

Effect of Calcium Carbonate on the Cadmium Content of Wheat After Addition of Large Amounts of Cds to Soil

Shigeki MURAMOTO, Hisao NISHIZAKI and Isao AOYAMA

In Japan, wheat is usually cultivated from December to June as a second crop in the same field as rice. In Cd-polluted areas, the fields are affected by both wastewater and the emissions from the chimneys of zinc refineries or plating factories³⁾. The application of inhibition agents, such as slaked lime, calcium silicate or fused magnesium are applied to inhibit the absorption of these metals by plants.

Many reports have been made on the decrease of metal absorption^{10,11,15)} through the application of some form of calcium, phosphate or silicate^{4,14,16)}. Also, it has been reported that wheat is more sensitive to CdS than to CdO⁸⁾.

However, almost all experiments were performed at less than 500 ppm Cd in soil, and these experiments have not been made at a concentration close to the level critical for wheat plants. There have been few reports on the effects of calcium carbonate on metal tolerance or metal uptake at the a level critical wheat. The typical example of using calcium carbonate was investigated by Maeda⁵⁾, and the application of phosphate by Koshino⁴⁾, and by Muramoto et al.¹²⁾.

The effects of calcium carbonate on the metal content of wheat to

Table 1. Coefficients of correlations between the Cd concentrations in soil and the growth indices of wheat plants.

Index of growth	CaCO ₃ treatment	Tested concentrations	Correlation Coefficient
Weight of straw	No	9	-0.959**
	Yes	9	-0.793**
Length of straw	No	9	-0.921**
	Yes	9	-0.768**
Weight of grain	No	9	-0.959**
	Yes	9	-0.915**
Yield(%)	No	7	-0.894**
	Yes	7	-0.917**

** : p < 0.01

the critical levels were examined.

MATERIALS AND METHODS

Cadmium sulfide, CdS (WAKO PURE CHEMICALS INDUSTRIES, LTD), was used at the nominal concentrations are shown in Table 1. CaCO₃ was administered, 350 g per 10 kg of alluvial soil in a pot. Two plants of wheat *Triticum estiva* L. per pot were planted from November to June for about 29 weeks. Four replicates were used. Each pot received as initial fertilizer 5 g ammonium sulfate, 4.3 g calcium phosphate, and 1.4 g potassium sulfate. It also received tap water containing less than 0.01 mg/L Cd to maintain good plant growth. After harvesting of wheat, samples were digested with HNO₃-HClO₄ (2 : 1) solution and were filled up to fixed volumes by the addition of 1N-HCl. These solutions were used for the determination of Cd and Zn with atomic absorption using the DDTC-MIBK extracting methods. The pH value of soil was 5.8 in the control and the range of pH values was 7.5-7.7 in the soil with CaCO₃ added. The soil contained as heavy metals : 0.3 µg/g Cd, 147 µg/g Zn, 37 µg/g Pb, and 42 µg/g Cu in dry matter.

RESULTS AND DISCUSSION

1. Growth indices of wheat

Figure 1a shows the relationship between the wheat yield and the

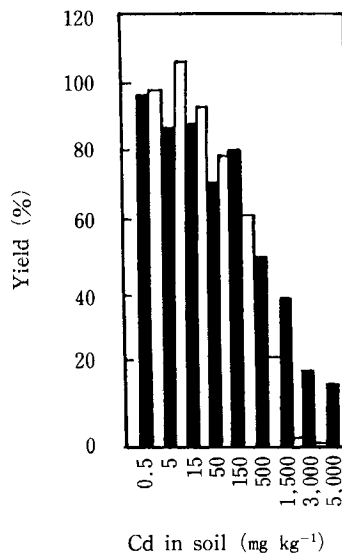


Fig. 1a. Relationship between Cd content in soil and the yields of grain in presence or absence of CaCO₃.

