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Compound pollution of Cd, Pb, Cu, Zn, As in plant-soil system and its prevention*

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Abstract——By means of both pot and field tests, this paper studied the contents of Cd, Pb, Cu, Zn and As and their ecological effects on plant-soil system, in tissues of crops and soil microorganisms. It was found that there exist synergistic effect among these five elements, especially for Cd in combination.

The reclamation of soil polluted by these elements in combination is rather difficult to be carried out. The distinctive ecological and chemical behaviors between Cd and As make various reclamation measures less applicable, and thus, further research measures are necessary.

Keywords: compound pollution; plant-soil system; heavy metals.

1 Introduction

In most cases, pollution is resulted by coexisting and co-functioning of multiple metals. The interactions between different elements make the toxic effect of pollutants in combination on ecosystem differ from that of single pollutants. In recent years, the study on compound pollution has become a focus in environmental science.

E. F. Bingham(Bingham, 1980), A. Wallace(Wallace, 1982), M. N. Azpiazu(Azpiazu, 1986) and F. Romero(Romero, 1987) investigated the compound pollution of heavy metals. In China, the research on environmental capacity of soil was conducted from 1983 to 1990, and the technical guidance of our research is adding single element into soil and observe its short-term effect in pot tests. The results obtained appeared to be deviated from actual situation. Zheng (Zheng, 1989) and Chen(Chen, 1992) studied the effect of Cu, Zn, Pb, Cd, Ni on lowland rice in seedling period in pot test. Xu(Xu, 1993) studied the effect of Cu, Pb, Cd, As on wheat seedling.

This experiment is characterized by:

Selecting a group of pollutants Cd, Pb, Cu, Zn and As in plant-soil system as tested objective, as these elements are representative pollutants coming from Pb-Zn mine, smelting wastewater discharge and gas emission and there are many areas polluted by these elements in China, for example, Zhangshi Irrigating Area in Shenyang.

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Designing three levels of pollutants: Change the large concentration intervals and design the maximum permissive concentration as the highest level (Wu, 1991).

Both field and pot test, focusing on long-term field test to approach the actual situation.

The pot and field tests had been conducted for five years from 1990 to 1991 and 1992 to 1994, respectively, including compound pollution test and pollution prevention test. The interaction among the elements will be discuss it in separate paper later.

2 Materials and methods

2.1 Tested soil

Soil tested is meadow burozem, collected from Ecological Station at Institute of Applied Ecology, the Chinese Academy of Sciences, Shengyang. Its physical and chemical properties as well as the metal background levels are shown in Table 1.

Table 1 Basic properties of tested soil*

Organic matter, %	pH (Water)	CEC, mol/100μg soil	Background value of heavy metal, mg/kg				
			Cd	Pb	Cu	Zn	As
1.79	6.5	23.7	0.13	25.7	19.1	49.8	10.4

* Surface soil(0—20cm) soil texture is medium loam

2.2 Selected crops

The crops selected are soybean intercropped with corn, wheat lowland rice, trees and so on. 2.5kg soil/pot in pot test with 3 replicates. $8m^2$ area in field plot.

2.3 Experimental design

2.3.1 Concentrations of pollutants

Level 1: Control

Level 2: low level, is one third of level 3

Level 3: high level, is the recommended standard of soil environment(Table 2).

Table 2 Input pollutant concentration*

(Unit: mg/kg)

Treatment	Element				
	Cd	Pb	Cu	Zn	As
Low dose	0.5	100	33	66	10
High dose	1.5	300	100	200	30

* Element compound are: Cd, $CdCl_2$; Pb, $Pb(CH_3COO)_2$; Cu, $CuSO_4$; Zn, $ZnSO_4$; As, Na_2HAsO_4

2.3.2 Reclamation design

Modifiers in pot test include lime, humic acid and mineral acids, their concentrations are illustrated in Table 6.

Modifiers in field test are lime plus Ca-Mg-P fertilizer, with 1875 kg lime/ha and 3750 kg Ca-Mg-P fertilizer/ha.

2.4 Analytical methods of determination

Soil and crops were prepared for As analysis by AgDDC-721 spectrophotometer, soil samples are digested in conc(3HCl:1HNO_3) and 1:1 H_2SO_4 and crops are digested by HNO_3-$HClO_4$.

For determining Cd, Pb, Cu and Zn in soil and crops, samples were digested in HNO_3-$HClO_4$ and analyzed by atomic absorption spectrophotometer, Hitach 180—80.

