

## Comparison of Metal Uptake between Glutinous and Non-glutinous Rice for Cadmium Chloride, Oxide and Sulfide at the Critical Levels

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Cadmium pollution has induced extreamly severe effects such as chlorosis is caused from damage to the function of phytosynthesis. There have been a lot of reports on the relationship between the metal contents in soil and in rice plants (Kobayashi and Muramoto et al. 1969, 1973, Lagerwerff and Specht 1971, Koshino 1973, Homma and Hirata 1974, Ito and Iimura 1976). However, these experiments have been performed at Cd levels up to 500 ppm. Cadmium chloride is a usual effluence from some factories waste water. Cadmium oxide is exhaused in vapour form from the chimneys of zinc refinery factories. Cadmium sulfide is a reduced form commonly found in soil. Average background level of cadmium in unpolished rice is lower 0.26  $\mu \rm g/g$  Cd (Muramoto 1989, Muramoto and Aoyama 1990). Also, Cd content in roots was about 800 times higher than that in unpolished rice at levels of 10,000 ppm Cd treated with CdO to soil (Muramoto 1989). In Japan, the safety standard for Cd content of unpolished rice was decided should be lower than 1.0  $\mu \rm g/g$  Cd by the Ministry of Health and Welfare.

In this paper, the effects of cadmium chloride, cadmium oxide and cadmium sulfide on the metal content of rice plants, non-glutinous rice and glutinous rice up to the critical levels are investigated.

## MATERIALS AND METHODS

Cadmium chloride (CdCl<sub>2</sub>. 2.5H<sub>2</sub>0), cadmium sulfide (CdS) and cadmium oxide (CdO) were used in these experiments and nominal concentrations of metals in soil are shown in Fig. 1a and Fig. 1b. Water solubility of these cadmium (g/100ml) is soluble at 54.7 g/100ml for CdCl<sub>2</sub>. 2.5H<sub>2</sub>0, in soluble for CdO, and trace for CdS, respectively. Two plants, Oryza sativa L. and Oryza sativa gluticum were planted in pots the size at 1/5,000 a. containing 10 kg of dry alluvial soil. The pH range was 5.8-6.0 and the soil contained heavy metals as follows; Cd 0.3  $\mu$ g/g, Zn 145  $\mu$ g/g, Pb 34  $\mu$ g/g and Cu 41  $\mu$ g/g in dry matter. Two plants per pot were planted from on 30th of June to on th 3rd of November for about 16 weeks. Four replicates were used. Test groups were divided into the following groups according to the treatment they received: (1)control, (2) CdCl<sub>2</sub>, (3) CdS, (4) CdO.

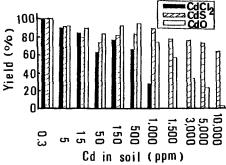


Figure la. Relatioship between Cd concentration in soil and yields of non-glutinous rice.

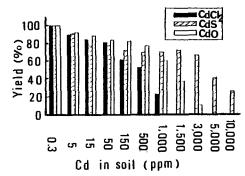


Figure 1b. Relarionship between Cd concentration in soil and yields of glutinous rice.

Table 1. Chemical composition of non-glutinous rice and glutinous rice (g per 100 g dry matter). A)

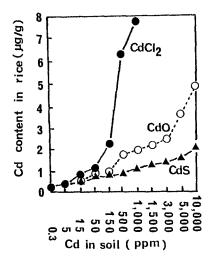
Rice plants		s Water	Pro-	Fat	Carbon	hydrate Fiber			al p	Fe
	(car	)	сели		Sugar-	LIDEL		IVCL		1.6
Non- glutinous	337	15.5	7.4	2.3	72.5	1.0	10	3	300	1.1
Glutinous	336	15.5	7.6	2.3	72.0	1.2	10	3	290	1.1

A) : cited from the table of standered chemical composition of Japanese food(1985).

Each pot received 5g ammonium sulfate, 4.3g calcium superphosphate, 1.4g potassium sulfate, and tap water containing < 0.01 ppm Cd to maintain good plant growth. After the croping, the rice grains and the plant roots were dried at 60 °C for 48h and digested with  $\rm HNO_3\text{-}HClO_4$  (2:1). After digestion, the solutions were 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 DISCUSSION

The chemical characteristics of glutinous and non-glutinous rice are shown in Table 1. The protein, ash and fiber contents of glutinous rice are higher. The relationships between rice yields and the Cd concentrations in soil are shown in Figs. 1a -1b.



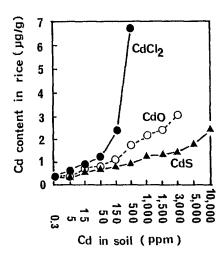


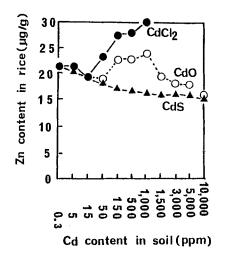
Figure 2a. Relationship between Cd concentration in soil and Cd content in non-glutinous rice.

Figure 2b. Relatioship between Cd concentration in soil and Cd content in glutinous rice.

