Effect of chemical fertilizers on the fractionation of Cu, Cr and Ni in contaminated soil

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Abstract Effect of chemical fertilizers (urea, NH_4Cl, $Ca(NO_3)_2$, KCl and KH_2PO_4) on the fractionation of Cu, Cr and Ni was studied by a 4-month incubation experiment. Using sequential extraction procedure, it was found that the application of fertilizers could change the distribution of Cu, Cr and Ni in the fractions of soil. Applying urea ($CO(NH_2)_2$) significantly decreased the concentrations of Cu, Cr and Ni in water soluble plus exchangeable (WE) fraction, but increased those in Fe–Mn oxides bound (FM) fraction ($p < 0.01$). However, application of NH_4Cl caused an increase in the WE fraction by 27.7% for Cu, 111.5% for Cr and 20.4% for Ni. The $CO(NH_2)_2$ raised the soil pH from 4.51 to 4.96, whereas NH_4Cl lowered the pH of soil by 0.44 units. The WE fraction of the three heavy metals was significantly increased, while the FM fraction was significantly decreased by adding KCl ($p < 0.01$). Moreover, the supply of KH_2PO_4 reduced the WE and carbonate bound (CB) fractions of Cu, Cr and Ni in the soil, however, it raised Cu and Ni in the residual (RS) fraction and Cr in the FM fraction. In addition, the mobility index indicated that KCl and NH_4Cl increased the mobility of Cu, Cr and Ni in the soil, whereas urea and KH_2PO_4 decreased the mobility of the three metals in the soil. These results suggest that applying chemical fertilizers does not only provide plant nutrients, but may also change the speciation and mobility of heavy metals in the soil.

Keywords Chemical fertilizer · Soil · Fraction · Copper · Chromium · Nickel

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Introduction

High level metals are usually found in superficial soil and vegetation in areas affected by mining activities, metal factories and traffic emissions (Tiller 1989; Krishna and Govil 2004; Liu et al. 2006). Generally, the total metal concentrations in polluted soils are required to assess the potential risk of these areas. However, there is usually a poor relationship between plant uptake and total content of heavy metals in soil (Xian 1989; Kabata-Pendias 1993; Wang et al. 2003). This is mainly due to different distributions of heavy metals in chemical fractions, which have different bioavailability (Maiz et al. 1997, 2000). Therefore, the assessment of the mobility, bioavailability and toxicity of metals requires not only the total amount of heavy metals in the soil to be measured, but also the amounts of heavy metals in each association form.

A five-step sequential extraction procedure proposed by Tessier et al. (1979) has been widely used to assess the mobility and availability of heavy metals in soils. According to this method, heavy metals in soil were separated into five different geochemical fractions: (1) soluble plus exchangeable (WE), (2) bound to carbonate (CB), (3) bound to Fe–Mn oxides (FM), (4) bound to organic matter (OC), and (v) residual (RS). The distribution of these fractions is greatly affected by soil properties such as pH, redox potential (Eh), cation exchange capacity (CEC), organic matter, clay content and so on. The WE fraction of Co, Ni, V and Zn was negatively correlated with pH (Gleyzes et al. 2002). The CB fraction was thought to have been present as co-precipitated with carbonate minerals and is sensitive to pH changes (Sims 1986). The FM metals were demonstrated to decrease with an increase in soil Eh, and be released under anoxic condition (Sims and Patrick 1978).The OC fraction of metals was reported to be positively correlated with soil organic matter (Tu 1996).

As an important way for increasing yield in agricultural production, fertilization can also alter soil properties and availability of heavy metals in soils. Malhi et al. (1998) reported that fertilization with ammonium nitrate reduced the soil pH from 6.85 to 4.10 in the 0–5 cm layer. Tsadilas et al. (2005) found that application of the ammonium fertilizer decreased the soil pH by 0.4 units, and increased the leaf Cd concentration of tobacco. It was well documented that supplying P effectively immobilized Pb in soil by formation of lead phosphates with reduced solubility (Ma et al. 1995; Boisson et al. 1999; Hettiarachchi et al. 2000; Cao et al. 2004). Addition of K was reported to significantly increase the soluble Cd in soils and Cd uptake by plants (Sparrow et al. 1994; Yi et al. 1996). These phenomena may relate to the transforms of soil metals in various fractions. Therefore, it is meaningful to study the effects of fertilizers on the fractions of soil metals.

