

Copper and Zinc Uptake by Spring Wheat (*Triticum aestivum* L.) and Corn (*Zea mays* L.) Grown in Baiyin Region

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Zinc (Zn) and copper (Cu) are essential to human beings due to their important roles in various metabolic processes, but they are toxic or can induce human health problems when their concentrations are excessive or deficient. Many works had been carried out on the transfer and accumulation of Cu and Zn, particularly in excess amount, to plant parts and to human beings (Zheng and Chen, 1990; Peles, et al., 1996; Wang and Wu, 1998; Herawati, et al., 2000; Barman, et al., 2000; Hu, et al., 2000). Interactions between the two metals had been reported (Reboredo, 1994). Because these reports were base on the works done in laboratory conditions or in highly industrialized regions, information were scarce on the status of trace metals in gray calcareous soils and crops receiving industrial effluent in industrializing regions (Mench, et al., 1994; Ramachandran and D'Souza, 1998; Barman, et al., 2000). However, accumulation ratios of potentially toxic metals may vary from plant to plant and soil to soil, and determination from greenhouse experiments may not provide an actual measure of toxicity of excess Cu and Zn under field conditions (Kisku, et al., 2000).

Baiyin region, in Gansu province and with a surface of about 501 km², is geographically located in gray calcareous soil zone, and one of the major nonferrous metals mining and smelting bases of P. R. China was built there in the 1950's. The cultivated soils there had been polluted by heavy metals due mainly to wastewater irrigation and partially to atmospheric element deposition (Nan and Zhao, 2000). Spring wheat (*Triticum aestivum* L.) and corn (*Zea mays* L.) were chosen for survey because they are staples in the diet of local people. The high contents of the two essential elements in crop parts can be dangerous to people health through food chain (Schuhmacher, et al., 1994). In this work, our purposes were (a) to study the translocation patterns of the two metals in economic crop parts, (b) to find out the differences of element accumulation patterns between two crops, and (c) to correlate the accumulation of selected metals in crop tissues with their levels in soils.

MATERIALS AND METHODS

Samples of crops and soils were randomly collected from the region studied during harvest time in 1998. The region studied was divided into four areas according to types of irrigating water and locations, i.e., two areas irrigated with Yellow River water in Dongdagou (YDA) and Xidagou (YXA) basins, one with the mixture of wastewater and Yellow River water in Xidagou basin (MXA), and one with wastewater in Dongdagou basin (WDA).

Entire crops were collected by way of digging and the roots were washed in place and again back to laboratory to clean further. Soil samples were vertically collected with a depth of 0 to 20 cm from each crop root zone. Crop sample was separated into roots, stems, and grains in laboratory. The specimens were washed with tap water and distilled water followed by de-mineralized water. Special attention was given to the roots, which were scrubbed free of soil and rinsed thoroughly. All crop samples were stored in brown paper bags, dried in oven at 70 °C for 12 hours, and then ground in a stainless steel mill for metal analysis. Soil samples were air-dried at room temperatures and purified by passing through a 1 mm sieve in order to eliminate foreign matters. Fractions less than 1 mm were ground further in an agate mortar. Homogenized samples were sealed in polyethylene bags for analysis.

2.0 g of crop (root, stem, and grain) sample was dissolved in the mixture of H_2O_2 - HClO_4 - HNO_3 , and 0.5 g of air-dried soil sample in the mixture of HCl - HNO_3 - HClO_4 - HF . These samples were digested in a Teflon-PFA using MDS-9000 (ORIENT). Concentrations of selected heavy metals were determined by inductively coupled plasma atomic emission spectrometry (Ilia, et al., 1999). For all analyses control standard solutions were run at the start, during and at the end of sample runs to ensure continued accuracy. Analytical precision of the method was improved by including several duplicate samples (10% of total). Reproducibility was within $\pm 5\%$.

Data were analyzed using one-way ANOVA (LSD) and Pearson correlation. All statistical analyses were done through using statistical package SPSS8.0 and Excel 97 for Windows.