The weight of rice, the length and the weight of stem showed significant correlation with the Cd concentration in soil. The yields of both non-glutinous and glutinous rice as well as the length and weight of stems significantly decreased with increasing Cd concentration in soil(p<0.01). The yield of non-glutinous rice decreased to 50% of the control at 500 ppm Cd, to 30% at 1,000 ppm Cd and to 0 % at 1,500 ppm Cd in the group treated with CdCl<sub>2</sub>.2.5H<sub>2</sub>O. In the group treated with CdO the yield decreased to 56 % of the control at 1,500 ppm Cd, to 36 % at 3,000 ppm and to 1 % at 10,000 ppm. In the CdS group for non-glutinous rice, there was a decrease by 28 % in comparison with control at 5,000 ppm and by 36% at 10,000 ppm Cd.

Therefore, the toxicity of cadmium to non-glutinous rice plants was in the order  $CdCl_2.2.5H_2O > CdO > CdS$ . This result is in agreement with other results (Muramoto 1990) and shows the dependence of Cd toxicity on the solubility of the Cd compounds. Also, for glutinous rice plants, the toxicity of cadmium was in the order  $CdCl_2 > CdO > CdS$ . The critical levels were 1,500 ppm Cd in the  $CdCl_2.2.5H_2O$  group, and 5,000 ppm Cd in the CdO group. The yield of glutinous rice decreased by 74 % at 10,000 ppm Cd in the CdS group compared with a decrease by 36 % for non-glutinous rice at the same concentration levels.

Figures 2a-2b show the relationship between the Cd concentration in soil and the Cd content of rice plants. The Zn content of brown rice for non-glutinous and glutinous rice is shown in Figures 3a-3b. The respective correlation equations and the correlation coefficients are shown in Table 2. The Cd accumulation in both non-glutinous and glutinous rice was in the same order as in previous results (Muramoto 1989):  $CdCl_2 > CdO > CdS$ .



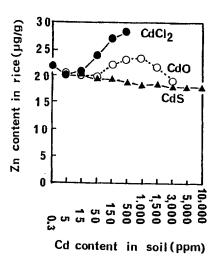


Figure 3a. Relatioship between Cd concentration in soil and Zn content in non-glutinous rice.

Figure 3b.Relatioship between Cd concentration in soil and Zn content in glutinous rice.

Table 2. Correlation coefficients and equations between Cd and Zn concentrations in rice plants and Cd concentrations in soil.

Metal	Cd form in soil	Rice variety	Tested concn.	Correlation coefficient	Correlation equation
	CdCl <sub>2</sub>	A	7	0.899*	y=0.983logx-0.983
	CdCl2	В	6	0.781*	y=0.75110gx-0.331
Cd	CdO <sup>2</sup>	A	11	0.887*	y=0.425logx-0.413
	CđO	В	11	0.925**	y=0.300logx+0.088
	CdS	Α	11	0.887*	y=0.425logx-0.413
	CdS	В	11	0.890**	y=0.174logx+0.715
	CdCl <sub>2</sub>	Α	7	0.849*	y=1.2621oqx+19.62
	CdCl <sup>2</sup>	В	6	0.820*	y=1.109logx+20.30
Zn	cđo <sup>2</sup>	Α	11	0.368	$y=-0.303\log x+21.32$
	CdO	В	11	0.040	y=0.022logx+21.32
	CdS	Α	11	-0.978**	y=-0.636log+20.59
	CdS	В	11	-0.950**	$y=-0.419\log x+21.21$

A :Non-glutinous rice plants, B :Glutinous rice plants,

\*\*: p>0.01, \*: p>0.05

There was a positive correlation between the concentration of cadmium in soil and the cadmium in brown rice of both non-glutinous and glutinous rice plants. The maximum concentration of Cd in non-glutionus rice was found to be 7.81  $\mu$ g/g at the critical levels of 1,000 ppm Cd in soil. In glutinous the maximum was 6.73  $\mu$ g/g at the critical levels of 500 ppm Cd in soil. These values for both rice varieties are higher than any others we have

Table 3. Correlation coefficients between the concentrations of Cd in soil in the form of CdCl<sub>2</sub>, CdO, and CdS and the growth indices of rice plants.

Index of arowth	Cd form in soil	Rice variety	Tested	Correlation coefficient	Correlation equation
9201141		Variety			- cquactor:
Weight	CdCl <sub>2</sub>	A	7	-0.860*	y=-7.9411ogx+105.1
of rice	CdCl2	В	6	-0.919*	$y=-8.975\log x+101.1$
grain	CdO 2	A	9	-0.848**	$y=-9.782\log x+118.7$
	CdO	В	9	-0.828**	$y=-8.315\log x+108.4$
	CdS	Α	9	-0.956**	y=-0.35010gx+101.9
	_CdS	B	9_	-0.859**	$y=-5.643\log x+100.2$
Length	CdCl <sub>2</sub>	Α	7	-0.835**	$y=-8.202\log x+109.2$
of	CdC15	В	6	-0.877**	$y=-7.141\log x+99.53$
stem	CđO Ž	A	9	-0.845**	$y=-4.781\log x+104.7$
	CdO	В	9	-0.908**	$y=-7.643\log x+104.8$
	CdS	A	9	-0.956**	y=-1.5711ogx+98.13
	CdS	B	9	-0.679	$y=-0.965\log x+101.5$
Weight	CdCl <sub>2</sub>	Α	7	-0.941**	y=-11.131ogx+98.35
of	CdC12	В	6	-0.916**	$y=-11.34\log x+99.28$
whole	CdO <sup>2</sup>	Α	9	-0.933**	$y=-7.30\log x+104.10$
body	CqO	В	9	-0.894**	$y=-6.61\log x+96.121$
_	CdS	Α	9	-0.870**	y=-18.281ogx $+100.9$
	CdS	B	9	-0.828**	y=-1.502logx+94.11

