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Phytoavailability of Copper, Zinc and Cadmium in Sewage Sludge-Amended Calcareous Soils*[1]

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ABSTRACT

The toxicity of trace elements (TEs), such as copper (Cu), zinc (Zn), and cadmium (Cd), often restrict land application of sewage sludge (SS) and there was little information about soil-plant transfer of TEs in SS from field experiments in China. In this study pot and field experiments were carried out for 2 years to investigate the phytoavailability of TEs in calcareous soils amended with SS. The results of the pot experiment showed that the phytoavailability of Zn and Cu in the SS was equal to 53.4%–80.9% and 54.8%–91.1% of corresponding water-soluble metal salts, respectively. The results from the field experiment showed that the contents of total Zn, Cu, and Cd in the soils increased linearly with SS application rates. With increasing SS application rates, the contents of Zn and Cu in the wheat grains initially increased and then reached a plateau, while there was no significant change of Cd content in the maize grains. The bioconcentration factors of the metals in the grains of wheat and maize were found to be in the order of Zn > Cu > Cd, but for the straw the order was Cd > Cu > Zn. It was also found that wheat grains could accumulate more metals compared with maize grains. The results will be helpful in developing the critical loads of sewage sludge applied to calcareous soils.

Key Words: bioconcentration factor, biosolids, metal transfer, trace elements

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INTRODUCTION

The phytoavailability and toxicity of trace elements (TEs) in biosolids, such as sewage sludge (SS), are key issues regarding land use of these materials, which depend on the accumulation of TEs in soils and their soil-plant transfer (Evanylo *et al.*, 2006). The concentrations of TEs in SS in China were lower than the limits of United States Environmental Protection Agency and decreased over time in the last two decades (Chen *et al.*, 2003); however, it is still dissident for land use of SS because there was no information about it from field conditions in China. Most of studies on soil-plant transfer of TEs in biosolids were carried out under laboratory and glasshouse conditions in China, which could lead to some experimental artifacts (McLaughlin *et al.*, 2006). It is necessary to study the transfer of TEs in soil-plant systems through the field experiments.

Generally, the bioavailability/toxicity of TEs (such as Cu and Zn) to plants is probably higher when they are added to soils as soluble salts compared to that added with biosolids (McLaughlin *et al.*, 2006). For example, the treatments with inorganic salts (Cd carbonates) resulted in relatively high concentrations of NH_4NO_3-extractable Cd in soils and high concentration of Cd in wheat grains compared with the equivalent salts in sludge treatments (Chaudri *et al.*, 2007). In the studies the TEs were added to soils as a single metal salt, but usually with co-contaminants, nutri-

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ents, or organic matter, which may markedly affect plant uptake of the TEs (McLaughlin *et al.*, 2006). Oliver *et al.* (2004) used isotopic exchange techniques to study the availability of Cu in biosolids and reported the low mobility of Cu in biosolids with the percentages of isotopically exchangeable Cu to total Cu less than 43%, which depended on the different sources of biosolids. However, Heemsbergen *et al.* (2010) compared the bioavailability of Cu and Zn in biosolids with the bioavailability of metal salts in the same soils using twelve Australian field trials and reported that bioavailability of Zn was similar in biosolid and salt treatments; for Cu, the results were inconclusive. Therefore, it is still needed to quantify the difference between the phytoavailability of TEs from biosolids and that from soluble salts in order to account for the risk from metals in biosolids in regulatory guidelines (Heemsbergen *et al.*, 2009).

The objectives of this study were to identify the difference of phytoavailability of TEs (Cu, Zn, and Cd) between SS and a mixture of water-soluble metal salts added with other co-contaminants and nutrients in a calcareous soil, and to investigate the phytoavailability and soil-plant transfer of TEs in SS in the calcareous soil.