RESULTS AND DISCUSSION

Table 1 shows the concentration of copper and zinc in the crop parts and soils from four areas and the results of one-way ANOVA, and Table 2 gives the contents of metals studied from literatures. Arithmetic mean contents in soils for Cu were 26.03 ± 2.56 , 87.40 ± 62.24 , 37.19 ± 17.41 , and 199.26 ± 66.54 mg kg^{-1} for YXA, MXA, YDA, and WDA, respectively. Mean contents in soil for Zn were 52.53 ± 6.32 , 160.95 ± 129.58 , 63.14 ± 8.55 , and 235.01 ± 73.48 mg kg^{-1} for YXA, MXA, YDA, and WDA, respectively. Only at MXA and WDA the element

contents were remarkably higher than the soil metal background levels (19.7 for Cu and 55.1 for Zn, mg kg⁻¹ DW) reported by Wang and Wei (1995). These findings indicated that metal contents at MXA and WDA were significantly elevated through irrigating with industrial wastewater. MXA is one place close to the copper processing plant and other factories and can use the mixture of effluents from these factories and water from Yellow River. WDA is another place nearby the nonferrous smelters and can be irrigated with the compound of mining and smelting industrial effluent and domestic wastewater (Nan and Zhao, 2000).

Table 1. Concentrations (arithmetic mean \pm standard deviations) of Cu and Zn in the crop parts and soils from different areas of Baiyin region (mg kg⁻¹, DW)

Area	N	spring wheat		N	corn	
		Cu	Zn		Cu	Zn
YXA	Grain 6	2.12 \pm 0.70	23.08 \pm 5.88	5	3.34 \pm 1.46	16.38 \pm 4.71
	Stem 6	4.62 \pm 0.79	36.96 \pm 4.14	5	5.40 \pm 2.30	15.43 \pm 1.25
	Root 6	7.34 \pm 0.78	37.41 \pm 5.05	5	16.74 \pm 2.10	33.24 \pm 7.80
	Soil 6	26.03 \pm 2.56	52.53 \pm 6.32	5	25.89 \pm 2.78	52.79 \pm 6.89
MXA	Grain 18	3.47 \pm 1.03	31.08 \pm 7.38	11	4.13 \pm 1.06	15.71 \pm 3.66
	Stem 18	5.62 \pm 1.37	33.31 \pm 6.70	11	10.14 \pm 2.74	21.27 \pm 7.66
	Root 18	15.63 \pm 9.67	33.94 \pm 10.11	11	25.37 \pm 5.87	61.40 \pm 18.23
	Soil 18	87.40 \pm 62.24	160.95 \pm 129.58	11	54.39 \pm 8.70	95.01 \pm 19.67
YDA	Grain 10	2.91 \pm 0.65	30.63 \pm 6.09	8	4.53 \pm 1.47	15.79 \pm 2.96
	Stem 10	4.54 \pm 0.65	33.05 \pm 5.96	8	6.61 \pm 3.40	20.16 \pm 3.67
	Root 10	8.68 \pm 7.18	33.80 \pm 9.74	8	22.28 \pm 9.43	50.25 \pm 6.40
	Soil 10	34.72 \pm 16.38	63.14 \pm 8.55	8	37.19 \pm 17.41	64.65 \pm 8.37
WDA*	Grain 13	6.84 \pm 1.34	42.03 \pm 17.92	9	3.60 \pm 1.31	22.85 \pm 3.20
	Stem 13	6.12 \pm 1.88	83.01 \pm 29.39	9	24.09 \pm 6.46	42.05 \pm 18.97
	Root 13	40.10 \pm 27.59	229.72 \pm 104.68	9	108.89 \pm 24.86	145.45 \pm 46.28
	Soil 13	199.26 \pm 66.54	235.01 \pm 73.48	9	181.68 \pm 49.12	227.35 \pm 67.33

N=Sample size. Detection limits: <0.005ppm for Cu, <0.005ppm for Zn. An asterisk indicates this area, except for grain copper of corn, has significant difference with others by LSD at p<0.05.

