It is possible that added Cu in this depth may be present mainly in non-extractable forms. The organic matter content and clay content in this soil layer was higher compared with other soil depths (Fig. 2). Clay and organic matter have strong affinity for Cu ions (Dhillon et al., 1981; Joshi, 1986; Yu et al., 2002) and thus may have reduced the DTPA extractable Cu in this experiment.

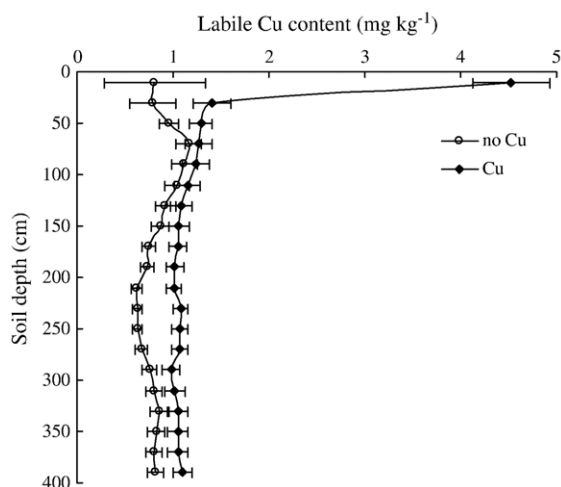


Fig. 1. Distribution of labile Cu in soil profiles after 17 years of Cu fertilizer applications (March 2001). Error bars indicate standard errors.

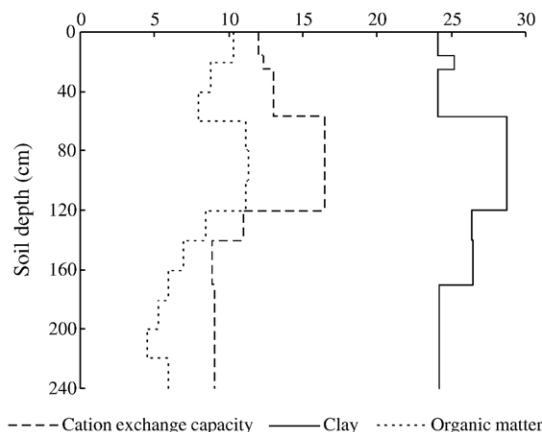


Fig. 2. Distribution of soil cation exchange capacity ( $\text{cmol kg}^{-1}$ ),  $<0.002 \text{ mm}$  clay content ( $10 \text{ g kg}^{-1}$ ), and organic matter content ( $\text{g kg}^{-1}$ ) in the soil at the beginning of the experiment.

In the no Cu fertilizer treatment, labile Cu was higher in the 60–120 cm soil layer compared to the 0–60 cm and 120–400 cm layers (Fig. 1). This suggests that Cu was being transported downward in the soil profile and that the 60–120 cm layer was a barrier against further downward transport. The observation that labile Cu was higher in the 120–400 cm depth of the fertilized treatment compared to the control indicates that the barrier function of the 60–120 cm layer was limited and that excess labile Cu can be leached down the soil profile in the upland soil of the Loess Plateau after long-term application of Cu fertilizers. The observation that labile Cu at the 400 cm depth was higher in the Cu fertilized treatment than in the control treatment suggests that labile Cu may have leached below 400 cm in the Cu fertilized treatment.

The distribution of labile Cu from 0–100 cm after 12 and 17 years of Cu fertilizer applications is shown in Fig. 3. Labile Cu content in the soil profile increased with increasing Cu inputs and application times. Twelve years of Cu fertilizer applications led to a significant increase of labile Cu in the 0–20 cm soil layer, while 17 years of Cu fertilizer applications caused a significant increase of labile Cu in the 0–45 cm soil layer. These results indicate that soil labile Cu is closely related to the amount of applied Cu. Fig. 4 presents changes in labile Cu of surface soil (0–20 cm) over different application times. Labile Cu in the control plot decreased gradually with time due to crop uptake. The decrease was more obvious in the first 3 years than in the last 14 years. Labile Cu in the Cu fertilized treatments increased rapidly during the first 7 years of the experiment, then increased more slowly until year 11 when it began to increase rapidly again.

The relationship between soil labile Cu in Cu treated soil and application time followed the linear model:

$$Y = 0.194t + 0.843 \quad r^2 = 0.937, \quad n = 9, p < 0.01$$

where  $t$  is the application time (years) and  $Y$  is labile Cu content in soil ( $\text{mg kg}^{-1}$ ).