MATERIALS AND METHODS

Characteristics of soils and sewage sludge

A field experiment was carried out in a fluvo-aquic soil in the Dezhou Experimental Station, Chinese Academy of Agricultural Sciences (37° 20′ N, 116° 38′ E). The soil used for the pot experiment was collected at a depth of 0–20 cm from the Research Station of Soil Fertility and Fertilizer Effects in Fluvo-Aquic Soil in Changping, Beijing (40° 13′ N, 116° 15′ E). Sewage sludge used for the field and pot experiments was from the Beijing Sludge Disposal Plant and collected in July, 2006. After air-drying, SS was ground to pass through a 2-mm sieve and contained 90.7 g kg^{-1} water. The characteristics of the soils and SS used in the experiments are shown in Table I.

Field experiment

The field experiment was started in October, 2006. The plant rotation was winter wheat-summer maize per year. There were five application rates of SS, 0 (CK), 4.5 (0.5S), 9 (1S), 18 (2S) and 36 t ha^{-1} (4S), and three replicates for each application rate. The 15 plots (5 m × 8 m each plot) were arranged in a randomized complete block design. The air-dried SS was applied as the basic fertilizer before wheat sowing every year and the weight of SS applied was in oven-dried base (60 °C). The fertilizers of phosphorus at 90 kg P_2O_5 ha^{-1} and potassium at 120 kg K_2O ha^{-1} were applied as basal fertilizers before seeding of winter wheat and summer maize. For wheat, a part of nitrogen fertilizer (60 kg N ha^{-1} as urea) was applied as a basal fertilizer prior to wheat seeding and the remaining nitrogen fertilizer (120 kg N ha^{-1} as urea) was applied during the wheat growing season; for maize, all

TABLE I

Basic characteristics of soils and sewage sludge (SS) used in the pot and field experiments

Item	Field soil	Pot soil	Field SS	Pot SS	GB15618-1995[a)]	GB18918-2002[b)]
pH	8.90	8.11	7.50	7.50	-	-
Organic matter (g kg^{-1})	12.2	15.9	355.2	310.1	-	-
Total N (g kg^{-1})	0.80	0.83	27.01	22.53	-	-
Total P (g kg^{-1})	0.66	0.63	16.59	16.92	-	-
Total K (g kg^{-1})	15.0	23.7	2.0	2.5	-	-
Zn (mg kg^{-1})	46.6	52.3	1 922.2	1 948.2	$\leq$ 300	< 3 000
Cu (mg kg^{-1})	17.1	20.2	238.0	277.0	$\leq$ 100	< 1 500
Cr (mg kg^{-1})	50.0	69.8	99.0	66.8	$\leq$ 250	< 1 000
Cd (mg kg^{-1})	0.11	0.13	1.50	1.90	$\leq$ 0.60	< 20
Pb (mg kg^{-1})	10.2	15.6	79.0	114.1	$\leq$ 350	< 1 000
Ni (mg kg^{-1})	27.0	32.1	46.0	35.0	$\leq$ 60	< 200
As (mg kg^{-1})	10.4	8.9	20.0	19.0	$\leq$ 25	< 75
Hg (mg kg^{-1})	0.10	-	13.00	7.00	$\leq$ 1.00	< 15

[a)] Environmental quality standards for soils (pH $\geq$ 7.5).

[b)] The limits for sewage sludge used to agricultural land (pH $\geq$ 6.5).

of nitrogen fertilizer (180 kg N ha^{-1}) was applied at small bell mouth stage of maize.

Soil samples were collected before fertilization (as a control) and after wheat harvest in June, 2008. The plant samples of straw and grains for wheat and maize were collected at maturity. Ten plants from each replication were randomly harvested in each plot. The aerial plant parts of wheat and maize were divided into grains and straw. The subsamples were washed carefully with tap water, and then with deionized water. Afterwards, the subsamples were oven-dried to constant weight at 70 °C (Sukkariyah *et al.*, 2005a). Then the oven-dried samples of grains and straw were ground separately using a stainless steel grinder (FW-100, China) to pass through a 100-mesh sieve for element analysis.