□ : Cd alone, ■ : Cd + CaCO₃

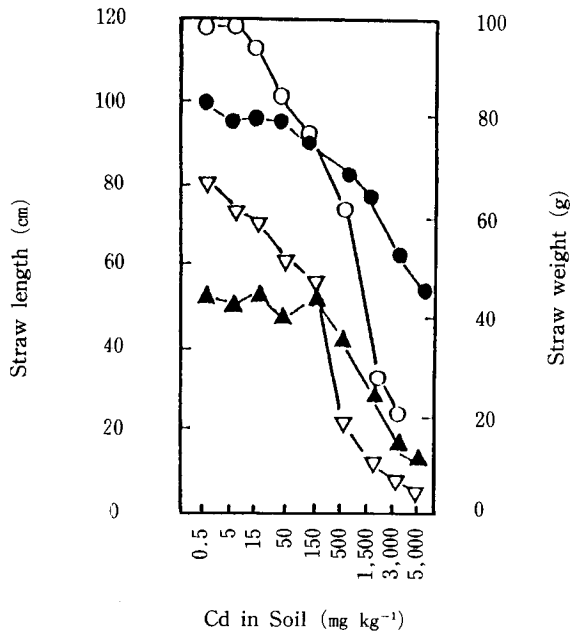


Fig. 1b. Relationship between Cd content in soil and the length or the weight of straw in presence or absence of CaCO₃.
 ○ : length, Cd alone, ● : length, Cd+CaCO₃
 ▽ : weight, Cd alone, ▲ : weight, Cd+CaCO₃

cadmium concentration in soil. Figure 1b shows the relationship between the length of straw or the weight of straw and Cd concentration in soil. Table 1 shows the coefficients of correlation between these growth indices and Cd concentration in soil.

A significant correlation ($p < 0.05$) was observed between the concentrations of cadmium in soil and the yields of wheat in both cases (Cd alone or Cd+CaCO₃). The yield of wheat decreased by 36%, 73%,

Table 2. T values (Student's t-test) for the differences in various growth indices of wheat between Cd alone and Cd+CaCO₃.

Cd content in soil (mg/kg)	Number of observation	A	B	C	D	E
0 - 500	6	-1.278	-0.297	-0.017	-0.292	-0.550
500 - 5,000	4	-1.826*	-1.912*	-2.411**	-2.804**	-1.776

* : $p < 0.05$, ** : $p < 0.01$,
 A : Length of straw, B : Weight of straw, C : Number of ears,
 D : Weight of grain, E : Yield of wheat

97% in the presence of 50 mg/kg Cd, 500 mg/kg Cd, and 1,500 mg/kg Cd, respectively. The critical level of CdS used alone for wheat was 1,500 mg/kg Cd in soil. However, when CaCO₃ was added, the yield of wheat decreased by 24%, 43%, and 57%, respectively at the same Cd levels in soil.

Table 2 shows the significance of the differences in some growth indices of wheat between the group treated only with Cd and the one treated with Cd and CaCO₃. The length of straw and the weight of wheat straw significantly decreased with the increase in Cd concentration in soil ($p < 0.01$). The critical level of wheat tolerance to Cd in the presence of CaCO₃ rose from 1,500 ppm to 5,000 ppm in soil.

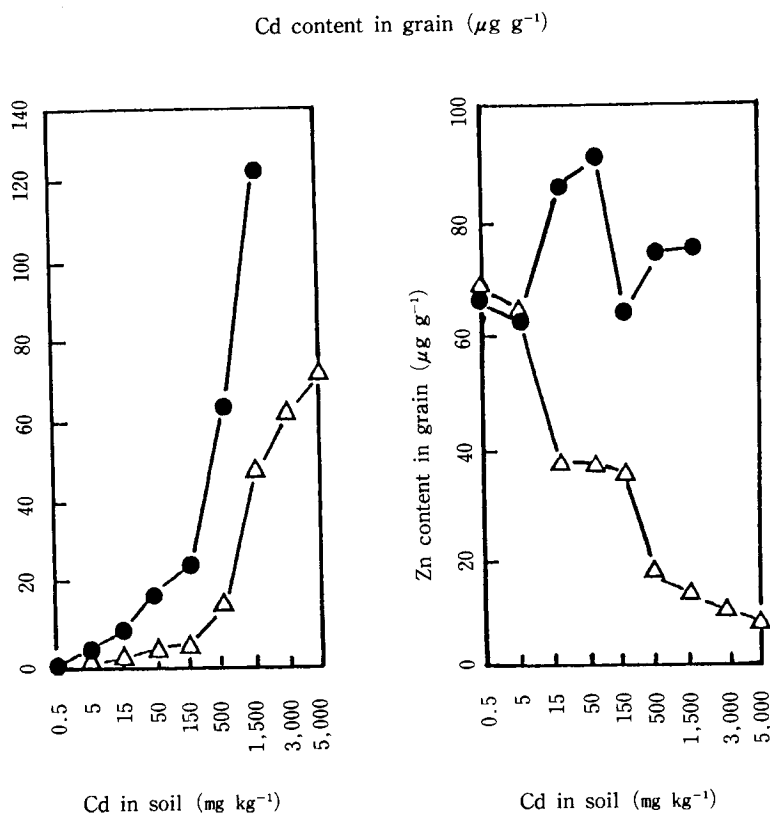


Fig. 2b. Relationship between Cd concentration in soil and Zn content of wheat, in presence or absence of CaCO₃.

