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Soil Amendment and Accumulation of Heavy Metals in Meadow Burozem-Crop Systems

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Soils polluted by heavy metals can induce various environmental problems. Generally speaking, soil pollution by heavy metals results from various human activities including discharge of industrial waste, metallurgical operations, battery-recycling and vehicle emissions (Peters and Shem, 1992; Zhou and Huang, 2001). As a result of increased input from industry, traffic and agriculture, the average content of heavy metals in soils of industrialized countries has increased considerably (Salomons and Stigliani, 1995). Soils polluted by heavy metals have been long recognized as a serious problem in the industrialized parts of Western Europe (Alloway, 1995) and North America (Hutchinson and Whitby, 1977) and it has recently become apparent that the problems in Russia and Eastern Europe countries are in many cases even more extensive (Kozlov *et al.*, 1993). In China, soil pollution by heavy metals is becoming increasingly serious. For example, soil Cd in the Zhangshi Agro-Irrigation Area of western Shenyang, China, was up to 7 mg kg^{-1} (Chen, 1985).

Metal leaching, toxicity and uptake by living organisms depend on soil chemical and physical properties as well as the physiological properties of organisms present in, or growing on the soil (Hopkin *et al.*, 1993). Soil parameters that affect metal solubility in soils include pH, organic matter, clay content, humidity, temperature, Eh and CEC (Sun *et al.*, 2001). With an increase in soil pH, organic matter and clay content, the solution concentrations of most cationic heavy metals decreases due to adsorption (McBride, 1994). The main emphasis on restoring industrial barren areas has been to treat the soil with limestone and phosphorus fertilizer, and to establish vegetation for covering of grasses and shrubs, on which a cover of broad-leaved trees gradually develops (Lautenbach *et al.*, 1995). Liming has been proved to be an appropriate measure for reducing heavy-metal toxicity (Chen, 1981).

Combined pollution is a common phenomenon in the soil environment, although pollution caused by individual heavy metals occasionally occurs in nature (Zhou,

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Table 1. Physical and chemical properties and heavy metal levels of the tested soil*.

Organic matter (%)	pH (soil:water= 1:10)	CEC meq (100g soil)$^{-1}$	Background level (mg kg^{-1})			
			Cd	Pb	Cu	Zn
1.55	6.5	23.7	0.13	25.7	19.1	49.8

* Surface soil, 0-20 cm; soil texture, medium loam.

1995). In most cases pollution results from the coexisting and co-functioning of multiple metals. In recent years, the study of combined pollution has become a focus in soil-environmental science (Zhu and Zhou, 1998; Zhou, 1999).

Thus, the main objectives of this study were to evaluate the effects of different modifier application rates on crop growth and metal accumulation by rice and soybean plants, and the joint effects of Cd, Pb, Cu, and Zn on migration and accumulation in soil-plant systems with different application of modifiers, and to determine concentrations of heavy metals accumulated in unpolished rice and soybean grains.

MATERIALS AND METHODS

The tested soil is meadow burozem, collected from the Ecological Station, Institute of Applied Ecology in Shilihe, Shengyang, China. Physical, chemical properties and heavy metal background levels of the soil are listed in Table 1. The tested crops are soybean *Glycine max* [L.] Merr Tie-Feng 24 and rice *Oryza sativa* No. 241.

There were 8 treatments in the pot-culture experiment. Each treatment duplicated 3 times. Each pot contained 2.5 kg of the tested soil. The tested modifiers added to pots were lime, humic acid and mineral acids. Forms of the tested heavy metals Cd, Pb, Cu and Zn were $CdCl_2{\cdot}2.5H_2O$, $Pb(CH_3COO)_2{\cdot}3H_2O$, $CuSO_4{\cdot}5H_2O$, and $ZnSO_4{\cdot}7H_2O$, respectively. Tested concentrations of the heavy metals and modifiers are showed in Table 2. Having been sieved at 5mm, soil samples were well mixed with various heavy metals and modifiers, China pots were then filled with the mixture (rice pot, Φ = 18cm, H = 20cm; soybean pot, Φ = 24cm, H = 22.5cm). Soybean and rice seedlings were planted in the potted soils after an equilibration for 2 wks.

After harvest, the soil samples were air-dried, sieved through 0.149 mm and stored in plastic bags for analysis. Crop samples (root, stem, grain) were air-dried in natural conditions and stored in paper bag for analysis. After the samples were digested in concentrated HNO_3 :$HClO_4$ (3:1), heavy metals Cd, Pb, Cu and Zn in

Table 2. Experimental treatment and tested concentrations of heavy metals and modifiers.