In this research, a paddy soil contaminated by electroplating wastewater was selected to examine the change of the distribution in different fractions of Cu, Cr and Ni after applying N, P and K fertilizers. The main objectives of this study were (1) to investigate the transforms of soil metals in each fraction as influenced by fertilizers; (2) to assess the effect of fertilizers on the mobility of heavy metals; (3) to give some advice for utilization of chemical fertilizers in metal-contaminated soil.

Materials and methods

Soil and incubation

The soil used for incubation in this study was collected from a paddy field near an electroplating factory (E110.38°, N24.51°) located in Guilin, China. Some properties of the soil were measured with routine analytical methods (AC 1983), and listed in Table 1. The collected soil was air-dried and passed through 2-mm sieves. The screened soil was then put into 11-cm diameter plastic pots (100 g dry soil per pot). Five fertilizers and non-fertilizer (control) were used for soil treatment. The fertilizer application was: (1) 200 mg N kg^{-1} as $CO(NH_2)_2$, NH_4Cl and $Ca(NO_3)_2$ respectively, (2) 80 mg P kg^{-1} as KH_2PO_4, and (3) 100 mg K kg^{-1} as KCl. Three replicates were used for each treatment. All soils were watered to field capacity and kept at room temperature (15–25°C).

Fractionation and analysis

Four months after addition of the fertilizers, all the soils were air-dried and mixed thoroughly. Then 1 g dry soil was taken from each pot according to the quarter method (Liu 1996) and sequentially extracted according to the procedure listed in Table 2. After each extraction, the mixture of soil and reagent was centrifuged at 3,500 rev min^{-1} for 20 min. The supernatant was then filtered and measured for the concentrations of Cu, Cr and Ni using flame atomic absorption spectrophotometer (PE-AA700).

Calculation of mobility index

The mobility of heavy metals could be assessed by the mobility index (MI) (Banat et al. 2003; Guo and Zhou 2005), which could be calculated according to the equation as followed:

$$MI = \sum_{i=1}^{n} \frac{F_i/T_i}{n}$$

where F_i is the metal concentration in WE fraction, T_i the total concentration of the metals, and n the number of the soil samples.

Statistical analyses

The significance of differences between the pairs of means was determined using one-way analysis of variance (ANOVA) performed with the statistical package SPSS. If the *F*-value showed significant differences ($p < 0.001$), the means were compared with least significant difference method (LSD).

Results and discussion

Effect of N supply on fractions of heavy metals

Application of 200 mg N kg^{-1} as CO $(NH_2)_2$ significantly decreased the WE fraction of Cu, Cr and Ni, and increased FM fraction of the three metals (Table 3).

Table 1 The properties of the soil used in the experiments

pH (H_2O)	CEC (cmol/kg)	Eh (mV)	SOM (%)	Clay (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Total Cu (mg/kg)	Total Cr (mg/kg)	Total Ni (mg/kg)
4.51	7.8	247	2.7	22.28	5.56	13.86	135.1	296.4	305.6

CEC cation exchange capacity; *Eh* redox potential; *SOM* soil organic matter

Table 2 Sequential fractionation procedure for speciation analysis of Cu, Cr and Ni in the soil