● : Cd alone, △ : Cd+CaCO₃

Table 3. Correlations and equations between Cd and Zn concentrations in wheat and Cd concentrations in soil, with or without addition of CaCO₃.

Metal	(Cd in soil) - (Metal in wheat)	Number of observations	Correlation coefficient	Correlation equation
Cd	A	7	0.838**	$Y=5.21 \log X+7.88$
	B	9	0.839**	$Y=13.2 \log X-7.89$
Zn	A	7	-0.669*	$Y=88.4 \log X+2.45$
	B	9	-0.956**	$Y=87.9 \log X-9.09$

* : p <0.05, ** : p <0.01

A: compared treatments between (Soil)-(Wheat, Cd alone), B :compared treatments between (Soil)-(Wheat, Cd+CaCO₃)Table 4. T values (Student's t-test) for the differences in metal content of wheat grain between the Cd alone and the Cd+CaCO₃ group.

Metal	Compared treatments	Significant differences (t-values)	Number of samples
Cd	(Cd) - (Cd+CaCO ₃)	14.62 **	7
Zn	(Cd) - (Cd+CaCO ₃)	39.08 **	7

** : p <0.01

2. Cadmium concentration in wheat grain

The relationship between the Cd concentration in soil and the Cd content or Zn content of wheat is shown in Figs. 2a-2b, respectively. Table 3 shows the correlation between the Cd concentration in soil and in wheat, and Table 4 shows the significance of the differences in Cd and Zn concentrations of wheat between the group treated only with Cd and that treated with Cd+CaCO₃.

The maximum concentration of cadmium in the wheat grain was 123.3 µg/g Cd at the critical level of 1,500 mg/kg Cd in soil. To our knowledge, these values for wheat grains are higher than any others in the literature concerning addition of CdS to soil. However, the maximum value for cadmium oxide (CdO) was 141 µg/g Cd in the wheat grain, at 10,000mg/kg in soil⁷⁾. Wheat may be more sensitive to CdS than to CdO.

On the other hand, in the group treated with CaCO₃, the Cd content of the wheat grain was 57.5 µg/g Cd at 1,500 mg/kg Cd in soil, lower than that of the group treated with Cd alone. The lethal level was not observed up to a concentration of 5,000 mg/kg in soil and the Cd content of wheat grain was 68.4 µg/g Cd at this level. Therefore, metal concentrations in wheat grain decreased and wheat growth as well as

tolerance to CdS increased in the presence of CaCO₃.

In Japan, the Cd content of unpolished rice should be kept lower than 1.0 µg/g Cd according to the Ministry of Health and Welfare⁶⁾. However, the safety standard for the Cd content of wheat grain has not been established yet⁹⁾.

3. Zinc concentration in wheat

The zinc concentration of wheat tended to increase with the increase in the Cd concentration in soil. However, an antagonism between Cd and Zn was observed when CaCO₃ was also added ($p < 0.01$). The Zn content in wheat treated in the presence of CaCO₃ significantly decreased ($p < 0.01$).

CaCO₃ is considered to decrease the Cd toxicity plants and keeps the Zn concentration in wheat at a normal range. The solubility of Cd and Zn decreased by an increase in the pH value by the addition of CaCO₃.

Cd becomes less soluble, at a pH above 6^{1,13)}. The pH value is increased up to 7.5-7.7 from around 5.8 by the addition of CaCO₃ to soil in this experiment. Addition of CaCO₃ is effective in keeping wheat yields high as well as in increasing cadmium uptake by the plant.

SUMMARY

The critical level of *Triticum estiva* L. wheat tolerance to Cds was 1,500 mg/kg Cd in soil. The yield of wheat decreased by 36% and 97% in the presence of 50 mg/kg Cd and 1,500 mg/kg Cd respectively, but in the presence of calcium carbonate it decreased by only 24% and 57% at the same Cd levels in soil.

The highest concentration obtained for wheat grain was 123.2 µg/g Cd in the 1,500 mg/kg Cd group, and this value was higher than any value we have seen in the literature for treatment with CdS.

On the contrary, the highest concentration in the presence of CaCO₃ was 57.5 µg/g Cd at the same Cd concentration in soil, and critical levels of wheat were increased up to 5,000 mg/kg in soil. When CaCO₃ was also applied to the soil, the growth damage was lower than that when CdS is applied alone.

Acknowledgements We thank Dr.J.Kobayashi, Dr.F.Morii, and Dr.M. Yagi for their valuable suggestions, and Dr.H.Yagi helpful advice.