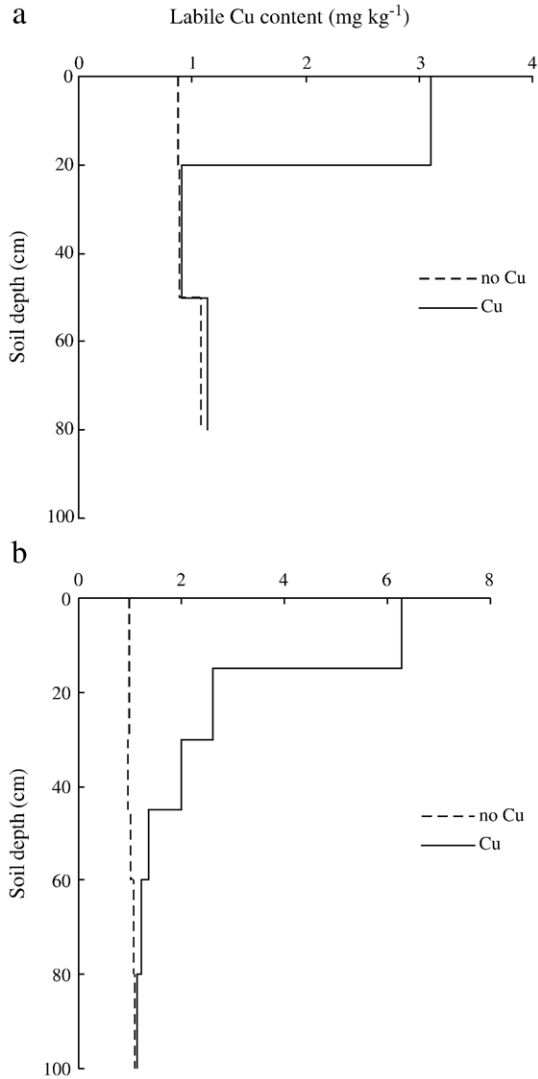


Fig. 3. Distribution of labile Cu in soil profiles after 12 and 17 years of Cu fertilization. (a) 12 years of Cu fertilizer applications (Sept. 1996); (b) 17 years of Cu fertilizer applications (Sept. 2001).

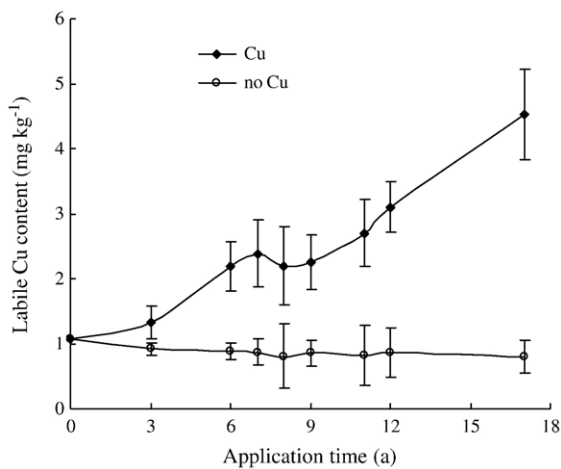


Fig. 4. Labile Cu in surface soils at different application times. Error bars indicate standard errors.

The increase of labile Cu in the 0–20 cm soil layer was also related to the fertilizer Cu rate (Fig. 5) and followed the linear relationship:

$$y = 0.06x - 0.145 \quad r^2 = 0.953, \quad n = 9, p < 0.01$$

where  $y$  is the increase of labile Cu (mg kg<sup>-1</sup>) and  $x$  is the fertilizer Cu rate (kg Cu hm<sup>-2</sup>).

### 3.3. Cu fractionation in soil profile

Copper bound to minerals (Min–Cu) contributed most to the total Cu in the soil, with amounts ranging from 55% to 78% of the total soil Cu (Fig. 6). Copper weakly bound to organic matter (Wbo–Cu) ranked second in content and accounted for 14% to 21% of the total Cu. These two fractions had a similar distribution pattern in the soil profile, i.e. decreasing with soil depth. Exchangeable Cu made up 2% to 11% of the total Cu in the soil. The contents of Exe–Cu, Carb–Cu, and MnOx–Cu had a similar profile distribution trend, which increased with soil depth. Generally, Cu content in different fractions followed the order of Min–Cu > Wbo–Cu > Exe–Cu > Sbo–Cu > Carb–Cu > MnOx–Cu regardless of Cu treatment.