No.	Treatment	Concentration	
		Heavy metal (mg kg^{-1})	Modifier
CK			
C	Cd + Pb + Cu + Zn	1.5 + 300 + 100 + 200	
$C + L_1$	Cd + Pb + Cu + Zn + lime	1.5 + 300 + 100 + 200	1.5 g kg^{-1}
$C + L_2$	Cd + Pb + Cu + Zn + lime	1.5 + 300 + 100 + 200	3.0 g kg^{-1}
$C + H_1$	Cd + Pb + Cu + Zn + humic acid	1.5 + 300 + 100 + 200	2.0 %
$C + H_2$	Cd + Pb + Cu + Zn + humic acid	1.5 + 300 + 100 + 200	4.0 %
$C + A_1$	Cd + Pb + Cu + Zn + acid	1.5 + 300 + 100 + 200	pH 5.0
$C + A_2$	Cd + Pb + Cu + Zn + acid	1.5 + 300 + 100 + 200	pH 4.0

the tested soil and crop samples were determined using the atomic absorption spectrophotometer method.

RESULTS AND DISCUSSION

The data in Table 3 and Table 4 indicated that the modifiers evidently affected crop growth in the pot-culture experiment. The height of soybean and rice plants treated with heavy metals (Cd + Pb + Cu + Zn) + lime and + humic acid was higher than that with only heavy metals (Cd + Pb + Cu + Zn). In other words, lime and humic acid treatment are of great advantage to growth of crops in soils polluted by heavy metals. The height of soybean and rice plants treated with heavy metals (Cd + Pb + Cu + Zn) + acid was greatly decreased, up to 10-18 cm as compared with only heavy metals (Cd + Pb + Cu + Zn) treatment. The yield of soybean and rice treated with mineral acids was decreased 28.21 % and 70.13 %, respectively. The acid treatment could greatly enhance the activity of heavy metals in soils, thus restrained crop growth. The height, dry weight of aboveground plant parts, and yield of soybean plants were lower than these of rice plants treated with heavy metals (Cd + Pb + Cu + Zn) + acid (pH4.0, 5.0). It indicated that soybean plants become more sensitive and easier to be harmed as compared with rice plants.

Synthetic effects of combined pollution of heavy metals on crops can be expressed in various patterns. For example, Zhang *et al.* (1986) put forward the Zn equivalent conception, Azpiazu (1986) adopted the iron impulsion, and Romero *et al.* (1987) deduced the pollution indexes of plants and soils. The ionic impulsion is the parameter related to heavy metals concentration and can be

Table 3. Effects of various modifiers on soybean in the pot-culture experiment.

Treatment No.	Plant height	Dry weight of aboveground parts (g pot^{-1})	Grain weight (g pot^{-1})	Yield (%)
CK	68.00	23.57	7.80	100.00
C	53.00	20.83	7.20	92.30
$C + L_1$	63.67	20.40	7.10	91.02
$C + L_2$	67.33	21.43	7.36	94.36
$C + H_1$	56.67	22.67	7.30	93.59
$C + H_2$	53.33	21.90	9.10	116.67
$C + A_1$	41.67	10.67	5.60	71.79
$C + A_2$	35.33	5.60	2.33	29.87

Table 4. Effects of various modifiers on rice in the pot-culture experiment.

Treatment No.	Plant height	Tillering No. (ind pot^{-1})	Dry weight of aboveground parts*	Grain weight*	Yield (%)
CK	91.25	16	72.80	34.80	100.00
C	89.00	13	63.57	31.40	90.23
$C + L_2$	93.00	14	67.25	35.50	102.01
$C + H_1$	93.70	14	63.73	30.86	88.69
$C + H_2$	93.00	14	69.40	32.90	94.54
$C + A_1$	86.70	11	48.57	22.83	65.60

* Unit is g pot^{-1}.

calculated using following formula:

$$I=\Sigma C_i^{1/n} \tag{1}$$

Where C_i is metal concentration (mmol l^{-1}), n represents metal oxidative number. The ionic impulsion of different treatment is showed in Table 5. The results showed that the ionic impulsion of roots treated with heavy metals (Cd + Pb + Cu + Zn) + lime was lower than that with only heavy metals (Cd + Pb + Cu + Zn). The lime treatment decreased heavy metal contents in the crops as compared with only heavy metals treatment and reduced the damage to the crops. The ionic impulsion of roots treated with heavy metals (Cd + Pb + Cu + Zn) + humic acid was close to that with only heavy metals (Cd + Pb + Cu + Zn), but the growth and development of the crops treated with the heavy metals + humic acid were better than these with only heavy metals treatment. Perhaps, humic acid had a definite fertility effect on crop development. The ionic impulsion of roots treated with acid (pH4.0, 5.0) was higher than that with other treatments.

The concentrations of heavy metals accumulated in different parts of the two

Table 5. The ionic impulsion of the crops with different treatments.