Pot experiment

To compare the bioavailability of Cu, Zn, and Cd in SS with that of soluble Cu, Zn, and Cd salts, a pot experiment was carried out in greenhouse. There were five treatments: a control with no SS and no metal salt addition (CK), two SS application rates at 50 (S5) and 100 g kg^{-1} soil (S10), and two metal application rates with the equal amounts of the metals in SS (M5 and M10). The sample of SS was thoroughly mixed with the soil while the metal salts of $CuSO_4{\cdot}5H_2O$, $CdSO_4{\cdot}8H_2O$, $CrCl_3{\cdot}6H_2O$, $ZnSO_4{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $PbCl_2$, $Na_3AsO_4{\cdot}12H_2O$, and $HgCl_2$ were spiked with solutions (200 mL solution for 2 680 g soil). The soil samples mixed with SS or metal salts were then put into plastic pots (670 g dry weight per pot). Eight seeds of maize (*Zea mays*) or ten seeds of tomato (*Lycopersicon esculentum*) were sown for each pot. In order to maintain plant nutrition, inorganic fertilizers of 0.4292 g urea kg^{-1}, 0.2632 g $KH_2PO_4{\cdot}H_2O$ kg^{-1}, and 0.428 g K_2SO_4 kg^{-1} were applied for the CK treatment and metal salt treatments. The pots were placed on a greenhouse in a completely randomized block design with four replicates for each treatment. The temperature in the greenhouse was maintained at 26 ± 2 °C during the daytime and 18 ± 2 °C at night. The pots were watered with deionized water (pH = 7.5, electrical conductivity < 1 μS cm^{-1}, Cu, Zn and Cd concentrations are lower than the detection limit as 0.52, 0.41 and 0.014 μg L^{-1}, respectively) daily to field capacity by weighing. Two weeks after sowing, seedlings were thinned to 5 plants per pot and grown for six weeks. At harvest, the aerial plant samples were washed carefully with tap water, and then with deionized water. Afterwards, the plant samples were oven-dried to constant weight at 70 °C (Sukkariyah *et al.*, 2005a) and then the metal concentrations in plant samples were determined.

Chemical analyses of sewage sludge, soil and plant samples

All samples of SS and soils were air-dried, ground, and then passed through a 2-mm sieve. Soil pH was measured in a water suspension (soil:deionized water = 1:2). Organic matter was determined using a digestion method. Total nitrogen (TN), phosphorus (TP) and potassium (TK) in the soils were determined using micro-Kjeldahl digestion, colorimetric analysis and a dissolution-flame photometer, separately (Page *et al.*, 1982). All the samples were digested using USEPA Method 3052 (USEPA, 1996): aliquots of dried SS and soil samples (0.25 g) were digested in HNO_3 (9 mL) + H_2O_2 (1 mL) + HF (0.5 mL) and aliquots of dried plant samples (0.25 g) were digested in HNO_3 (5 mL) + H_2O_2 (1 mL) in polyfluorocarbon pressure vessels and a microwave oven. The concentrations of TEs in digested solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a, USA). Blank and a standard material of soil sample (GBW-07403) and wheat (GBW-10011) provided by the China National Center for Standard Materials were used as quality control. The Cd, Cu, and Zn recovery rates in the soil and plant samples were 90%±10%, 95%±10%, and 95%±10%, respectively.

Data analyses

Phytoavailability coefficients (PC), which represents the equivalent phytoavailability of metals in SS to that in water-soluble salts, could be used to compare the difference in phytoavailability of TEs in SS and metal salts. The phytoavailability coefficient in the present study was calculated as follows:

$$\mathrm{PC} = \frac{C_{\mathrm{S}} - C_{\mathrm{CK}}}{C_{\mathrm{M}} - C_{\mathrm{CK}}} \times 100\% \qquad (1)$$

where C_{CK} is the concentration (mg kg^{-1}) of a trace element in plant shoots from control treatment; C_{S} is the concentration (mg kg^{-1}) of a trace element in plant shoots from the treatment amended with SS; C_{M} is the concentration (mg kg^{-1}) of a trace element in plant shoots from treatment amended with metal salts.