3 Results

3.1 Ecological effect of compound pollution

3.1.1 Effect of compound pollution on yield of selected crops

It is demonstrated in Table 3 that the tested concentrations of the pollutants resulted in a decreased crops yield by 5%—10%, with smaller drop in field than in pot test. There are no significant inhibition on crop growth, which meets the requirement designed.

3.1.2 Effect of compound pollution on element content in crops tissue

Element contents in various parts(root, stem and leaf, grain) of selected crops were analyzed and the results obtained can be seen in Figs, 1, 2, and 3(data in the appendix).

Table 3 Effect of compound pollution on biomass of crops

Test	Crop	Treatment	Plant height, cm	Dry weight of above-ground of plant*	Grain weight*	Yield, %
Pot test	Soybean	Control	68.0	23.57	7.8	100
		Low dose	63.3	23.23	7.1	91.02
		High dose	53.0	20.83	7.2	92.30
	Lowland rice	Control	91.3	92.80	34.8	100
		Low dose	90.0	70.40	32.1	92.40
		High dose	89.0	63.57	31.4	90.23
Field test	Soybean	Control	85	5.16	2.42	100
		Lowdose	88	5.95	2.45	101.20
		High dose	78	5.00	2.35	97.10
	Lowland rice	Control	84	14.44	7.92	100
		Low dose	79	14.14	7.67	96.84
		High dose	81	13.53	7.38	93.18

* The unit is g/plot test and kg/plot in field test

The contents of Cd and Zn in soybean grain of pot test are 0.228 and 54.42 mg/kg, respectively. With field test, Cd and Pb in rice gain are 0.389 and 2.250 mg/kg, Cd and Zn in wheat grain are 0.323 and 62.26 mg/kg, Cd in soybean grain is 0.200 mg/kg. All these values are beyond the standard for food and health in China(Cd 0.2mg/kg, Pb 1.0mg/kg, Cu

20mg/kg, Zn 50mg/kg and As 0.7mg/kg), which suggests that the application of environmental standard based on single element will cause the going beyond of standard for the food produced in area with compound pollution.

Compound pollution enhances the adsorption of Cd and causes the drop of threshold level of Cd in soil. The adsorption of Cd will be stimulated by the coexisting of Cu, Zn and As. It also can be enhanced by low level of Pb, inhibited while Pb is at higher level(Yu, 1995).

Based on the single element pot test with meadow burozem in the past, 10 mg/kg of Cd, > 2000mg/kg of Pb and > 60mg/kg of As in soil will cause 0.15mg/kg Cd, 1.0mg/kg Pb and 0.4 mg/kg As in rice, respectively. Now, only adding 1.5mg/kg Cd, 300mg/kg Pb and 30mg/kg As into soil can cause 0.21—0.85mg/kg Cd, 1.19-2.25 mg/kg Pb and 0.576—0.79 mg/kg As in rice for compound pollution, thus resulting in soil threshold level of Cd in soil dropping by 4—6 times, Pb dropping by 7 times and As dropping by 2 times.

3.1.3 Effect of compound pollution on absorption coefficient of the crops

The ration of crop grain absorption to the input is assumed as absorption coefficient. By comparing the absorption coefficients of single element with those of pollutants in combination in the same type of soil, it is found that the latter is larger, with the absorption of Cd, Pb, Cu and As increasing by 10—100 times(Table 4).

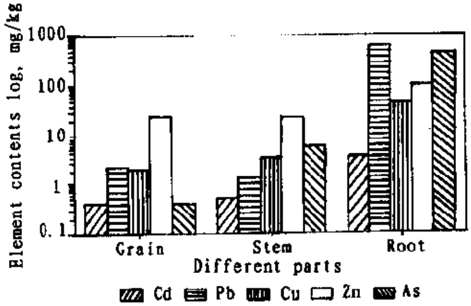

Fig. 1 Heavy metal contents in rice

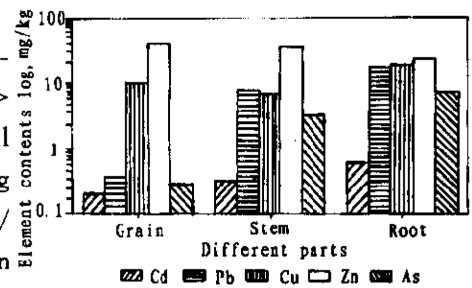

Fig. 2 Heavy metal contents in soybean

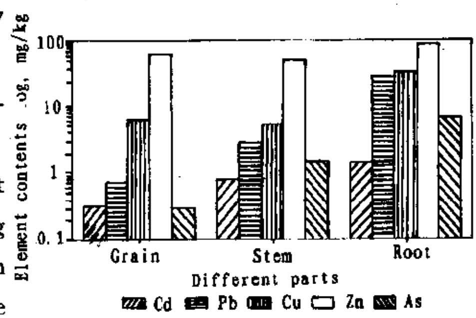

Fig. 3 Heavy metal contents in wheat

Table 4 Coefficient of absorption by grain of selected crops(pot test)