Copper added to soil quickly reacted with organic matter, oxides, carbonates and other soil components. Copper increased more in the Min, Exe, Wbo, and Carb than other fractions. This means that a minimal amount of the added Cu entered into the Sbo and MnOx fractions. The distribution of added Cu to different fractions is the result of various soil processes and the equilibrium of these processes, which depend on soil physical–chemical conditions, crop cultivation, tillage, and other soil management practices. In the soil studied, high soil organic matter and carbonate are the main factors that control the fate of fertilizer Cu. Although there are considerable amounts of oxides in the soil and Cu is readily retained on the surface of oxides, it generally takes years for Cu to enter the crystalline lattice of soil oxides. Due to the annual application of Cu fertilizer, Cu ions in

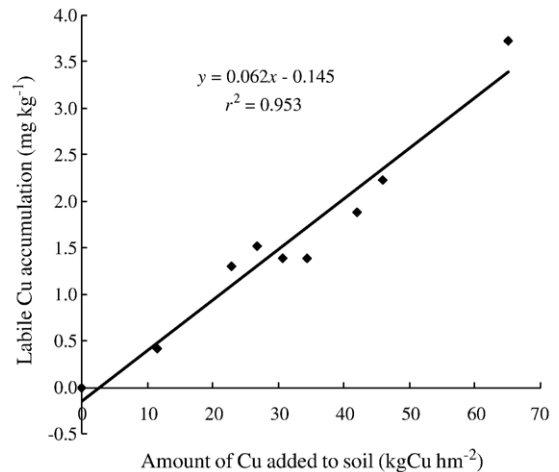


Fig. 5. Relationship between labile Cu accumulation in surface soil and the amount of Cu added to soil as fertilizers.

soil solution are regularly supplemented and exchangeable Cu therefore significantly increased.

Correlation analysis between Cu fractions and several soil properties (Table 3) showed that soil pH values were negatively correlated with Exe-Cu, Wbo-Cu, Carb-Cu and labile Cu at  $p < 0.05$ , while CEC was positively correlated with Exe-Cu, Carb-Cu and MnOx-Cu. Such relationships agree with results of other researchers (Zou and Mo, 1995; Alva et al., 2000). Organic matter and labile Cu were also positively related with Wbo-Cu, Min-Cu and total Cu. These relationships can be explained by the inter-relationship among organic matter, labile Cu, Min-Cu and total Cu reported by Yuan (1983).

### 3.4. Vertical transport of Cu in soil profile

To further understand vertical transport of Cu, we determined the distribution of labile Cu and Cu fractions along the soil profile (Table 4). Generally, the distribution of labile Cu in

the profile, which can be used to assess the vertical transport of Cu, was similar to the distribution of Exe-Cu, Wbo-Cu, and Carb-Cu fractions. Therefore, these three fractions are mobile and can be used to predict Cu leaching in soil.

Salbu et al. (1998) and Narwal et al. (1999) used the ratio of the sum of mobile Cu fractions to the total Cu as an index to evaluate the vertical transport of Cu in soil profiles. In this study, we used the Exe-Cu, Wbo-Cu, Carb-Cu fractions to assess the downward movement of Cu in soil profiles. The relative index of Cu transport was therefore calculated as a “Transport Factor” on the basis of the following formula:

$$TF = (\text{Exe-Cu} + \text{Wbo-Cu} + \text{Carb-Cu}) / \text{Total Cu} \times 100$$

Since the transport ability of Exe-Cu, Wbo-Cu, and Carb-Cu are not constant, the “Transport Factor” (TF) describes the potential transport ability. The percentage of each Cu fraction in the soil profile indicates the mobility of the fraction. The TF of