Bioconcentration factor (BCF) was used to evaluate the relative plant availability and food chain risk of biosolids (McLaughlin *et al.*, 2006), which was the ratio of metal concentration (mg kg^{-1}) in plant tissues at harvest and initial concentration (mg kg^{-1}) of metals in external environment (Zayed *et al.*, 1998).

A statistical comparison of the data was examined with one-way analysis of variance (ANOVA) and the least significant difference (LSD) test at the 5% probability level as available in the SPSS statistical package.

RESULTS AND DISCUSSION

Phytoavailability of Cu, Zn and Cd from sewage sludge and metal salts added to soils

In pot experiment, the concentrations of Zn in tomato seedlings were lower than those in maize seedlings, while the concentrations of Cu in tomato seedlings were higher than those in maize seedlings (Table II), probably because maize was a Zn-philic plant while tomato favored Cu more than maize. However, no information was found about comparison in metal concentrations between these two plants in literature. The concentrations of Zn and Cu in tomato and maize seedlings increased significantly by both SS and metal salts applied, but the increases in the concentrations of Zn and Cu in tomato and maize seedlings by SS were less than those by metal salts (Table II). The PC values of Zn were found to range from 53.4% to 80.9% and those of Cu from 54.8% to 91.1% (Fig. 1), which indicated that the phytoavailability of Zn and Cu in SS was lower than the corresponding water-soluble metal salts. The reason for the low phytoavailability of Zn and Cu in SS, compared with metal salts, is that there were certain non-extractable or available Cu and Zn in SS. For examples, about 5% to 50% of Cu and 5% to 30% of Zn in SS of China were in residual fractions, which could not be extracted by acetic acid, hydroxylammonium chloride (pH 2) and hydrogen peroxide (pH 2) in sequential extraction (Wang *et al.*, 2005, 2006). Also, the low exchangeability of Cu was found in 24 Australia biosolids with only 7% to 43% isotopically exchangeable Cu in biosolids (Oliver *et al.*, 2004). However, after long-term aging (3 years) in field experiments, Heemsbergen *et al.* (2010) found low phytoavailability of Zn in biosolids compared with $ZnSO_4$ only in one of four sites. It is reasonable that the differences in phytoavailability of Cu and Zn between SS and metal salts will probably decrease with the aging time because of the fixation of Cu and Zn in soils. The results also showed that the PC values of Zn and Cu were affected by the levels of metals added as salts and SS; with the increasing levels of added metals, the PC values of Zn or Cu increased (Fig. 1).

For Cd, similar to Cu and Zn, it was also found that the concentrations of Cd in maize and tomato seedlings from SS-amended soils were less than those from the soils amended with metal salts, which suggested that the bioavailability of Cd in SS was less than that of soluble Cd salts. Similar results were reported by McLaughlin *et al.* (2006) in field soils (pH from 4.04 to 7.9) and Street *et al.* (1977) in sandy soil (pH > 7.0). However, the application of biosolids to soil can reduce phytoavailability of Cd in some contaminated soils (Street *et al.*, 1977; Brown *et al.*, 1998). In the present study, similarly the concentrations of Cd in the plant shoots from SS-amended soils were lower than CK (Table II). The low availability of Cd in SS may be explained by two reasons: one is the addition of co-cations (such as Ca) in SS, which competitively inhibit uptake of Cd by plants; the other is the disso-

TABLE II

Metal concentrations of tomato and maize seedlings in different treatments: a control with no sewage sludge and no metal salt addition (CK), two sewage sludge application rates at 50 (S5) and 100 g kg^{-1} soil (S10), and two metal application rates with the equal amounts of the metals in sewage sludge (M5 and M10)

Treatment	Maize			Tomato		
	Zn	Cu	Cd	Zn	Cu	Cd
	mg kg^{-1}					
CK	38.46±1.91[a)]	6.97±0.07	0.36±0.01	22.03±1.73	8.32±0.69	0.65±0.02
S5	129.19±0.75	8.80±0.23	0.23±0.02	72.92±2.37	15.17±0.52	0.21±0.04
S10	215.76±14.68	9.11±0.40	0.23±0.01	-[b)]	-	-
M5	208.32±14.22	9.43±0.49	0.48±0.01	84.92±1.85	20.82±1.96	0.43±0.03
M10	290.70±8.27	9.32±0.25	0.86±0.07	-	-	-

[a)] Means±standard errors.