Elements	Compound pollution, high dose	Single element pollution
Cd	Cd 1.5mg/kg	Cd 5—10mg/kg
	$6.13-11.47\times10^{-2}$(lowland rice)	$4.9-5.32\times10^{-4}$(lowland rice)
	$2.2\times10^{-2}-0.45$ (soybean)	
Pb	Pb 300mg/kg	Pb 100—500mg/kg
	$2.6-4.5\times10^{-4}$(lowland rice)	$1.26\times10^{-5}-2.43\times10^{-6}$(lowland rice)

Table 4 (continued)

	3.5－7.1×10^{-4}(soybean)	
Cu	Cu 100mg/kg	Cu 100－200mg/kg
	9.3－25.1×10^{-3}(lowland rice)	4.6－6.8×10^{-5}(wheat)
	2.4－4.1×10^{-2}(soybean)	1.08－1.96×10^{-4}(soybean)
Zn	Zn 200mg/kg	
	4.69×10^{-2}－0.298(soybean)	not detect
	7.4－33×10^{-3}(soybean)	
As	As 30mg/kg	Ca－As 40mg/kg 5.64×10^{-5}(lowland rice)
	1.73－2.8×10^{-3}(soybean)	Fe－As 40mg/kg 4.71 ×10^{-5}(lowland rice)
	6.59 －15×10^{-3}(lowland rice)	Na－As 40mg/kg 3.24 ×10^{-6}(lowland rice)
		Na－As 40mg/kg 2.86 ×10^{-6}(soybean)

3.1.4 Effect of compound pollutants on microbial ecology

Wilke B. M. (Wilke, 1988) found that adding 3 ppm Cd, 50ppm Cu, 100ppm Pb and 200 ppm Zn singly caused no effect on soil respiration and dehydrogenase activity, while addition of these pollutants in combination would inhibit them significantly.

In this test, the soil dehydrogenase activity, soil respiration and microbial biomass, are selected as these have ecological significance and represent the activity of soil microorganisms. Samples of corn and trees were collected in summer and autumn of 1994 in field, and the analytical results are shown in Table 5.

Table 5 Results of field experiments with compound effects of heavy metal pollutants on microbial activity in soils (dehydrogenase activity)

Plant	Pretreatment	Summer		Autumn	
		DHA	*R*, %	DHA	*R*, %
Poplar	Control	10.69		17.57	
	Low dose	7.63	28.6	15.67	10.9
	High dose	7.28	31.9	10.32	41.3
Pine	Control	13.27		12.71	
	Low dose	13.04	1.7	9.73	23.5
	High dose	8.01	39.6	8.10	36.3
Corn	Control	12.81		8.44	
	Low dose	13.28	-3.7	7.59	25.1
	High dose	9.35	27.0	4.92	32.6

It can concluded from the above results that compound pollution of heavy metals can decrease the activity of dehydrogenase, the respiration and the biomass of microorganisms in soil, the inhibition rates increase with increasing concentration of pollutants. If 10% inhibition rate is assumed as the threshold of significant effect, even the low level of the five elements in combination will inhibit the activity of soil microorganisms significantly (Gong, 1995). That is to say, the additive and synergistic effect will be reproduced by these five heavy metals in combination.

3.2 Effect of reclamation measures on compound pollution

In early 70's, scientists in Japan put forward the method for reclaming the soil contaminated by single heavy metal, especialy for Cd (EPA in Japan, 1973). In China, Wu (Wu, 1984), Cao (Cao, 1992) and Li (Li, 1986) worked out the measures to decrease Cd and As pollution in soil, by increasing pH, spreading organic manure, changing lowland into upland and adding various oxidizers. F. T. Bingham, A. L. Page (Bingham, 1980) and A. Wallace (Wallace, 1989) studied the reclamation of heavy metals contaminated soil with lime application. However, the compound pollution of Cd, Pb, Cu, Zn and As causes new problems and needs to be further discussed.