Copper contents in wheat grain were 2.12 \pm 0.70, 3.47 \pm 1.03, 2.91 \pm 0.65, and 6.84 \pm 1.34 mg kg⁻¹ for YXA, MXA, YDA, and WDA, respectively. Zinc contents in wheat grain were 23.08 \pm 5.88, 31.08 \pm 7.38, 30.63 \pm 6.09, and 42.03 \pm 17.92 mg kg⁻¹ for YXA, MXA, YDA, and WDA, respectively. Most of the metal contents were either below or practically identical to the background values (BV) (6.72 for Cu and 34.6 for Zn, mg kg⁻¹ DW) reported by Chen (1996). Only at WDA the content of zinc in wheat grains was slightly higher than the BV. However, all levels of the trace metals studied were lower than the hygienic standards of P. R. China (Table 2).

Table 2. Concentrations of selected heavy metals from the literatures (mg kg⁻¹, DW)

Element	Cu	Zn	Reference
Background value ^a			Chen H. (1996)
Wheat	6.72	34.6	
Corn	1.47	16.6	
Maximum safe intake level	30.0		FAO/WHO
Hygienic standards for grain	10.0	50.0	NSBC ^b
Maximum safe intake content	6.0	40.0	Bowen (1979)

^a = The value indicates that in grain in P. R. China.

^b = National Standard Bureau of P. R. China (GB15199-94, GB13106-91)

The levels of copper in corn grain were 3.34 ± 1.46 , 4.13 ± 1.06 , 4.53 ± 1.47 , and 3.60 ± 1.31 mg kg⁻¹ for YXA, MXA, YDA, and WDA, respectively. These values were 2, 3, 3, and 2 times higher than the BV (Table 2). The levels of zinc in corn grain were 16.38 ± 4.71 , 15.71 ± 3.66 , 15.79 ± 2.96 , and 22.85 ± 3.20 mg kg⁻¹ for YXA, MXA, YDA, and WDA, respectively. These values had the same magnitude with the BV. All measures of the trace elements in grains were lower than the hygienic standards of P. R. China (Table 2).

The results of one-way ANOVA showed that the metal contents in the crop parts and soils from YXA, YDA and MXA were not different. However, the levels of the two metals in the crops parts and soils from WDA significantly different at $p < 0.05$ from those from others except for zinc concentration of corn grain can be observed. These findings suggest that the increasing in grain contents of the elements studied in agro-system be confirmed in the region investigated, especially at WDA, although contents of the trace metals studied in crop grains were safe to local people.

Table 3. Accumulation ratios of heavy metal concentration between crop parts and soils and their proportions

	Cu				Zn			
	G/S	St/S	R/S	G:St:R	G/S	St/S	R/S	G:St:R
Spring wheat (<i>Triticum aestivum</i> L.)								
YXA	0.08	0.18	0.28	1:2:4	0.44	0.70	0.71	1:2:2
YDA	0.09	0.13	0.25	1:1:3	0.48	0.52	0.54	1:1:1
MXA	0.04	0.06	0.18	1:2:5	0.19	0.21	0.21	1:1:1
WDA	0.03	0.03	0.20	1:1:7	0.18	0.35	0.98	1:2:5
Corn (<i>Zea mays</i> L.)								
YXA	0.13	0.21	0.65	1:2:5	0.31	0.29	0.63	1:1:2
YDA	0.12	0.18	0.90	1:2:8	0.24	0.31	0.78	1:1:3
MXA	0.08	0.19	0.47	1:2:6	0.17	0.22	0.65	1:1:4
WDA	0.02	0.13	0.60	1:7:30	0.10	0.19	0.64	1:2:6

G:St:R denotes grain:stem:root. G = grain. St = stem. R = root. S = soil.