[b)] Data not available because of no survivor of tomato plants.

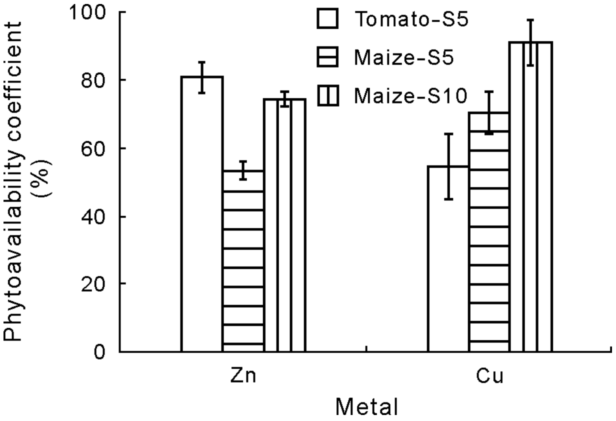

Fig. 1 Phytoavailability coefficients of Zn and Cu in sewage sludge at application rates of 50 g kg^{-1} soil (S5) and 100 g kg^{-1} soil (S10) for tomato and maize.

lved organic matter, probably reducing the availability of Cd in soil solution to plants through complexation of free Cd^{2+} (McLaughlin *et al.*, 2006).

Metal accumulation in soils amended with sewage sludge

The concentrations of total Zn, Cu and Cd in the soils increased linearly with the increasing application rates of SS and the linear correlation coefficients (R^2) ranged from 0.850 to 0.992 ($P < 0.05$, Fig. 2), because above 95% of the metals applied by SS remained in the top 20 cm of soils (Sukkariyah *et al.*, 2005b). The results are similar to those reported in the literature (Al-Najar *et al.*, 2005; Cooper, 2005; Sukkariyah *et al.*, 2005a). When the SS application rate reached to 36 t ha^{-1}, the concentrations of total Zn, Cu, and Cd in the soils were significantly higher ($P < 0.05$) than those in the control.

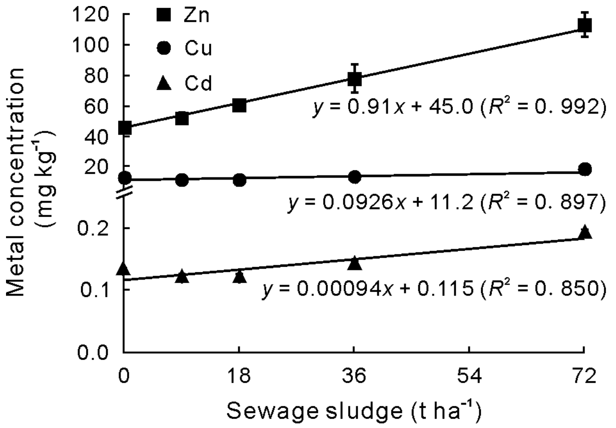

Fig. 2 Relationships between soil metal concentrations and the amounts of sewage sludge applied to soil from 2007 to 2008.

The changes in the concentrations of total Zn, Cu, and Cd in the soils (ΔZn, ΔCu, and ΔCd) could be described by the equations as follows:

$$\Delta\text{Zn (mg kg}^{-1}) = 0.475 \times \text{Zn added as SS (kg ha}^{-1}) \quad (R^2 = 0.992, P < 0.05) \qquad (2)$$

$$\Delta\text{Cu (mg kg}^{-1}) = 0.382 \times \text{Cu added as SS (kg ha}^{-1}) \quad (R^2 = 0.897, P < 0.05) \qquad (3)$$

$$\Delta\text{Cd (mg kg}^{-1}) = 0.473 \times \text{Cd added as SS (kg ha}^{-1}) \quad (R^2 = 0.850, P < 0.05) \qquad (4)$$