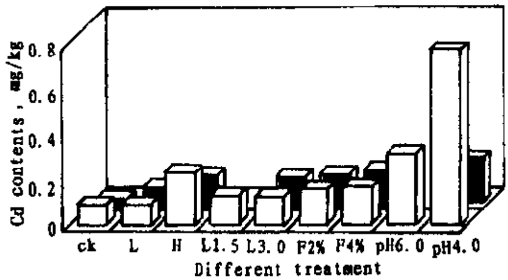

Fig. 4 Cd content in grain

L: low dose; H: high dose; L1.5: lime 1.5g/kg soil; L3.0: lime 3.0g/kg soil; F2%: fumic acid 2%; F4%: fumic acid 4%; pH 4.0, pH 5.0 mineral acid

3.2.1 Comparison of reclamation measures on lowlands and upland cultivation

The best method for reclamation of As contaminated soil is to turn lowland into upland and grow soybean instead of lowland rice. Under the condition of the same dose addition of pollutants into soil, solely due to the different measures used in lowland and upland, the absorption of As in lowland rice differs from that of soybean with its increment in grain, stem and root by 1.3—7.8, 2.03—4.17 and 1.37—64.0 times, respectively. Upland cultivation can decrease As content while increase adsorption of Cd and Zn. Cd absorption by grains of soybean and wheat is higher than that of lowland rice by 1.3—2.5 time (Fig. 4 and Fig. 5).

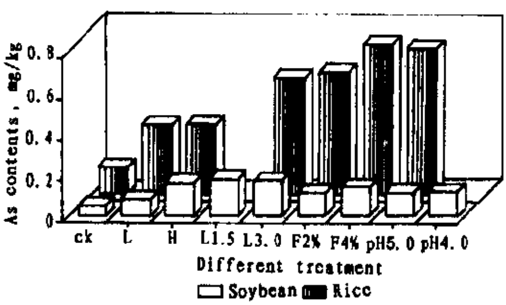

Fig. 5 As content in grain

(The abbreviations are the same as to Fig. 4)

The above results may result from the transformation of As species enhanced by varied environmental conditions. In the oxided conditions of upland, As occurs mainly as arsenate and is readily compound by metal hydroxide and therefore, its available As is rather low with less toxicity, which results in the absorption of As difficulty by crops. Under the reduced conditions of lowland, arsenate transforms into arsenite with higher toxic effect and provides more available As, which is readily absorbed by rice.

3.2.2 Comparison of effects among various modifiers

Table 6 represents the results obtained by applying methods of adding acids, lime, Ca-Mg-P fertilizers or Fumic acid. By addition of acid, the absorption of Cd, Pb, Cu and Zn can be enhanced by crops. With As, its absorption will be inhibited by acid in crops. Adding lime to increases soil pH, the absorption of heavy metals, especially of Cd, will be inhibited by plants, for Pb, Cu and Zn not significant. Pb and Cd absorption are apparently inhibited by both lime and Ca-Mg-P fertilizers, while the effect on Cu and Zn is not significant due to the increase of bound species of carbonate and Fe-Mn oxide and decrease of exchangeable Cd species. Application of Fumic acid inhibits Cd absorption in upland. In lowland, this inhibition effect is offset by the reduction.

Table 6 Efficiency of various modifiers on reclaiming pollution of Cd, Pb, Cu, Zn and As in combination

(Unit: mg/kg)

Test	Treatment	Soybean grain					Lowland rice grain				
		Cd	Pb	Cu	Zn	As	Cd	Pb	Cu	Zn	As
Pot test	Control	0.091e	0.38ab	9.31b	46.13d	0.050b	0.019d	0.216ab	3.02b	25.86	0.129c
	Low dose	0.095de	0.389ab	10.13	54.42c	0.082b	0.064c	0.340a	3.80b	24.76	0.336b
	High dose	0.228c	0.232b	11.55ab	57.79c	0.162a	0.119b	0.293a	3.95	25.74b	0.399b
	H+lime 1.5%	0.132de	0.358ab	8.42b	55.76c	0.181a	—	—	—	—	—
	H+lime 3.08%	0.124de	0.291ab	8.25b	55.50c	0.178a	0.111b	0.305ab	4.06b	26.14	0.561a
	H+humic acid 2%	0.159d	0.489ab	99.96b	72.17	0.119b	0.121b	0.352a	4.53ab	7.33	0.590ab
	H+humic acid 4%	0.168cd	0.350ab	8.62b	65.88b	0.147a	0.138	0.187ab	5.18ab	30.51ab	0.730a
	H+acid pH 5.0	0.314b	0.351ab	8.47b	85.85a	0.116a	—	—	—	—	—
	H+acid pH4.0	0.767a	0.596a	13.40a	—	0.128ab	0.191a	0.122b	5.53a	32.50a	0.711a
Field test	Control	0.038	0.018	10.86	29.03	0.264	0.044	0.091	1.38	16.17	0.039
	Low dose	0.049	0.125	10.51	38.76	0.460	0.081	0.168	1.27	14.14	0.260
	High dose	0.200	0.349	10.07	38.65	0.550	0.389	2.250	2.03	16.16	0.380
	High dose+lime+Ca-Mg-P fertilizer	0.199	0.180	9.88	44.46	0.104	0.193	0.506	1.62	14.84	0.596