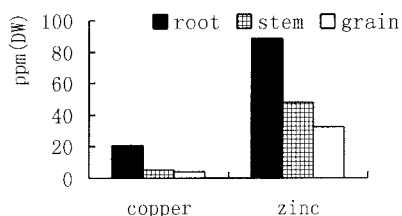


Figure 1. Boxplots of Cu and Zn contents in roots, stems and grains of wheat for whole region

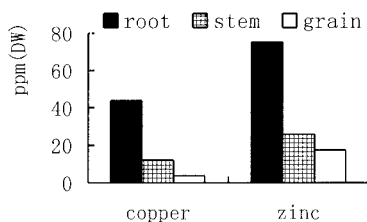


Figure 2. Boxplots of Cu and Zn contents in roots, stems and grains of corn for whole region

Ratios of selected element contents between crop tissues and soils are listed in Table 3. Significant difference among these two element concentrations in the crop parts and soils can be observed. Copper contents in plant parts were several or even dozens fold lower than the metal levels in corresponding soils, and zinc contents only several fold lower than the soil content. The metal concentrations at four areas studied were highest in roots, followed by stems, and then low in grains (Fig.1, 2). These findings were in agreement with the previous experiment results (Wang and Wu, 1998). In our investigation, wheat roots contained 3 to 7 times the content found in grains for Cu, and 1 to 5 times for Zn. Corn roots contained 5 to 30 fold the content determined in seeds for Cu, and 2 to 6 fold for Zn. These findings confirmed that the order of element translocation proportions from root to other crop parts was $Zn > Cu$, and the ability of crop roots absorbing metals was ranked in the following order: corn root $>$ wheat root. The reasons for these results may be that element Zn is the most bio-available metal in polluted soils, and the absorption rate of Cu by plant roots are among the lowest for essential elements (Adriano, 1986). The metal accumulation in crop tissues are generally a function of the metal concentration in soil and the soil factors but the levels of absorption differs according to crop species and tissues.

These findings suggest that the crops studied be selected for cultivation on the field having high levels of the metal pollutants due to least quantity of metals accumulation within limits of the hygienic standards in edible parts. They also make a suggestion that the soils contaminated by element Zn and Cu be phyto-remedied by way of digging out the roots during harvest time in order to minimize the soil metal contents.

Pearson correlation coefficients were found between concentrations of the metals studied in the soils and crop structures (Table 4). The relationships between metals studied in the soil and plant parts were positively significant except for Cu in corn

grain and Zn in wheat grain. These findings confirmed that increasing of the soil metal contents can elevated the metal concentrations in crop parts. These discoveries in present investigation are in accordance with the previous field reports. Hu et al.(2000) pointed out that there existed a positive index equation (line equation) of relationships between copper contents in the soil and rice parts (straw, shell, and grain). Dudka et al. (1996) described the tranfer of zinc from soil to barley parts (straw and grain) with the positive plateau models.

Table 4. Pearson correlation analysis of selected element concentrations in the soil (s) and plant parts: root (r), stem (st), and grain (g)

	Cur	Cust	Cug	Znr	Znst	Zng
Spring wheat (<i>Triticum aestivum</i> L.)						
Cus	0. 732**	0. 295*	0. 769**	0. 733**		
Zns	0. 498**			0. 463**	0. 478**	ns
Corn (<i>Zea mays</i> L.)						
Cus	0. 968**	0. 909**	ns	0. 680**		
Zns	0. 796**			0. 861**	0. 733**	0. 491**

ns = not significant. ** Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Interactions of copper and zinc may be expounded by the positive significant Pearson's correlation among the two elements in the soil and crop parts (Table 4). The coefficients between root copper content and soil zinc content were 0.5 and 0.79 for wheat and corn ($p<0.01$), respectively, and those between root zinc level and soil copper level 0.73 and 0.68 for wheat and corn ($p<0.01$), respectively. These findings implicated that the two elements acted synergistically on the root metal absorption under field condition, which agrees with the previous pot experiment findings of Zheng and Chen (1990) who pointed out that the coexist of the metals can elevate the absorption of rice root for each other. However, the results in present work are contrary to those of Adriano (1986) who reported that copper interacted antagonistically with zinc on plant growth, and not in consistent with the findings of Reboredo (1994) who concluded that the uptake and accumulation of copper by *Halimione* was independent of soil zinc level. These divergent and sometimes contrary findings agree with Wong and Beaver (1981), who stated "simulations of metal interactions in laboratories are not likely to produce similar toxic effects to those observed in the field". These differences of results between pot experiments and field studies suggest that the mechanisms of interaction among metals under field conditions be exploit further in the following researches in order to set up some proper guidelines for human behaviors.

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