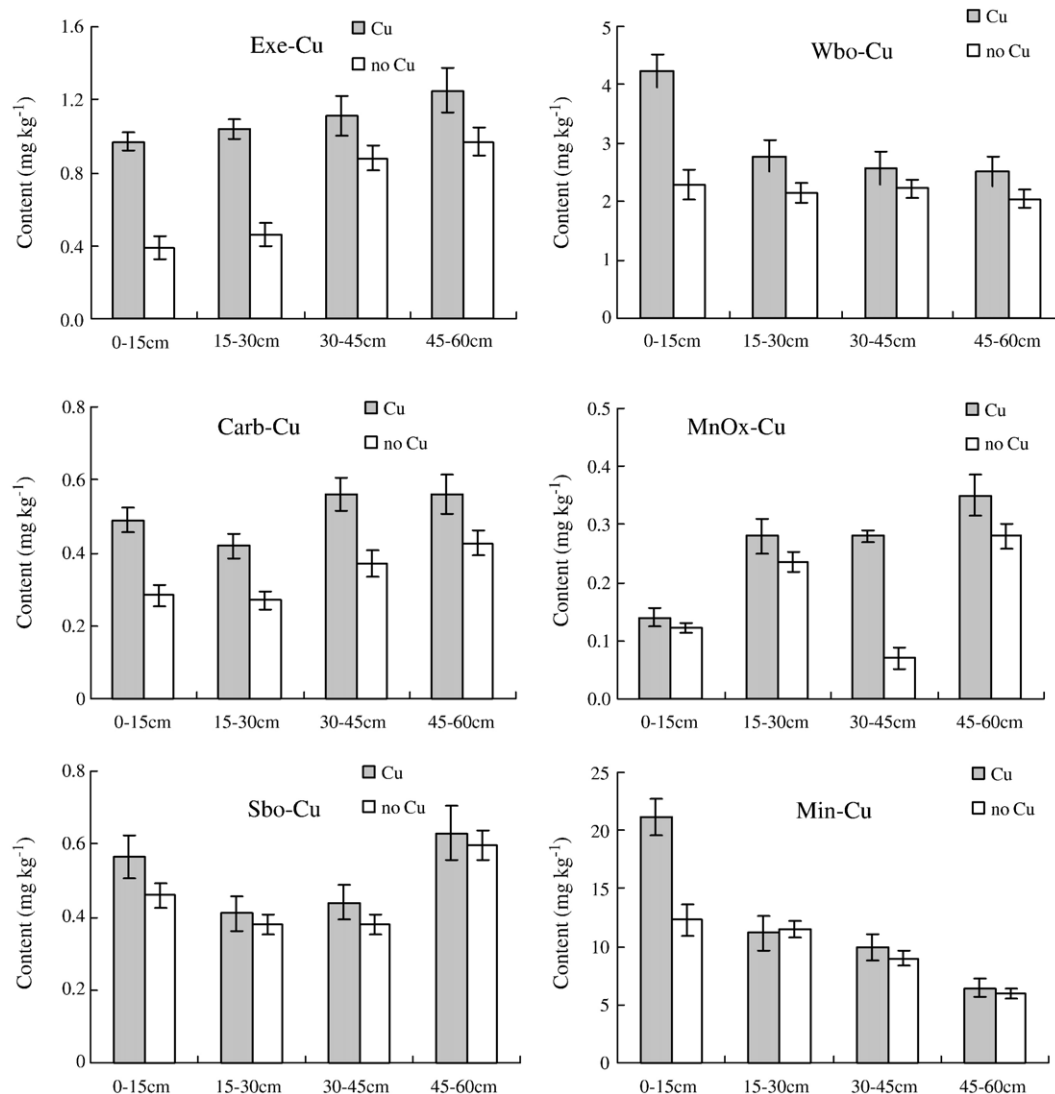


Fig. 6. Distribution of various Cu fractions in soil profiles after 17 years of Cu fertilizer applications. Exe-Cu=Exchangeable Cu; Wbo-Cu=Organic matter weakly bound Cu; Carb-Cu=Carbonates bound Cu; MnOx-Cu=Manganese oxide bound Cu; Sbo-Cu=Organic matter specifically bound Cu; Min-Cu=Minerals bound Cu. Error bars indicate standard errors.

Table 3  
Correlation coefficients between copper fractions and soil properties

	Exe-Cu	Wbo-Cu	Carb-Cu	MnOx-Cu	Sbo-Cu	Min-Cu	Total Cu	Labile Cu	pH	CEC	OM
Exe-Cu	1.000	0.283	0.926***	0.539	0.496	-0.230	-0.072	0.249	-0.753*	0.910**	-0.386
Wbo-Cu		1.000	0.402	-0.181	0.280	0.859**	0.931***	0.983***	-0.764*	0.006	0.713*
Carb-Cu			1.000	0.525	0.574	-0.073	0.084	0.351	-0.827*	0.835**	-0.195
MnOx-Cu				1.000	0.418	-0.491	-0.396	-0.196	-0.421	0.734*	-0.478
Sbo-Cu					1.000	-0.078	0.035	0.226	-0.594	0.488	-0.121
Min-Cu						1.000	0.986***	0.870**	-0.357	-0.461	0.917**
Total Cu							1.000	0.935***	-0.502	-0.320	0.880**
Labile Cu								1.000	-0.719*	0.016	0.691
pH									1.000	-0.575	-0.251
CEC										1.000	-0.616
OM											1.000