Fraction	Extractant and brief procedure
Soluble and exchangeable	1 mol/l $MgCl_2$ 8 ml, pH 7 (adjust with HCl), 18°C, agitated for 1 h
Bound to carbonate	1 mol/l NaOAc 8 ml, pH 5 (adjust with HOAc) at 20°C, agitated for 17.5 h
Bound to Fe–Mn oxides	0.04 mol/l NH_2OH HCl in 25% (v/v) HOAc 20 ml, pH 2 (adjust with HOAc), 96°C (in water bath), intermittent agitating for 3 h
Bound to organic matter	0.02 mol/l HNO_3 3 ml, 30% H_2O_2 5 ml, pH 2 (adjust with HNO_3), 83°C, occasionally agitated for 1.5 h, 30% (v/v) H_2O_2 3 ml was added, pH 2 (adjust with HNO_3), 83°C, intermittent agitated for 1.1 h, 3.2 mol/l NH_4OAc in 20% (v/v) HNO_3 5 ml was added, 18°C, diluted to 20 ml, agitated for 0.5 h
Residue	HF–$HClO_4$–HNO_3 digestion

Other fractions of the three metals were not consistently affected by urea. However, the supply of NH_4-containing fertilizer (as NH_4Cl) significantly increased WE fraction of Cu, Cr and Ni by 27.7, 111.5, and 20.4%, respectively. Moreover, the CB fraction of Cu, Cr and Ni was significantly reduced by adding NH_4Cl ($p < 0.01$). The effect of $Ca(NO_3)_2$ on all fractions of Cu, Cr and Ni was not pronounced. The relative concentrations of Cu, Cr and Ni in all fractions as influenced by applying $Ca(NO_3)_2$ were not significantly different from those of the control (Fig. 1).

The reduction in the WE fraction of heavy metals can be explained by the increased soil pH because of urea application (Xian and Shokohifard 1989). In the present work, it was observed that the soil pH was significantly increased by 0.45 units after urea supply

Table 3 Cu, Cr and Ni concentrations in the fractions of soils as influenced by applying chemical fertilizers

Fertilizers	Fractions (mg/kg)					Sum (mg/kg)	Recoveries (%)