From the above equations, it was found that the increased rates of soil Zn, Cu, and Cd per kg Zn, Cu, and Cd added as SS per year were about 0.475, 0.382, and 0.473 mg kg^{-1}, respectively. Compared with the results that the increased rates of soil metals per kg metals added as biosolids per year were 0.28 and 0.39 for Zn and 0.27 and 0.35 for Cu in two acidic soils in Australia (Cooper, 2005), the increased rates of soil metals per kg biosolid metals per year were more in calcareous soils than in acidic soils. However, the accumulation rate of metals caused by SS application depends not only on soil properties, but also on the change of soil properties caused by SS application, metal removal by plant uptake, and metal loss by leaching. For example, addition of SS increased the amount of dissolved organic carbon (DOC) in the soils, which facilitated the transport of metal contaminants through the formation of soluble metal-DOC complexes to a deep soil (Antoniadis and Alloway, 2002). Also, when the amounts of SS applied to soils are enough to increase the depth of top soil, the accumulation rates will depend on the mixture of SS with soils and the depth of soil sampling.

Metal accumulation in plant grains

The concentrations of Zn, Cu, and Cd in two successive crop grains under different SS application rates are presented in Table III. It was found that the concentrations of Zn and Cu in wheat grains were much higher than those in maize grains, which indicated wheat grains can accumulate more Cu and Zn than maize grains. The application of SS to soils significantly increased the concentrations of Zn and Cu in wheat grains, but the changes of Zn and Cu concentrations in crop grains were usually much less than those in the soils. For example, the concentrations of Zn in the soil increased by 7.3 times with the treatment of 4S (36 t ha^{-1}) in 2008, while Zn concentrations in wheat grains increased only 2.2 times.

TABLE III

Concentrations of Zn, Cu and Cd in crop grains at sewage sludge application rates of 0 (CK), 4.5 (0.5S), 9 (1S), 18 (2S), and 36 t ha^{-1} (4S)

Crop	Year	Metal	MPC[a]	GB2715-2005[b]	Treatment				
					CK	0.5S	1S	2S	4S
			mg kg^{-1}						
Wheat	2007	Zn	150	-	20.30±1.79[c] a[d]	27.22±1.85b	29.53±1.15bc	33.52±0.81c	42.81±7.74d
		Cu	10	-	4.74±0.35ab	5.21±0.35bc	5.70±0.29c	5.61±0.12c	6.02±0.23c
		Cd	0.10	0.10	0.026±0.001c	0.024±0.002bc	0.020±0.001ab	0.024±0.002bc	0.027±0.001ab
	2008	Zn	150	-	19.38±1.96ab	24.91±1.96b	29.61±3.87bc	33.92±0.69c	36.58±0.87cd
		Cu	10	-	4.32±0.29ab	4.71±0.12b	4.94±0.40b	5.04±0.06b	5.01±0.06b
		Cd	0.10	0.10	0.021±0.001a	0.027±0.010a	0.029±0.017a	0.049±0.033a	0.041±0.027a
Maize	2007	Zn	150	-	16.85±0.13a	18.77±0.48b	19.18±0.29b	20.40±0.27c	21.63±0.14d
		Cu	10	-	1.51±0.09a	1.84±0.37a	1.62±0.01a	1.48±0.23a	1.49±0.23a
		Cd	0.10	0.10	0.0048±0.0012a	0.0073±0.0001a	0.0059±0.0043a	0.0074±0.0033a	0.0019±0.0002b
	2008	Zn	150	-	14.42±0.69a	15.51±0.87ab	15.01±0.20ab	17.90±0.87b	18.02±0.98b
		Cu	10	-	3.12±0.17a	2.89±0.29a	3.10±0.27a	3.30±0.34a	2.99±0.24a
		Cd	0.10	0.10	0.015±0.003ab	0.019±0.004ab	0.021±0.005ab	0.023±0.006b	0.011±0.002a

[a] Maximum permitted concentrations from Food Standards Australia New Zealand (2002).