Exe-Cu=Exchangeable Cu; Wbo-Cu=Organic matter weakly bound Cu; Carb-Cu=Carbonates bound Cu; MnOx-Cu=Manganese oxides bound Cu; Sbo-Cu=Organic matter specifically bound Cu; Min-Cu=Minerals bound Cu; CEC=Cation exchange capacity; OM=Organic matter.

\*  $p < 0.05$ .

\*\*  $p < 0.01$ .

\*\*\*  $p < 0.001$ .

Cu tended to increase with soil depth in both the Cu fertilizer and noCu fertilizer treatments (Table 5). A comparison of corresponding layers in the two treatments showed a large difference in the TF values at the 15–30 cm depth, which indicated the accumulation of mobile Cu in the 15–30 cm layer of the Cu fertilized treatment. There are two possible explanations for this phenomenon. First, organic matter was lower in the 15–30 cm depth compared to the surface soil (Fig. 2). This means that Cu fixation by organic matter would be relatively low in the 15–30 cm depth and a greater proportion of the fertilizer Cu would remain in mobile forms. Secondly, CEC was higher in the 15–30 cm depth compared to the surface soil (Fig. 2). High CEC favors the transformation of immobile Cu into mobile forms. These explanations are supported by the finding that the TF of Cu was positively correlated with CEC ( $r=0.873$ ,  $p=0.005$ ,  $n=8$ ) and negatively related with organic matter content ( $r=-0.783$ ,  $p=0.022$ ,  $n=8$ ). Among the three mobile Cu fractions, Wbo-Cu contributed most to Cu vertical transport, and accounted for half of the Cu mobility factor. The next main contributors to Cu vertical transport were Exe-Cu and Carb-Cu.

Table 4  
Increases in Cu fractions and labile Cu in soil profile after 17 years of Cu fertilization ( $\text{mg kg}^{-1}$ )

Soil layer (cm)	Exe-Cu	Wbo-Cu	Carb-Cu	MnOx-Cu	Sbo-Cu	Min-Cu	Labile Cu
0–15	0.58 a	1.95 a	0.21 a	0.02 b	0.11 a	8.83 a	5.31 a
15–30	0.58 a	0.62 b	0.15 bc	0.04 b	0.03 b	-0.37 c	1.64 b
30–45	0.23 b	0.34 b	0.19 ab	0.21 a	0.06 b	0.93 b	1.04 b
45–60	0.28 b	0.46 b	0.13 c	0.07 b	0.03 b	0.45 bc	0.06 c

Exe-Cu=Exchangeable Cu; Wbo-Cu=Organic matter weakly bound Cu; Carb-Cu=Carbonates bound Cu; MnOx-Cu=Manganese oxides bound Cu; Sbo-Cu=Organic matter specifically bound Cu; Min-Cu=Minerals bound Cu. Means in the same column with different letters are significantly different at  $p < 0.05$ .

As indicated in Table 4, labile Cu and the mobile Cu fractions tended to change in the soil profile in a similar pattern, we therefore calculated the “Transport Factor” for labile Cu using the following formula to compare the potential transport of labile Cu with mobile Cu fractions.

$$TF_{\text{labile Cu}} = \text{Labile Cu} / \text{Total Cu} \times 100$$

In the no Cu fertilizer plot, the distribution of  $TF_{\text{labile Cu}}$  was similar to that of  $TF_{\text{Exe-Cu}}$ ,  $TF_{\text{Wbo-Cu}}$ ,  $TF_{\text{Carb-Cu}}$  and  $TF_{\text{Cu}}$ , i.e. increasing with soil depth. Values of  $TF_{\text{labile Cu}}$  were about one-third as much as  $TF_{\text{Cu}}$ . In contrast,  $TF_{\text{labile Cu}}$  decreased with soil depth in Cu fertilized plots because the increase of labile Cu in upper soil layers was much larger than the increase in Wbo-Cu, Exe-Cu and Carb-Cu after repeated Cu fertilization. Labile Cu was measured using a DTPA procedure in this experiment. The Cu extracted by DTPA includes some fractions that are not readily mobile. This may explain why  $TF_{\text{labile Cu}}$  decreased in the Cu fertilizer treatment but increased in the no Cu fertilizer treatment. Although labile Cu can be used to indicate Cu