	WE	CB	FM	OC	RS		
Cu							
Control	10.1 ± 0.5c	10.3 ± 1.2a	41.5 ± 2.1b	32.6 ± 2.7a	38.0 ± 3.1b	130.8 ± 6.5	98.2 ± 2.5
$CO(NH_2)_2$	4.2 ± 0.5e	9.6 ± 1.3ab	53.3 ± 2.1a	31.9 ± 6.7a	37.6 ± 3.3b	131.9 ± 5.1	101.2 ± 6.1
NH_4Cl	12.9 ± 0.5b	7.4 ± 0.8b	43.2 ± 1.2b	30.7 ± 1.4a	37.2 ± 2.9b	132.2 ± 2.4	97.9 ± 1.8
$Ca(NO_3)_2$	10.7 ± 0.1c	11.2 ± 0.2a	42.6 ± 2.8a	31.7 ± 1.3a	37.2 ± 2.2b	133.2 ± 0.5	98.7 ± 0.3
KCl	15.4 ± 1.3a	10.2 ± 0.1a	34.9 ± 1.4c	32.4 ± 3.9a	37.1 ± 1.1b	130.0 ± 6.7	96.3 ± 4.9
KH_2PO_4	6.0 ± 0.5d	7.6 ± 0.3b	40.8 ± 0.2b	31.7 ± 3.0a	47.5 ± 3.2a	133.6 ± 6.1	98.9 ± 4.6
Cr							
Control	6.1 ± 0.5c	20.1 ± 1.9a	156.1 ± 1.5c	56.1 ± 1.8a	39.2 ± 1.6a	277.6 ± 7.3	93.7 ± 2.5
$CO(NH_2)_2$	2.5 ± 0.1e	20.2 ± 1.8a	167.5 ± 1.7b	57.2 ± 5.1a	38.3 ± 3.9a	285.8 ± 12.5	96.4 ± 4.2
NH_4Cl	12.9 ± 2.5b	12.9 ± 1.0b	155.4 ± 2.2cd	56.5 ± 3.9a	42.3 ± 12.2a	280.0 ± 21.7	94.5 ± 7.3
$Ca(NO_3)_2$	5.9 ± 0.4cd	20.2 ± 0.6a	154.4 ± 4.8cd	57.8 ± 1.3a	38.3 ± 0.8a	276.6 ± 7.8	93.3 ± 2.6
KCl	20.1 ± 1.9a	20.6 ± 0.3a	146.0 ± 5.8d	52.3 ± 1.4a	36.9 ± 2.0a	275.9 ± 11.3	93.1 ± 3.8
KH_2PO_4	2.8 ± 0.3de	14.8 ± 0.9b	185.0 ± 7.0a	50.3 ± 0.3a	36.2 ± 3.2a	289.1 ± 11.7	97.5 ± 3.9
Ni							
Control	79.8 ± 5.0b	14.1 ± 1.3a	55.4 ± 1.1b	44.3 ± 3.2a	109.5 ± 7.9b	303.2 ± 8.8	99.2 ± 2.9
$CO(NH_2)_2$	43.2 ± 4.4d	13.7 ± 1.2a	87.4 ± 10.7a	43.0 ± 8.1a	104.6 ± 6.1b	292.0 ± 6.9	95.9 ± 2.3
NH_4Cl	96.1 ± 6.6a	9.3 ± 1.3c	55.1 ± 2.4b	40.3 ± 3.8a	102.0 ± 14.1b	302.8 ± 8.6	99.1 ± 2.8
$Ca(NO_3)_2$	77.3 ± 3.3b	13.3 ± 1.4ab	52.3 ± 4.4b	42.1 ± 5.2a	106.2 ± 5.0b	291.3 ± 8.1	95.3 ± 2.6
KCl	94.9 ± 1.6a	12.5 ± 0.1ab	47.2 ± 3.2b	43.3 ± 1.9a	103.2 ± 8.6b	301.0 ± 5.1	98.5 ± 1.7
KH_2PO_4	58.2 ± 1.4c	10.7 ± 0.6bc	52.7 ± 1.7b	43.6 ± 7.2a	130.3 ± 6.9a	295.6 ± 1.7	96.7 ± 0.6

