Ber. Ohara Inst. landw. Boil., Okayama Univ. 20 : 1 ~ 9 (1991)

THE EFFECT OF SEVERAL CADMIUM COMPOUNDS IN SOIL ON THE METAL CONTENT OF UNPOLISHED RICE

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There are many reports on the effect of cadmium mixed with soil on the growth of plants[3, 4, 6, 7, 10]. However, the metal content and the growth of the rice plants as influenced by several kinds of cadmium compounds added to soil have not been investigated.

Thus, a pot-experiment was established to determine the metal content of the unpolished rice and the response of rice plants to twelve kinds of cadmium compounds in soil, at the average range of cadmium pollution in Japan.

For the sake of convenience, we divided the twelve compounds of cadmium into two groups: soluble and insoluble. Then we compared the metal content of unpolished rice between the two groups.

MATERIALS AND METHODS

Twelve kinds of Cd compounds were used in this experiment. Table 1 and Table 2 show the nominal concentrations of the metals in soil, containing 10 kg of dry alluvial soil. The twelve test groups were 1) $CdSO_4.2\frac{2}{3}H_2O$, 2) $Cd(CH_3COO)_2.2\frac{1}{2}H_2O$, 3) $CdCl_2.2\frac{1}{2}H_2O$, 4) $Cd(NO_3)_2.4H_2O$, 5) $CdBr_2.4H_2O$, 6) CdI_2, 7) CdF_2, 8) $Cd(OH)_2$, 9) $Cd(CN)_2$, 10) CdO, 11) $CdCO_3$; 12) CdS, and control.

The pH range of control soil was 5.9-6.1 and the soil contained heavy metals as follows: 0.28 μg/g Cd, 138 μg/g Zn, 35 μg/g Pb and 39 μg/g Cu in dry matter. Two plants per pot were planted from 4, July to 7 November for about 16 weeks. Four replicates were used.

To each pot was added 5 g ammonium sulfate, 4.3 g calcium superphosphate, 1.4 g potassium sulfate, and tap water containing <0.01 ppm Cd to maintain good plant growth. After cropping, the rice grains were grained to obtain unpolished rice. Each sample was dried at 80 ℃ for 48-hr in a hot air drier and was digested with HNO_3-$HClO_4$ (2 : 1).

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Received November 30, 1990

TABLE 1. Twelve kinds of cadmium compounds used for the pot-experiment.

Cadmium compounds	Chemical formula	Formula (g)	Solubility (g/100ml)
cadmium sulfate hydrate	$CdSO_4 \cdot 2\frac{2}{3}H_2O$	208.46	76.4
cadmium acetate dihydrate	$Cd(CH_3COO)_2 \cdot 2H_2O$	266.53	61.0
cadmium chloride semipentahydrate	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	228.36	54.7
cadmium nitrate tetrahydrate	$Cd(NO_3)_2 \cdot 4H_2O$	308.47	61.3
cadmium bromide tetrahydrate	$CdBr_2 \cdot 4H_2O$	344.31	52.7
cadmium iodide	CdI_2	366.26	46.3
cadmium fluoride	CdF_2	150.40	4.35
cadmium hydroxide	$Cd(OH)_2$	146.43	Tr.
cadmium cyanide	$Cd(CN)_2$	164.45	Tr.
cadmium oxide	CdO	128.41	—
cadmium carbonate	$CdCO_3$	172.42	—
cadmium sulfide	CdS	144.48	Tr.

* : The values in g/100ml at 20℃, Tr : Trace, — : Insoluble

TABLE 2. Effects of the addition of cadmium to soil on the growth and the yield of rice plants.