REFERENCES

1. Iimura,K. and Ito,H. 1971. Abstract of papers, Annual Meeting of Society of the Science of soil and Manure, Japan 17 : 167-175. (in Japanese).
2. Iimura,K. 1972. Movement of heavy metals in the soil. Bull. Hokkaido. Nat'l. Agric. Exp. stn. 15 : 46-52. (in Japanese).
3. Kobayashi, J.,Morii,F., Muramoto,S., Nakashima,S. 1970. Effects of air and water pollution on agricultural products by Cd,Pb, and Zn attributed to a mine and refinery in Annaka City, Gumma Prefecture. Jap.J.Hyg. 25 : 364-375. (in Japanese).
4. Koshino,M. 1972. Cadmium uptake by rice plant and wheat as affected by the application of phosphate and several metal elements. Bull. Nat'l. Agric. Exp. stn. b-24 : 1-51. (in Japanese).
5. Maeda,M. 1968. Diagnosis and measures of some elements excess to plants. Noson-gyoson-Bunnka Kyokai : 141-147, 154-160. (in Japanese).
6. Ministry of Health and Welfare. 1972. The essentials of tentative countermeasures against environmental pollution by cadmium, in Environmental Agency : 3-20.
7. Muramoto,S. 1989. Heavy metal tolerance of rice plants (*Oryza sativa* L.) to some metal oxide at the critical levels. J.Environ.Sci. Health. A-25 : 629-635.
8. Muramoto,S. 1990a. The critical levels and the maximum metal uptake for wheat and rice plants when applying metal oxides to soil. J.Environ. Sci.Health B-25 : 273-280.
9. Muramoto,S. 1990b. Comparison of metal uptake between glutinous and non-glutinous rice for cadmium chloride, oxide and sulfide at the critical levels. Bull.Environ. Contam.Toxicol. 45 : 415-421.
10. Muramoto,S. and Aoyama,I. 1990c. Effects of fertilizers on the vicissitude of cadmium in rice plant. J.Environ.Sci. Health. A-25 : 629-635.
11. Muramoto,S. 1991a. The effect of several cadmium compounds in soil on the metal content of unpolished rice. Ber.Ohara Inst.landw.Biol.,Okayama Univ. 20 : 1-9.
12. Muramoto,S. 1991b. Changes in concentration of cadmium,zinc,and iron in glutinous and non-glutinous rice for cadmium sulfide with or with calcium carbonate. Ber. Ohara Inst.landw.Biol.,Okayama Univ. 20 : 11-18.
13. Ninaki,M and Got,I. 1980. Effect of calcium carbonate to acid soil. The ninety anniversary thesis of Tokyo Agr.Univ. 276-293. (in Japanese).
14. Takijima,Y. and Katsumi,F. 1973. Cadmium contamination of soils and rice plants caused by zinc mining. IV. Use of soil amendment materials for the control of Cd intake by plants. Soil.Sci.Nutr. 19 (4) : 235-244. (in Japanese).
15. Yamagata,N. and Shigematsu,I. 1970. Cadmium pollution in perspective. Bull.Inst-Public Health (Tokyo). 19 : 1-7. (in Japanese).
16. Williams,C.H. and David, D.J. 1973. the effect of superphosphates on the cadmium content of soils and plants. Aust.J.Soil.Res. 11 : 43-51.

硫化カドミウムの高濃度添加時における小麦の生育と カドミウム集積濃度に対する炭酸カルシウムの影響

村本 茂樹、西崎日佐夫、青山 勲

植物に対する有害金属の生育限界濃度域での実験は極めて少ない。ここでは、小麦の硫化カドミウム (CdS) に対する生育限界濃度と小麦穀粒中カドミウム含有量に及ぼす炭酸カルシウム添加栽培の影響を調べた。その結果、硫化カドミウムに対する小麦の生育限界濃度は1,500ppmであり、その時の小麦穀粒中のカドミウム含有量は123.2 μ g/g(乾燥物中)であることが判明した。すなわち溶解度の低いカドミウムの化学形においても、穀粒中への集積が生じる結果が示された。また、炭酸カルシウムの同時添加により、無添加に対して1,500ppm区では穀粒中のカドミウム含有量は57%減少し、小麦の生育限界濃度は5,000ppmに拡大された。茎葉長、茎葉重、穀粒重等の各生育項目において炭酸カルシウムの添加効果が見られ、特にカドミウム濃度500—5,000ppmの間では炭酸カルシウム添加によるカドミウム毒性の抑制現象が有意に認められた。このことは高濃度カドミウム汚地域における炭酸カルシウムによる植物保護の一策としての有効性を示唆したと考えられる。