[b] Hygienic standard for grains in China (Ministry of Health, PR China, 2005).

[c] Means±standard errors.

[d] Means followed by the same letter(s) within each row are not significantly different at $P < 0.05$ by the least significant difference test.

When the concentrations of Cu or Zn in plants were plotted against the application rates of sewage sludge (data from Table III), the pattern of metal accumulation in wheat and maize was found to be different. The concentrations of Zn and Cu in wheat grains initially increased with the increase of SS application rates, and then reached a plateau, which can be well described by Mitscherlich equations: Zn in wheat grain (mg kg^{-1}) = $37.3 - 18.1\mathrm{e}^{-0.46x}$ ($R^2 = 0.998$) and Cu in wheat grain (mg kg^{-1}) = $5.0 - 0.67\mathrm{e}^{-0.099x}$ ($R^2 = 0.997$), where x is the amounts of applied SS (t ha^{-1}). For maize, the concentrations of Zn in grains were increased linearly and significantly with SS application rates and can be described by the following equation: Zn in maize grain (mg kg^{-1}) = $14.1 + 0.0589x$ ($R^2 = 0.998$). However, there were no significant effects on Cu concentrations in maize grains when the SS application rates were increased. There was also no significant difference of Cd concentrations in both wheat and maize grains when the SS application rates were increased (Table III). When the SS was applied to the soil, the added Zn will have a competitive absorption with Cd, which may decrease the Cd uptake by plants (Oliver *et al.*, 1994); the high soil organic matter content after the application of sludge can also reduce the crop uptake of Cd (McLaughlin *et al.*, 2006; Chaudri *et al.*, 2007).

The concentrations of Zn, Cu, and Cd in wheat and maize grains from the soils amended with SS in the present study, even at the highest application rates, were still below the maximum permitted concentrations as specified in the national control standard in China (GB2715-2005, Ministry of Health, PR China, 2005) and Food Standards Australia New Zealand (2002). The contents of TEs in crop grains tended to reach a plateau with the increased amounts of SS applied (Barbarick *et al.*, 1995). Therefore, the allowable amounts of SS estimated by the maximum of soil metals are probably conservative for food safety.

The amounts of Zn, Cu and Cd uptake by wheat and maize plants were lower than 1% of the added metals by SS to the soils (Table IV). This result indicated that the amounts of these metals transferred to straw and grains of wheat and maize was small. The amounts of Zn and Cu uptake by wheat were higher than those by maize. Cadmium uptake by wheat and maize was the lowest. Because of the low uptake and mobility of these metals in soil-plant system in the calcareous soil, the cumulative rates of these metals in the soils were mainly affected by the rates of SS application.

Bioconcentration factors

Bioconcentration factors (BCF), also known as ab-

TABLE IV

Amounts of metal uptake[a)] by wheat and maize in sewage sludge treatments of 4.5 (0.5S), 9 (1S), 18 (2S), and 36 t ha^{-1} (4S)

Plant	Metal	Treatment				Average
		0.5S	1S	2S	4S	
		%				
Wheat	Zn	0.72	0.43	0.27	0.22	0.41
	Cu	0.51	0.37	0.15	0.08	0.28
	Cd	0.06	ND[b)]	0.05	0.03	0.05
Maize	Zn	0.24	0.12	0.16	0.08	0.15
	Cu	0.27	0.06	0.04	0.02	0.10
	Cd	ND	0.07	0.16	ND	0.12

[a)] Calculated as the percent of added metal.

[b)] Not detectable.

sorption coefficients, reflect the ability of TEs transfer in soil-plant systems. The BCF values of Zn, Cu and Cd in wheat and maize are shown in Table V. For wheat, the BCF values of grains for Cu (0.297) and Zn (0.546) were significantly higher than those of straw (0.137 for Cu and 0.140 for Zn), while the BCF values of grains for Cd (0.204) was significantly lower than those of straw (0.506). However, for maize, the BCF values of straw for Cu (0.424) and Cd (0.495) were significantly higher than those of grains (0.088 for Cu and 0.036 for Cd), which indicated lower translocation of Cu and Cd from maize straw to maize grains.