Table 5  
Transport factor of Cu in soil profile

Treatments	Layers (cm)	$TF_{\text{Exe-Cu}}$	$TF_{\text{Wbo-Cu}}$	$TF_{\text{Carb-Cu}}$	$TF_{\text{Cu}}$	$TF_{\text{labile Cu}}$
Cu fertilizer	0–15	3.5 c	15.4 bc	1.8 d	20.7 c	22.8 a
	15–30	6.5 b	17.3 b	2.6 c	26.3 b	16.2 b
	30–45	7.4 ab	17.2 b	3.8 b	28.4 b	13.4 bc
	45–60	10.6 a	21.4 a	4.8 a	36.8 a	9.0 c
No Cu fertilizer	0–15	2.5 c	14.4 c	1.8 d	18.7 c	6.1 d
	15–30	3.1 c	14.3 c	1.8 d	19.2 c	6.4 d
	30–45	6.8 b	17.2 b	2.9 c	26.8 b	7.4 cd
	45–60	9.4 a	19.8 ab	4.1 ab	33.4 a	9.6 c

$TF_{\text{Exe-Cu}}$ =Transport factor of exchangeable Cu;  $TF_{\text{Wbo-Cu}}$ =Transport factor of organic matter weakly bound Cu;  $TF_{\text{Carb-Cu}}$ =Transport factor of carbonates bound Cu;  $TF_{\text{Cu}}$ =Transport factor of mobile Cu;  $TF_{\text{labile Cu}}$ =Transport factor of labile Cu.

Means in the same column with different letters are significantly different at  $p < 0.05$ .

vertical movement,  $TF_{\text{labile Cu}}$  can not reflect the potential transport of Cu in the soil profile after Cu fertilization.

#### 4. Conclusions

Repeated application of Cu fertilizer to upland soil of the Loess Plateau resulted in Cu accumulation in the surface soil and transport deeper into the soil profile. Labile Cu moved more than 400 cm deep in the soil profiles. Copper added to soil in fertilizers was mainly distributed in the Min, Exe, Wbo, and Carb fractions. Exchangeable Cu, Wbo-Cu, and Carb-Cu are the readily mobile fractions in the soil. The transport ability of different fractions followed the order of Wbo-Cu > Exe-Cu > Carb-Cu, and was higher in the 15–60 cm layer than in the 0–15 cm soil layer. Results from this study show that prolonged application of Cu fertilizer may pose an environmental risk due to the potential for Cu leaching.