Cd compounds	A		B		C		D		E	
	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm
$CdSO_4 \cdot 2.\frac{2}{3}H_2O$	72.2	76.5	151	188	76.5	70.0	64.5	59.0	86	79
$Cd(CH_3COO)_2 \cdot 2H_2O$	77.0	79.2	203	207	79.5	78.5	68.3	67.4	91	90
$CdCl_2 \cdot 2\frac{1}{2}H_2O$	85.0	79.8	248	231	75.3	70.2	66.0	62.0	88	83
$Cd(NO_3)_2 \cdot 4H_2O$	70.0	74.0	209	207	76.5	77.5	65.7	66.6	88	82
CdI_2	0	0	0	0	0	0	0	0	0	0
CdF_2	80.2	78.5	214	205	78.5	80.0	67.4	68.7	90	92
$Cd(OH)_2$	78.5	74.2	221	194	76.0	69.0	65.3	59.3	87	79
$Cd(CN)_2$	77.8	77.2	215	209	80.0	81.0	68.7	69.6	92	93
CdO	96.9	88.9	282	260	85.6	78.8	45.0	69.0	100	92
$CdCO_3$	72.5	78.2	216	189	65.5	63.0	56.3	54.1	75	72
CdS	94.0	91.4	274	268	83.0	81.3	73.0	71.0	97	95
M ± S.D.	79.9 ± 8.8	79.0 ± 5.6	223 ± 35.7	214 ± 27.2	78.5 ± 5.8	74.6 ± 6.1	67.7 ± 6.3	64.4 ± 5.5	86.0 ± 7.4	86.9 ± 7.1
Control	96.1		293		85.6		75.0		100	
Significant difference	NO		NO		NO		NO		NO	

* : Percentage of decrease in comparison with control.

A : Length of stem(cm), B : Weight of stem(g), C : Weight of unpolished rice(g), D : Weight of unpolished rice, E : Decrease of yield compared with control(%).

This solution was made up to a fixed volume by the addition of 1N-HCl and used for the determination of Cd, Zn, Pb, and Cu with atomic absorption using the DDTC-MIBK extracting method.

RESULTS AND DISCUSSIONS

Table 2 shows the relationship between the Cd content in soil and the growth of rice plants. Addition of cadmium markedly affected the growth,[6,10,11] and the yield of rice plants. The occurrence of chlorosis[6] at the early stage of rice plant growth after cadmium addition to soil, induced by cadmium toxicity, might be related to decreased iron uptake of plants[1,2]. Rice grain yield was calculated to decrease by 9 %, and 14 % with addition of 10 ppm Cd, and 50 ppm Cd, respectively. The weight of the stem of rice plants decreased by about 17-18 %, and 24-27 %, with addition of 10 ppm Cd and 50 ppm Cd, respectively. However, there was no significant difference between the two groups. Table 3 shows the cadmium, zinc, and copper concentrations in unpolished rice. A significant difference in cadmium between

TABLE 3. Relationship between metal content in soil and in unpolished rice.

Cd compounds	Metal content ($\mu g/g$)							
	Cd		Zn		Cu		Pb	
	*10ppm	50ppm	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm
$CdSO_4.2.\frac{2}{3}H_2O$	0.62	1.04	22.1	22.5	3.59	4.34	0.01	0.01
$Cd(CH_3COO)_2.H_2O$	0.84	1.18	21.8	21.4	4.11	3.98	0.01	1.33
$CdCl_2.\frac{1}{2}H_2O$	0.82	1.02	21.9	24.8	4.68	4.40	0.77	0.33
$Cd(NO_3)_2.4H_2O$	0.61	1.02	19.3	22.3	3.81	4.14	0.81	0.01
$CdBr_2.4H_2O$	0.69	1.19	22.6	20.7	3.56	4.08	1.46	1.53
CdI_2				(None Yields)				
CdF_2	0.52	0.94	21.5	21.0	4.01	4.04	0.69	0.81
$Cd(OH)_2$	0.47	0.81	20.3	22.7	3.73	4.56	1.09	0.01
$Cd(CN)_2$	0.42	0.88	20.7	23.7	3.92	4.43	1.13	1.84
CdO	0.46	1.14	24.5	26.0	5.23	5.14	1.57	0.33
$CdCO_3$	0.36	0.69	20.1	21.1	4.04	4.55	1.41	0.01
CdS	0.41	0.73	25.8	25.7	5.78	4.96	0.01	0.52
M ± S.D.	0.56 ± 0.06	1.02 ± 0.29	21.9 ± 2.0	22.9 ± 1.9	4.22 ± 0.7	4.42 ± 0.4	0.81 ± 0.6	0.61 ± 0.7
Control	0.14		22.1		1.02		1.85	
Significant difference	**		No		No		No	

** : $p<0.01$, * : Cadmium concentration in soil(mg/Kg).

10 ppm Cd and 50 ppm Cd added to soil was recognized at the level of 1 % error.

In the group of CdI_2 added to soil, rice plants did not grow because of the damage of root tissues due to the combined toxicity of cadmium and iodide ions. These results indicated that the Cd content of unpolished rice in the group treated with 50 ppm Cd was higher than that in the group treated with 10 ppm Cd[6, 8, 9].