Results are means ± SD, $n = 3$. Values followed by same letters are not significantly different at $p < 0.01$, according to least significant difference method (LSD)

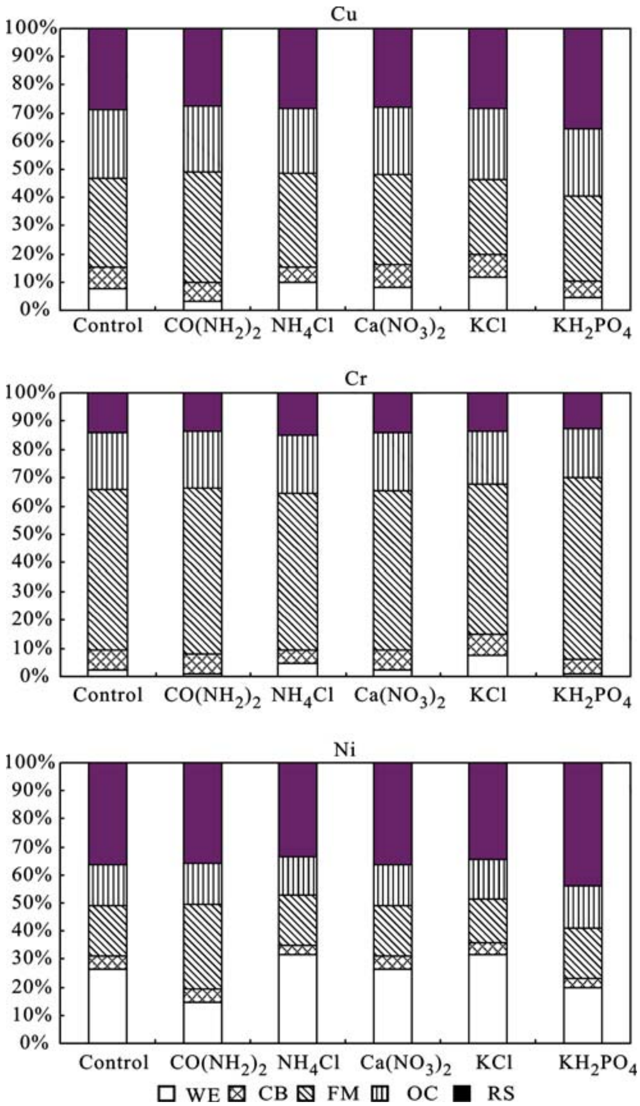

Fig. 1 Relative concentrations of Cu, Cr and Ni in each fraction of soil. *WE* water soluble and exchangeable; *CB* Carbonate; *FM* Fe–Mn oxide; *OC* Organic matter; *RS* Residual

(Fig. 2). In acid soil, hydrolyzation of urea would consume hydrion in the soil solution, and thus increase soil pH (Tu et al. 2000). On the contrary, NH_4Cl addition increased the WE fraction of Cu, Cr and Ni, but decreased the CB fraction of the three metals, which also could be ascribed to the changes of soil pH. The metal in the CB fraction is sensitive to pH change, and the CB fraction of Cu, Cr and Ni will dissolve to the WE fraction when soil pH is decreased (Yuan et al. 2004). The application of ammoniacal fertilizer could induce the soil acidification due to the microbial nitrification during formation of nitrate from ammoniacal fertilizers (Eriksson 1990; Patriquin et al. 1993). Figure 2 showed that application of NH_4Cl lowered the soil pH from 4.51 to 4.07.

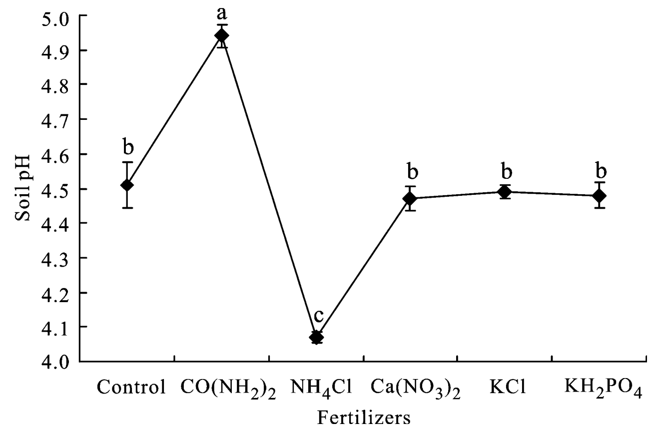

Fig. 2 Effect of fertilizers on the soil pH. Different letters denote that differences are statistically significant according to the LSD ($p < 0.01$)

Effect of P supply on fractions of heavy metals

Cu, Cr and Ni concentrations in the WE and CB fractions as influenced by applying phosphorus fertilizer (as KH_2PO_4) were significantly decreased ($p < 0.01$). Moreover, phosphate treatment increased the residual Cu by 25.0% and the residual Ni by 19.0% (Table 3). These results were similar to the findings of Cao et al. (2003), who reported that the addition of P could transform soil Cu, Pb and Zn from the non-residual to the residual phase. The possible reason for this is that phosphorus can react with metals to form indissoluble metal phosphates (Cotter-Howells 1996; Xie et al. 2006). It was noticed that application of KH_2PO_4 did not increase the RS fraction of Cr, but increased the FM fraction of Cr. After four months incubation, the percentage of Cr in the FM fraction increased from 55.9% to 64.1% in P-treated soil as compared to the control (Fig. 1), which means that the reduction in WE and CB fractions of Cr by phosphorus can be due to binding to the Fe and Mn oxide rather than formation of chromium phosphates. Phosphorus can be bound to oxide surface in soil, which increases specific sorption sites for Cr (Bolland et al. 1977; Xie and MacKenzie, 1988).