For different metals in grains of wheat and maize, the BCF values were in the order of Zn > Cu > Cd, but in straw of wheat and maize the BCF values were in an order of Cd > Cu > Zn. Jamali *et al.* (2009) also reported that the BCF values for wheat grains in the same order (Zn from 0.460 to 0.600, Cu from 0.207 to 0.526, and Cd from 0.179 to 0.417). But in the literature there was not always the case. Karami *et al.* (2009) studied heavy metal uptake by wheat from a SS-amended calcareous soil and observed that BCF values of metal in both grains (0.85, 0.20, and 0.09 for Cd, Zn, and Cu, respectively) and stalk (0.93, 0.12, and 0.10 for Cd, Zn, and Cu, respectively) followed the order of Cd > Zn > Cu. The higher BCF values of Cd and the lower BCF values of Zn and Cu were found in the study of Karami *et al.* (2009), compared to the study of Jamali *et al.* (2009) and the present study. Logan *et al.* (1997) concluded that crop uptake of Cd from the soil treated with low-Cd sludge would be less than that from the soil treated with a high-Cd sludge, even when actual Cd loadings were similar. Apparently, besides of soil properties, the Cd concentration as well as the ratio of Cd/Zn in SS may be important factors to control the transfer of Cd in soil-plant systems.

For SS treatments, the BCF value of Cd in wheat grains was lower and that of Zn in maize straw was higher than those of control (Table V). All other BCFs were not significantly different. The BCF value for Cd in wheat grains was 0.204. If the limit value of Cd in hygienic standard for grains (0.1 mg kg^{-1}, GB2715-2005) and the BCF value of 0.204 were used, the possible limit value of Cd in the soils can be calculated as 0.49 mg kg^{-1}, which is lower than the current standard of 0.6 mg kg^{-1} for the soils with pH > 7.5 from GB15618-1995 (SEPAC, 1995). The BCF value for Cd in maize grain (0.036) is much lower than that in wheat, which suggested that the transfer of Cd to maize grains was more difficult than that to wheat.

CONCLUSIONS

The low phytoavailability of Zn and Cu in SS was found when compared with corresponding water-solu-

TABLE V

Bioaccumulation factors of Zn, Cu, and Cd in plant straw and grains under the control and sewage sludge treatments

Crop	Item	Treatment	Zn	Cu	Cd
Wheat	Straw	Control	0.125±0.009[a)]	0.132±0.012	0.541±0.030
		Sewage sludge	0.137±0.009	0.140±0.004	0.516±0.025
	Grains	Control	0.489±0.015	0.281±0.003	0.270±0.019
		Sewage sludge	0.546±0.028	0.297±0.009	0.204±0.024*
Maize	Straw	Control	0.307±0.030	0.410±0.033	0.447±0.094
		Sewage sludge	0.394±0.0364*	0.424±0.007	0.495±0.079
	Grains	Control	0.406±0.007	0.091±0.010	0.044±0.017
		Sewage sludge	0.357±0.033	0.088±0.007	0.036±0.014

*Significant from the control at $P < 0.05$ level, as determined by the least significant difference test.

[a)] Means±standard errors.

ble metal salts in a short-term pot experiment, however, the difference in phytoavailability of Cu and Zn between SS and metal salts would decrease with long-term aging time in fields. The low phytoavailability of Cd from SS was also found when compared with Cd salt. Furthermore, there was a decrease in phytoavailability of soil Cd by SS application. Total Zn, Cu, and Cd in the soils increased linearly with SS application rates because there was relatively little amount removed by plant uptake ($< 1\%$). When SS application rates increased, Zn and Cu in wheat grains initially increased and then reached a plateau, while there was no significant effect on Cd in maize grains. The orders of bioconcentration factors of the metals were different between grains and straw (grains: Zn > Cu > Cd and straw: Cd > Cu > Zn). It was also found that wheat grains could accumulate more metals compared to maize grains. The results will be helpful in developing the critical loads of sewage sludge applied to calcareous soils.

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