Also, the average zinc concentrations was 19.3 to 25.8 μg/g with an average of 21.9 ± 2.0 μg/g in the group treated with 10 ppm Cd, and 20.7 to 26.0 μg/g with an average of 2.9 ± 1.9 μg/g for 50 ppm Cd, respectively.

There was a significant difference in zinc concentration of unpolished rice between the plants treated with cadmium, and the control. However, the concentrations of copper and lead in unpolished rice in the plants treated with cadmium were similar to those of the control.

Figures 1 and 2 show the relationship between Cu and Zn in unpolished rice. The correlation coefficients for [Cd] - [Cu] was evaluated to be, $r = 0.78$ ($p < 0.1$) and $r = 0.80$ ($p < 0.1$) in the 10 ppm Cd group and the 50 ppm Cd group added to soil, respectively.

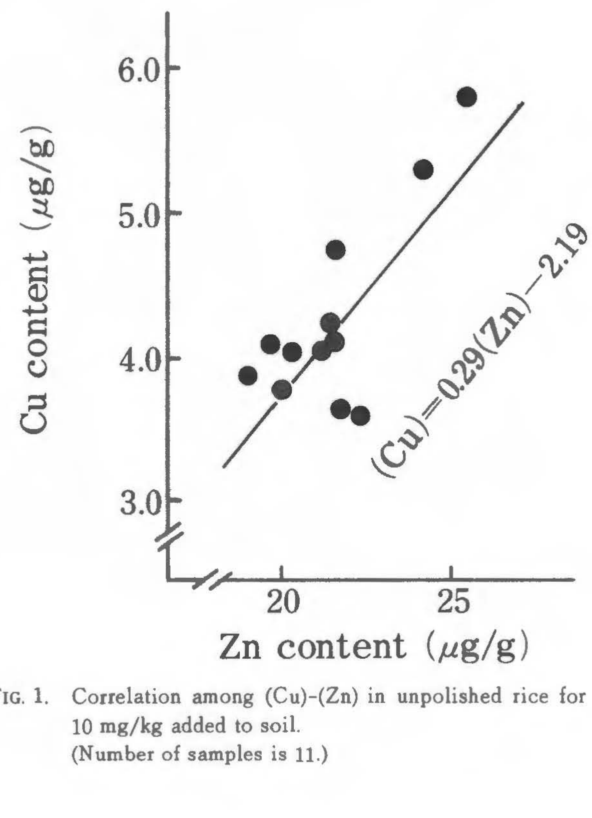


FIG. 1. Correlation among (Cu)-(Zn) in unpolished rice for Cd 10 mg/kg added to soil.
(Number of samples is 11.)