Treatment	Ionic impulsion	
	Soybean root	Rice root
CK	2.31	2.76
C	3.74	5.55
$C + L_1$	3.13	
$C + L_2$	2.90	4.01
$C + H_1$	4.32	5.59
$C + H_2$	4.32	4.39
$C + A_1$	4.90	
$C + A_2$	6.85	6.94

Table 6. Content of heavy metals in different tissue parts of soybean plants (mg kg^{-1})*.

		CK	C	$C+L_1$	$C+L_2$	$C+H_1$	$C+H_2$	$C+A_1$	$C+A_2$
Cd	Root	0.21^e	1.45^c	1.00^d	0.70^{de}	1.00^d	1.33^{cd}	3.57^b	10.90^a
	Stem	0.19^d	0.68^c	0.29^d	0.25^d	0.78^c	0.81^c	2.75^b	8.27^a
	Grain	0.09^e	0.23^c	0.13^{de}	0.12^{de}	0.16^d	0.17^{cd}	0.31^b	0.77^a
Pb	Root	3.46^f	43.5^d	37.8^d	23.1^e	43.0^d	58.9^c	122.3^b	252.9^a
	Stem	2.90^d	13.0^{bc}	11.5^c	8.40^c	16.7^b	15.1^{bc}	17.90^b	44.00^a
	Grain	0.38^b	0.23^b	0.36^{ab}	0.29^{ab}	0.49^{ab}	0.35^{ab}	0.35^{ab}	0.60^a
Cu	Root	12.1^d	36.0^c	30.4^c	26.1^{cd}	26.2^c	34.8^c	86.2^b	158.7^a
	Stem	5.54^c	6.79^c	6.83^c	6.64^c	6.86^c	7.15^c	15.10^b	29.70^a
	Grain	9.31^b	11.6^{ab}	8.42^b	8.25^b	9.96^b	8.62^b	8.47^b	13.4^a
Zn	Root	50.7^d	140.2^c	72.2^d	57.1^d	300.9^b	275.3^b	508.9^a	
	Stem	50.6^d	135.5^c	53.3^d	51.2^d	224.8^b	209.0^b	287.9^a	
	Grain	46.1^d	57.8^c	55.8^c	55.5^c	72.2^b	65.9^b	85.9^a	

* a, b, c, d, and e represent the result of multi-comparison among different treatments (significance level $\alpha < 0.05$).

crops are showed in Table 6. The heavy metal contents absorbed by the crops were decreased with increasing lime application rates. Because the lime treatments significantly increased soil pH as compared with the control (soil pH was from 6.30 to 6.72-7.42), the activity of heavy metals in the soil-crop systems were weaken. The element contents with heavy metals + lime treatment were thus decreased comparing with only heavy metals treatment in crops.

The lime treatments increased soil pH as compared with only heavy metals treatment (soil pH was increased from 6.30 to 7.46). The content of heavy metals accumulated in rice plants treated with heavy metals + lime was close to those treated with only heavy metals. This is mainly caused by different biological

Table 7. Content of heavy metals in different tissue parts of rice plants (mg kg^{-1})*.

		CK	C	C + L_2	C + H_1	C + H_2	C + A_2
Cd	Root	0.41^{c}	2.50^{c}	2.33^{b}	2.46^{b}	2.30^{b}	4.98^{a}
	Stem	0.095^{d}	0.62^{c}	0.60^{c}	1.00^{b}	1.37^{a}	1.12^{ab}
	Grain	0.019^{d}	0.12^{c}	0.11^{b}	0.12^{b}	0.14^{b}	0.19^{a}
Pb	Root	14.9^{e}	425.0^{b}	354.6^{c}	413.4^{bc}	328.5^{c}	570.1^{a}
	Stem	5.39^{b}	6.57^{b}	7.23^{b}	9.65^{ab}	12.3^{a}	9.48^{ab}
	Grain	0.22^{ab}	0.29^{ab}	0.31^{ab}	0.35^{a}	0.19^{ab}	0.12^{b}
Cu	Root	12.8^{e}	85.2^{c}	85.2^{c}	104.2^{b}	107.1^{b}	151.4^{a}
	Stem	6.13^{c}	8.86^{c}	10.3^{bc}	12.8^{b}	13.7^{b}	18.2^{a}
	Grain	3.02^{b}	3.95^{b}	4.06^{b}	4.53^{ab}	5.18^{ab}	5.53^{a}
Zn	Root	80.1^{d}	123.2^{bc}	123.7^{bc}	148.6^{bc}	179.8^{b}	273.2^{a}
	Stem	63.4^{b}	71.9^{b}	68.7^{b}	124.2^{a}	112.4^{ab}	148.3^{a}
	Grain	25.9^{b}	25.7^{b}	26.1^{b}	27.3^{b}	30.5^{ab}	32.5^{a}

* a, b, c, d, and e represent the result of multi-comparison among different treatments (significance level $\alpha < 0.05$).