Appendix: Content of heavy metal elements in different parts of crops (mg/kg)

Test	Crop	Treatment	Cd			Pb			Cu		
			Root	Stem	Grain	Root	Stem	Grain	Root	Stem	Grain
Pot test	Soybean	Control	0.210	0.189	0.091	3.46	2.99	0.383	12.05	5.54	9.31
		Low	0.499	0.249	0.095	8.64	7.56	0.389	15.30	6.54	10.13
		High	1.450	0.682	0.228	43.52	12.98	0.232	35.98	6.79	11.55
	Lowland rice	Control	0.409	0.095	0.019	14.91	5.39	0.216	12.81	6.13	3.02
		Low	0.967	0.139	0.064	194.43	6.42	0.340	59.72	7.96	3.80
		High	2.500	0.624	0.119	425.03	6.57	0.293	85.19	8.86	3.95

Table 6 (continued)

	Lowland	Control	0. 134	0. 072	0. 044	5. 53	1. 29	0. 306	12. 87	2. 93	1. 38
Field	rice	Pollutant	3. 448	0. 469	0. 389	624. 57	2. 25	1. 196	42. 49	3. 48	2. 03
test	Wheat	Control	0. 150	0. 460	0. 062	1. 01	4. 25	0. 329	12. 58	5. 55	5. 14
		Pollutant	1. 420	0. 790	0. 323	28. 06	2. 82	0. 719	31. 98	5. 53	6. 45
	Soybean	Control	0. 187	0. 099	0. 088	2. 00	2. 22	0. 019	11. 12	6. 82	9. 42
		Pollutant	0. 591	0. 316	0. 200	16. 40	6. 10	0. 349	17. 83	7. 00	10. 07

Test	Crop	Tretment	Zn			As		
			Root	Stem	Grain	Root	Stem	Grain
	Soybean	Control	50. 65	50. 63	46. 13	28. 65	1. 28	0. 050
Pot		Low	74. 36	67. 98	54. 42	20. 08	5. 67	0. 082
test		High	140. 21	135. 46	57. 79	59. 08	6. 76	0. 162
		Control	80. 14	63. 39	25. 86	39. 27	2. 93	0. 129
	Lowland	Low	119. 03	67. 92	24. 76	263. 53	11. 77	0. 336
		High	132. 23	71. 88	25. 74	476. 75	11. 45	0. 339
	Lowland	Control	41. 39	19. 36	16. 17	23. 61	2. 62	0. 039
field	rice	Pollutant	102. 13	24. 24	23. 62	461. 54	5. 91	0. 380
test	Wheat	Control	29. 93	26. 73	32. 21	0. 45	0. 84	0. 110
		Pollutant	88. 50	51. 99	62. 26	6. 58	1. 50	0. 285
	Soybean	Control	26. 06	20. 39	29. 00	0. 74	1. 71	0. 210
		Pollutant	23. 41	35. 47	38. 65	7. 16	3. 10	0. 282

Because of the difference between As and Cd with respect to their chemical behaviors in soil, all these reclamation measures are found to be invalid. Thus reclamation for comprehensive prevention of contaminated soil needs further study.

4 Conclusion

Select a typical group of pollutants Cd, Pb, Cu, Zn and As and their ecological effects were observed in meadow burozem. It was found that their effect on crop yield at the level of recommended environmental standard ranges from 5% to 10%.

The coexisting of these five elements appearance to have synergistic effect, especially on the enhancement of Cd absorption. The absorption coefficient is larger than that of single element by 10—100 times. The activity of soil microorganisms is inhibited by compound pollution, and hence, aggravates the environmental pollution and the risk for human health.

As the ecological and chemical behaviors of Cd, Pb, Cu and Zn are different from that of As, various reclamation measures contradict with each other. To turn lowland into upland can decrease the effect of As but increase the effect of Cd; while turning upland into lowland the effect of As will be increased. As a result, better prevention measures should be worked out further.

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