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#### References

- Ahumada, I., Mendoza, J., Ascar, L., 1999. Sequential extraction of heavy metals in soils irrigated with wastewater. *Commun. Soil Sci. Plant Anal.* 30, 1507–1519.
- Alva, A.K., 1993. Copper contamination of sandy soils and effects on young Hamlin orange trees. *Bull. Environ. Contam. Toxicol.* 51, 857–864.
- Alva, A.K., Huang, B., Paramasivan, S., 2000. Soil pH affects copper fraction and phytotoxicity. *Soil Sci. Soc. Am. J.* 64, 955–962.
- Bengtsson, H., Alvenäs, G., Nilsson, S.I., Hultman, B., Öborn, I., 2006. Cadmium, copper and zinc leaching and surface run-off losses at the Öjebyn farm in Northern Sweden—temporal and spatial variation. *Agric. Ecosyst. Environ.* 113, 120–138.
- Dhillon, S.K., Sidhu, P.S., Sinha, M.K., 1981. Copper adsorption by alkaline soils. *J. Soil Sci.* 32, 571–578.
- FAO/Unesco, 1988. *Soil Map of the World, Revised Legend*. FAO, Rome.
- Flores-Veles, L.M., Ducaroir, J., Jaunet, A.M., Robert, M., 1996. Study of the distribution of copper in an acid sandy vineyard soil by three different methods. *Eur. J. Soil Sci.* 47, 523–532.
- Jiang, T., Hu, A., Qin, H., 1990. Fractionation of soil zinc, copper, iron and manganese. *Acta Sci. Circumstantiae* 10, 280–286 (In Chinese).
- Joshi, D.C., 1986. Studies on the adsorption and availability of copper in some arid soils. *Plant Soil* 94, 357–367.
- Kabata-Pendias, A., Pendias, H., 1992. *Trace Elements in Soils and Plants*, 2nd ed. CRC Press, Boca Raton, FL.
- Landing, B., 1992. Copper concentrations in Lake Jackson (Florida) sediments. *Proceedings of the Bioavailability and Toxicity of Copper*. Florida University Press, Gainesville, FL, pp. 121–145.
- Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* 42, 421–428.
- Mapanda, F., Mangwayana, E.N., Nyamangara, J., Giller, K.E., 2005. The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. *Agric. Ecosyst. Environ.* 107, 151–165.
- Msaky, J.J., Calvert, R., 1990. Adsorption behavior of copper and zinc in soil— influence of pH on adsorption characteristics. *Soil Sci.* 150, 513–522.
- Muchuweti, M., Birkett, J.W., Chinyanga, E., Zvauya, R., Scrimshaw, M.D., Lester, J.N., 2006. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: implications for human health. *Agric. Ecosyst. Environ.* 112, 41–48.
- Narwal, R.P., Singh, B.R., Salbu, B., 1999. Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions. *Commun. Soil Sci. Plant Anal.* 30, 1209–1230.
- Nyamangara, J., 1998. Use of sequential extraction to evaluate zinc and copper in a soil amended with sewage sludge and inorganic metal salts. *Agric. Ecosyst. Environ.* 69, 135–141.
- Nyamangara, J., Mzezewa, J., 1999. The effect of long-term sewage sludge application on Zn, Cu, Ni and Pb levels in a clay loam soil under pasture grass in Zimbabwe. *Agric. Ecosyst. Environ.* 73, 199–204.
- Page, A.L., Miller, R.H., Kenney, D.R., 1982. *Methods of Soil Analysis Part 2*. Agronomy Monographs, vol. 9. American Society of Agronomy, Madison, Wisconsin, USA.
- Pietrzak, U., McPhail, D.C., 2004. Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma* 122, 151–166.
- Prasad, B.R., Basavaiah, S., Subba Rao, A., Subba Rao, I.V., 1984. Forms of copper in soils of grape orchards. *J. Indian Soc. Soil Sci.* 32, 318–322.
- Rattan, R.K., Datta, S.P., Chhonkar, P.K., Suribabu, K., Singh, A.K., 2005. Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. *Agric. Ecosyst. Environ.* 109, 310–322.
- Salbu, B., Krekling, T., Oughton, D.H., 1998. Characterization of radioactive particles in the environment. *Analyst* 123, 843–849.
- SAS Institute, 1989. *SAS/STAT User's Guide Version 6*, fourth ed. SAS Inst., Cary, NC.
- Shuman, L.M., 1985. Fractionation method for soil micronutrients. *Soil Sci.* 140, 11–22.
- Shuman, L.M., 1988. Effects of phosphorus level on extractable micronutrients and their distribution among soil fractions. *Soil Sci. Soc. Am. J.* 52, 136–141.
- Singh, B.R., 1997. Soil pollution and contamination. In: Lal, R. (Ed.), *Methods for Assessment of Soil Degradation*. CRC Press, Boca Raton, FL, pp. 279–299.
- Sposito, G., Lund, L.J., Chang, A.C., 1982. Trace metal chemistry in arid zone field soils amended with sewage sludge. I. Fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. *Soil Sci. Soc. Am. J.* 46, 260–264.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Yu, C.Z., Peng, L., Liu, Y.H., Dai, M.J., Peng, X.L., 1991. Content and distribution of trace elements and fertilizer efficiency in soils of Loessal region. *Acta Pedol. Sin.* 28, 317–326 (In Chinese).
- Yu, S., He, Z.L., Huang, C.Y., Chen, G.C., Calvert, D.V., 2002. Adsorption-desorption behavior of copper at contaminated levels in red soils from China. *J. Environ. Qual.* 31, 1129–1136.
- Yuan, K.N., 1983. *Soil Chemistry of Plant Nutrients*. Science Press, Beijing. (In Chinese).
- Zou, B.J., Mo, R.C., 1995. Distribution of soil zinc, iron, copper and manganese fractions and its relationship with plant availability. *Pedosphere* 5, 35–44.