properties between rice and soybean plants and reductive conditions of rice plants. The humic acid treatments led to a decrease in Cd concentration of soybean plants as compared with only heavy metals treatments, the element concentration with other treatments was close to those treated with only heavy metals (Cd + Pb + Cu + Zn). Because the humic acid treatments decreased soil pH from 6.30 to 5.06-5.53, heavy metals in soils became volitant and were easily translated to crops and accumulated in crops. The humic acid can influence bioavailability of heavy metals in soils by way of this pattern. The contents of Cd, Pb, Cu and Zn absorbed by rice plants could be enhanced under the condition of the acid treatment, because soil pH was decreased from 6.3 to 5.69-5.85 by acid addition. After having added acid, heavy metals accumulated in the crops were evidently higher than these treated with only heavy metals (Cd + Pb + Cu + Zn). The concentrations of Cd, Pb, Cu, Zn in soybean grains were higher than these in rice grains. As for different treatment , the contents of Cd and Cu in soybean stems were lower than those in rice stems, the accumulation of Pb and Zn in soybean stems was higher than that in rice stems, the absorption of Cd, Pb and Cu by soybean roots was lower than that by rice roots. This indicated that the characteristic of accumulation and translation of different heavy metals is greatly different. The distribution pattern of heavy metals in soybean and rice plants was in sequence root > stem > grain. The distribution pattern of Cu was different from that of other heavy metals in soybean and was in the order of root > grain > stem. Heavy metal contents in roots of rice and soybean plants were higher than those in aboveground plant parts. Heavy metals were mostly accumulated in roots of crops.

Many factors affect migration ability of heavy metals in soils, such as pH, organic matter, clay contents, CEC and Eh. The migration of Cd, Pb, Cu, and Zn were affected by some modifiers (humic acid, lime, acid). An increase in soil pH can usually reduce the activity of heavy metals and decrease the accumulation of heavy metals in grain. Because negative charges on soil colloid are decreased with acid treatments, absorption of heavy metals on soils is decreased. The activity of heavy metals in soils is thus increased and easily translated to crop seeds. Generally speaking, organic matter can fix heavy metals in soils. The content of organic matter was increased from 1.5 % to 1.8-2.0 % by the addition of humic acid, but the concentrations of heavy metals in the crops treated with humic acid were higher than those treated with only heavy metals. On the one hand soil pH was decreased from 6.3 to 5.69-5.85 by the application of humic acid, on the other hand new activated humic matter was formed by application of humic acid. Thus heavy metals are not easy to fix, and new activated humic matter can greatly promote the movement of heavy metals in soils. Effects of the modifiers on migration of heavy metals is in the sequence acid treatment > humic acid treatment > lime treatment.

Absorption coefficients can indirectly reflect the migration properties of heavy metals in soil-plant systems and can be expressed by following formula:

$$K_{ac} = P_{crop}/P_{soil} \tag{2}$$

Where K_{ac} is absorption coefficient, P_{crop} is the accumulation of heavy metals in crop grain, and P_{soil} is the amount of heavy metals added to soils. According to the formula calculation, the absorption coefficient of Cd, Pb, Cu and Zn by soybean plants was 0.022-0.45, 0.00035-0.00071, 0.024-0.041 and 0.0469-0.298 respectively. The absorption coefficient of Cd, Pb, Cu and Zn by rice plants was 0.061-0.115, 0.00026-0.00045, 0.0093-0.025 and 0.007-0.033 respectively. The absorption coefficient of heavy metals by crops is in the order Cd > Zn > Cu > Pb. The migration ability of Cd and Zn is higher than that of Cu and Pb, in particular, most of the Pb in crops was detained in roots, in other words, some Pb from soils was translated to grain. Zn should be relatively mobile in soils. Similar results were reported by Ma and Rao (1997). Although Cd generally is present in much smaller concentrations than Zn, Cd is also considered to be mobile. Similar results can be found in references (Alloway and Jackson, 1991; Schmitt and Sticher, 1991). Heavy metals Zn and Cd have similar chemical properties and behavior in soils (Tyler, 1978; Bergkvist,1986), but Pb is much less mobile (Camobreco *et al.*, 1996). The 40% amount of crop absorption moves to grain for Cd and Zn elements. Cd and Zn are easily accumulated in grain. Cd is harmful to human health. The excessive Cd in grain can damage human health. Zn is an essential element for the growth of the human body and crop growth. If excessive Zn occurred in crops, it is not advantageous to crop growth and damages human health via the food chain. The migration ability of different heavy metals is related to the absorption characteristics of heavy metals in soils. After Cd, Pb, Cu and Zn were added to soils, soils can better absorb Pb and Cu; absorption ability for Cd and Zn is weak. The migration of Cd and Zn are stronger than Pb and Cu in soil.

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