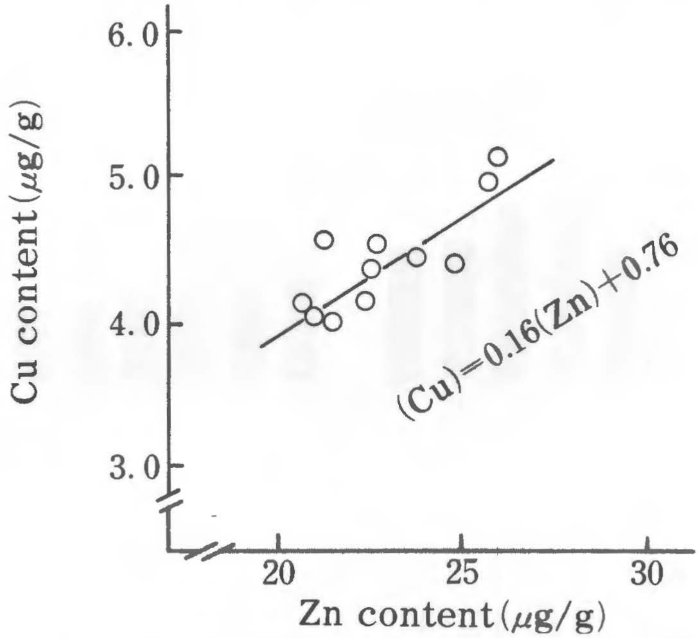
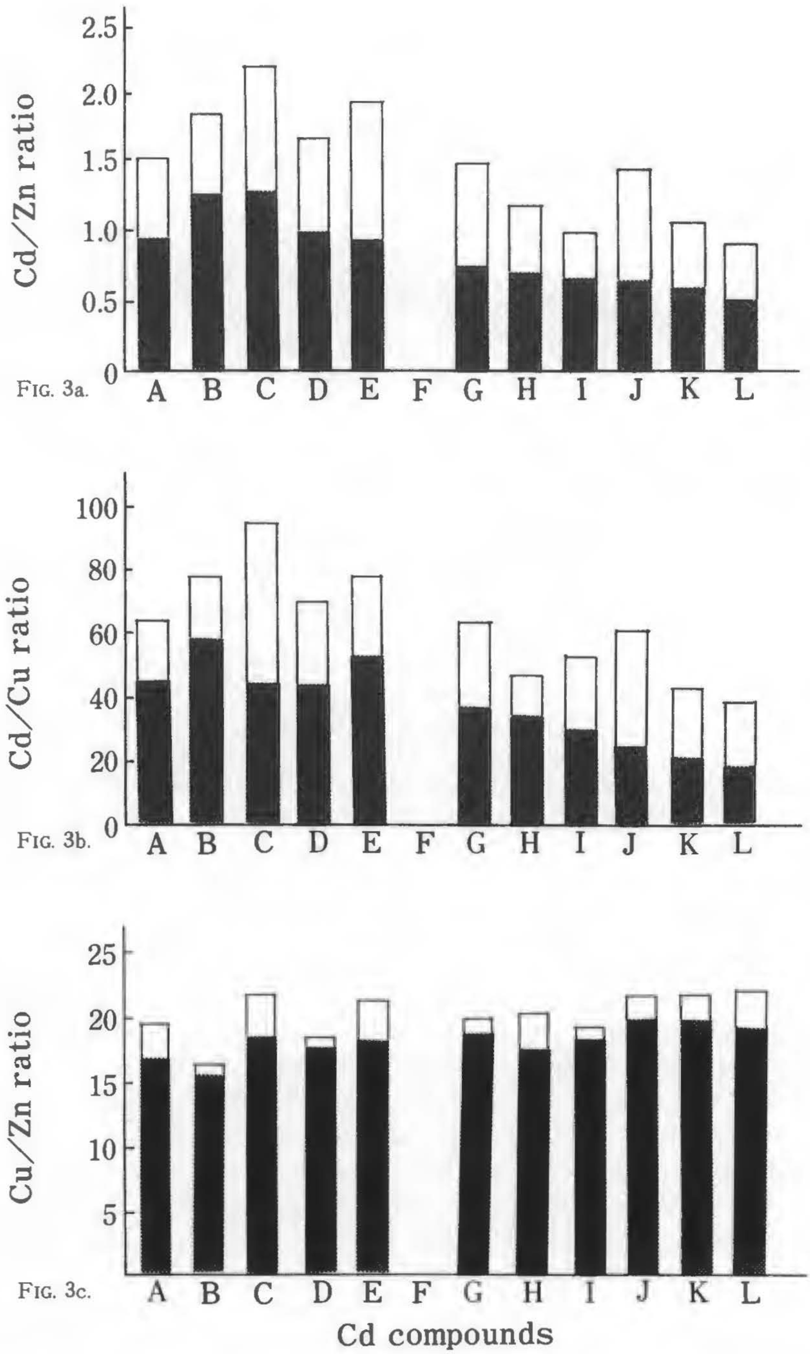


FIG. 2. Correlation among (Cu)-(Zn) in unpolished rice for Cd 50 mg/kg added to soil.
(Number of samples is 11.)

There was a significant difference ($p<0.01$) in cadmium content of unpolished rice between the soluble compounds, $Cd(CH_3COOH).2\frac{1}{2}H_2O$, $CdCl_2.2\frac{1}{2}H_2O$, $Cd(NO_3).4H_2O$, $CdSO_4.2.\frac{2}{3}H_2O$, CdF_2 except for CdI_2 and the insoluble compounds $Cd(OH)_2$, $Cd(CN)_2$, CdO, $CdCO_3$, and CdS.

However, the concentrations of Zn and Cu were similar in the 10 ppm Cd group and in the 50 ppm Cd group. The correlation coefficient for the concentrations of Zn and Cu was evaluated to be 0.78 in the 10 ppm Cd group and 0.80 in the 50 ppm Cd group ($p<0.01$).