Effect of K supply on fractions of heavy metals

The WE fraction of Cu, Cr and Ni was significantly increased by K (as KCl) application (Table 3). After using potash fertilizer, the relative concentrations of Cu, Cr and Ni in WE fraction of soil were raised from 7.6, 2.0 and 26.3% to 11.9, 7.3 and 31.5%, respectively (Fig. 1). However, K supply caused a significant reduction in the FM fraction of Cu, Cr and Ni

($p < 0.01$). The increase of WE fraction was in agreement with the observation of Tu et al. (2000), who reported that addition of KCl increased Cd and Pb in the WE fraction by 2–25% and 0.2–7%, respectively. The increase of WE fraction and the decrease of FM fraction may be due to the competitive exchange between K and heavy metal ions on soil surfaces (Mandal et al. 1996) and the reacting of the accompanying anion Cl^- with metal cations to form soluble complex (Bingham et al. 1984).

Effect of fertilizers on mobility of heavy metals

The mobility of heavy metals can be assessed by the mobility index (Banat et al. 2003; Guo and Zhou, 2005). The mobility indexes of Cu, Cr and Ni as influenced by fertilizers are shown in Fig. 3. It was observed that the mobility indexes of Cu, Cr and Ni increased by adding NH_4Cl and KCl, which could enhance the potential Cu, Cr and Ni threat to eco-environment in soil contaminated by heavy metals. However, the application of urea and KH_2PO_4 lowered the mobility indexes of Cu, Cr and Ni. It was mainly attributed to the reduction of metal concentrations in WE fraction. Additionally, there was no significant change in mobility indexes of the three metals after $Ca(NO_3)_2$ supply.

Because of the different effects of fertilizers on mobility of heavy metals, fertilizers should be reasonably used during cultivation in heavy metal contaminated soil in order to avoid the heavy metal mobilization. According to the result of this study, the application of N fertilizer as $Ca(NO_3)_2$ is superior to using NH_4Cl in the soil contaminated by heavy metals. In acidic soil, applying of excessive KCl should be avoided to reduce the leaching of heavy metals. Addition of P fertilizer as KH_2PO_4 was effective in metal immobilization because it significantly reduced the WE and CB fractions of metals with less impact on soil pH.

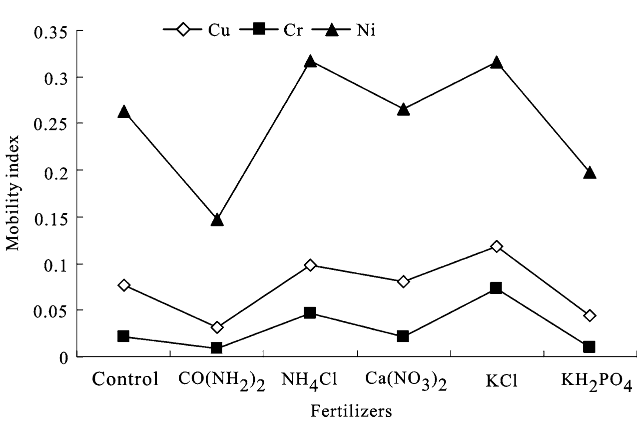

Fig. 3 Mobility index of Cu, Cr and Ni as influenced by applying chemical fertilizers

Conclusions

The effects of various chemical fertilizers on the fractions of heavy metals were quite different. Application of urea lowered the WE fraction of Cu, Cr and Ni, but raised the FM fraction of the three metals. Supply of NH_4Cl caused an increase in the WE fraction of the three metals, while a decrease in the CB fraction. Applying $Ca(NO_3)_2$ had no or less effect on all fractions of Cu, Cr and Ni. The P application (as KH_2PO_4) significantly decreased the WE and the CB fractions of Cu, Cr and Ni, whereas increased Cu and Ni in the RS fraction and Cr in the FM fraction. However, supplying KCl led to an increase in the WE fraction of the three metals and a decrease in the FM fraction. In heavy metal contaminated soils, therefore, application of fertilizers not only provides plant nutrients, but may also change the speciation and mobility of heavy metals. In order to avoid the heavy metal mobilization, it is suggested that chemical fertilizers should be reasonably used during cultivation in soil contaminated by heavy metals.

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