A :Non-glutinous rice plants, B :Glutinous rice plants, \*\*: p < 0.01, \*: p < 0.05

seen in the literature for treatment with CdCl<sub>2</sub>.2.5H<sub>2</sub>O. In the group treated with CdO, the maximum concentration of Cd in non-glutinous rice was 3.04  $\mu g/g$  at the critical level of 3,000 ppm Cd in soil. In glutinous rice the maximum concentration was 4.96  $\mu g/g$  at the critical levels of 10,000 ppm in soil. In the group treated with CdS, the Cd content was relatively low compared with that of the other two groups and the lethal level was not observed up to the levels of 10,000 ppm Cd in soil. The maximum Cd content of rice was 2.11  $\mu g/g$  in non-glutinous and 2.44  $\mu g/g$  in glutinous rice at 10,000 ppm Cd in soil.

As for the changes in the amount of Zn in both non-glutinous and glutinous rice it decreased with increasing Cd content in the groups treated with CdO and CdS. On the contrary there was significant increase in the Zn content of plants with increasing Cd concentration in soil in the form of CdCl<sub>2</sub>.  $2.5\text{H}_2\text{O}$  with the exception of the concentration of 15 ppm in soil (p<0.05). It is assumed that the high solubility of chloride compounds allows higher uptake of both Zn and Cd.

Table 3 shows the correlation coefficients between the concentrations of Cd treatment in the forms of CdCl<sub>2</sub>. 2.5H<sub>2</sub>O, CdO, CdS and the growth indices of non-glutinous and glutinous rice plants. Table 4 shows that significant differences of Cd content between non-glutinous rice and glutinous rice were recognized in all the three groups tested (p<0.05, or p<0.01). Also, the Zn content of glutinous rice was higher than that of non-glutinous rice. Significantly higher Zn content of glutinous rice was found in the group treated with CdS. There were significant differences of rice yields between the two varieties in both CdO and CdS treatment groups (p<0.01).

Table 4. T-values (Student's t-test) for the significance of differences between non-glutinous and glutinous rice plants for various indices.

Metal treatment group	Cd content of rice	Zn content of rice	Yields	Length of stem
CdCl <sub>2</sub>	-3.24*	-0.99	0.06	1.48
CdO 2	-0.525**	-5.94**	3.74**	-8.17**
CdS	-3.63**	-2.03**	4.49**	2.86*

<sup>\*\*:</sup> p < 0.01, \*: p < 0.05

Table 5. The range of cadmium concentration in unpolished rice, straw, root of rice plant, and soil in two characteristics area in Japan.

Area	Range of	Range of Cd content(dry matter, µg/g)					
	Unpolished rice	Straw	Root	Soil			
Area not polluted with Cd A	0.05_0.1	0.05-1.2	10-30	0.5-1.0			
Cd-polluted area B	) 0.5–5	18.5	200-700	1-60			

A):Kurashiki City(1983), B):Annaka City

The length of stem had a tendency to be higher in non-glutinous rice when applying CdCl<sub>2</sub>.2.5H<sub>2</sub>O or CdO in soil. Table 5 shows the Cd content in soil and rice plants in Cd-polluted and not polluted areas in Japan. The content of cadmium in rice plant was in the order Root > Straw > Rice grain (Koshino 1973, Muramoto 1989). The maximum value of Cd accumulated in unpolished rice was 5.02  $\mu \mathrm{g/g}$  in Annaka City where pollution is due to a zinc refinary factory (Kobayashi et al. 1973 ). In areas with Zn refinery factories the dominant form of Cd is CdS in the paddy fields and CdO in other fields.

Also, average background level of cadmium in soil ranges from 0.06  $\mu$ g/g Cd to 1.00  $\mu$ g/g Cd (Muramoto 1990). The content of cadmium in rice from control areas differed more greately with locality than with the nature of soil or variety of rice. The general average content of cadmium in all Japanese polished rice was 0.066  $\mu$ g/g Cd wet weight with 0.005  $\mu$ g/g Cd of standard deviation (Moritsugi and Kobayashi 1964).

With our experiments we showed that Cd in the form of CdCl<sub>2</sub> or CdSO<sub>4</sub> (encountered in factory effluents) an have higher bioaccumulation than CdO or CdS in rice plants(Figs 2a-2b). These results are in agreement with earlier published ones (Muramoto 1989).

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