Fig 3 and Table 4 show the molecular equivalent ratio of metal content for Cd/Zn, Cd/Cu, Cu/Zn in unpolished rice are shown. The Cd/Zn ratio in unpolished rice was 1.59 to 3.85 with an average of 2.6 $\pm$ 0.77 in the 10 ppm Cd group, and 2.84 to 6.45 with an average of 4.46 $\pm$ 1.1 in the 50 ppm Cd group. There was a significant difference in the metal concentration ratio of Cd/Cu in unpolished rice between the 10 ppm Cd group and the 50 ppm Cd group ($p<0.5$). Table 5 show the concentration of some metals in the soil after cropping. Twelve cadmium compounds were divided into two groups: the soluble group (solubility at 20 ℃, more than 4.5 g/100 ml) and the insoluble group (solubility at 20 ℃, less than 1.0 g/100 ml). The concentration in soil



FIGS. 3a-3c. The relationship between the amount of Cd added to soil (mg/kg) and the molecular equivalent ratio of metal content in unpolished rice.
■ : 10 ppm Cd group, □ : 50 ppm Cd group

TABLE 4. Significant differences of the metal content ratio in unpolished rice between the soluble-Cd and the insoluble-Cd compounds.

Cd added to Soil (mg/kg)	Metal content ratio	Significant difference	Number of Samples
	Cd/Zn	**	11
10	Cd/Cu	**	11
	Cu/Zn	—	11
	Cd/Zn	*	11
50	Cd/Cu	*	11
	Cu/Zn	—	11

** : $p<0.1$, * : $p<0.05$, — : no significant

TABLE 5. The content of Cd, Zn, Cu, and Pb in the soil of the bottom layer after cropping.

Cd compounds	Metal content (in dry matter, $\mu g/g$)							
	Cd		Zn		Cu		Pb	
	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm	10ppm	50ppm
$CdSO_4 . 2\frac{2}{3} H_2O$	11.0	51.1	128	117	44.8	48.2	28.5	34.6
$Cd(CH_3COO) . 2H_2O$	9.7	49.5	140	130	47.7	48.1	29.8	35.7
$CdCl_2 . 2\frac{1}{2} H_2O$	14.9	47.2	139	130	47.3	48.0	45.0	35.9
$Cd(NO_3)_2 . 4H_2O$	9.0	41.2	132	148	49.4	50.0	32.6	31.0
$CdBr_2 . 4H_2O$	9.9	45.8	133	120	47.2	44.0	21.6	22.3
CdI_2	10.5	50.8	152	124	44.9	43.2	31.2	31.7
CdF_2	10.7	53.3	118	135	52.0	47.9	32.4	35.3
$Cd(OH)_2$	9.6	41.2	132	131	46.0	56.8	38.2	30.2
$Cd(CN)_2$	9.1	41.1	127	129	51.1	47.9	28.1	35.5
CdO	9.4	40.9	167	137	54.4	47.7	50.8	40.1
$CdCO_3$	8.3	37.9	120	120	48.1	48.5	37.2	37.2
CdS	9.8	38.0	134	137	47.9	48.0	39.1	32.4
M ± S.D.	10.2 ± 1.61	47.3 ± 9.4	134 ± 12	130 ± 8.8	48.8 ± 3.3	48.2 ± 3.3	34.5 ± 7.9	33.6 ± 4.5
Control	0.45		173		51.9		49.5	
Significant difference	**		No		No		No	

** : $p < 0.01$ (Significant differences between the 10 mg/kg Cd group and the 50 mg/kg Cd group).

was 8.3 to 14.9 $\mu g/g$ with an average of 10.4 ± 1.61 $\mu g/g$ in the 10 ppm Cd group, and 37.9 to 53.3 $\mu g/g$ with an average of 47.3 ± 9.4 $\mu g/g$ in the 50 ppm Cd group.

SUMMMARY

The metal uptake of rice plants grown on soil treated with twelve kinds of cadmium compounds was investigated at the cadmium concentration levels of polluted districts in Japan. There is a significant difference in cadmium content of unpolished rice between the soluble compounds and the insoluble ones. The cadmium contents of unpolished rice from soil treated with 50 ppm cadmium was in the following order of magnitude: cadmium chloride semipentahydrate, cadmium bromide tetrahydrate, cadmium acetate dihydrate, cadmium oxide, cadmium cyanide, cadmium hydroxide, cadmium sulfide, cadmium carbonate.

The plants that were treated with cadmium iodide did not grow, because of root tissue damage due to the combined toxicity of cadmium and iodide ions.

Acknowledgements The author thanks Dr. J. Kobayashi, Dr. F. Morii, and Dr. K. Nakagawa for their valuable suggestions.

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