Studies on Soil Pollution by Cadmium, a Heavy Metal

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Soil pollution by heavy metals is recognized in many places of Japan where many mines exist. A notable example is the crop damage caused by waste water of Ashio cupper mine that created serious social problems since old time. The Itai-Itai disease which occurred in the Jintsu River basin, Toyama Prefecture, was identified as a chronic toxicity of cadmium coming from a mine located at the upper stream of the river, according to the official view of the Ministry of Welfare (May 1968). Since that time, problems of soil pollution have evoked strong public concern. The government recognized soil pollution as one of the typical public nuisance, and promulgated a law with objectives of protecting agricultural land from specific toxic substances including cadmium in December 1970. Under such a situation, Ministry of Agriculture and Forestry organized a special research project in order to make clear causal relationships between toxic substances contained in soil and crop damage or crop and livestock products possibly harmful to human being, and to establish effective measures to alleviate crop damage and to prevent soil pollution in a shortest time. With the participation of 13 research institutions of the Ministry of Agriculture and Forestry and one of the prefectural agricultural experiment stations, the project was carried out for 3 years, starting from 1971. Results of this project will be presented in brief.

Natural background content of cadmium

Many data on the natural content of cadmium under non-polluted condition were obtained by the survey on cadmium content for different land utilization and different crops. These data were utilized as a standard for judging soil pollution. As shown in Table 1 and 2, natural content of cadmium in top soil of paddy fields averages about 0.45 ppm (as determined by the method of perchloric acid digestion of soil samples), although it varys with soil groups⁷⁾. No big difference was found with soils of upland farms, tea gardens, and orchards.

Survey on non-polluted forest soil and Ando soil (virgin soil) indicated a tendency of lower

Table 1. Average concentrations of cadmium in plow layers of non-polluted paddy fields (air-dried basis)

Soil group	Cd (ppm)			
Gley soil	0.27±0.11			
Grayish brown soil	0.31±0.12			
Peat soil	0.34±0.24			
Gray soil	0.39±0.19			
Yellowish brown soil	0.44±0.11			
Strong gley soil	0.54±0.30			
Black soil	0.55±0.31			
Average (Total 53 sites)	0.45±0.23			

Area	Number of	Brown rice (air-dry basis)			
	sampling site	Mean	Range		
Kantō-Tōsan	10	0, 05	0. 02—0. 09		
Tōhoku	25	0. 04	0, 02-0, 09		
Hokuriku	28 (26)	0. 12 (0. 09)	0. 02—0. 56 (0. 02—0. 29)		
Chūgoku	18	0.06	0. 03-0. 13		
Kyūshū	7	0.06	0. 03-0. 09		
		Wheat & barley grain (air-dry basis)			
		Mean	Range		
Tōhoku	14	0. 05	0. 02-0. 08		
Hokuriku	7	0. 05	0. 03—0. 10		
Chūgoku	19	0. 07	0. 03-0. 13		
Kyüshü	18	0. 04	0. 00—0. 17		
		Soil (dry basis)			
		Mean	Range		
Kantō-Tōsan (paddy field)	10	0. 52	0. 29—0. 84		
Hokuriku (paddy field)	28	0.46	0. 28—0. 78		
Hokuriku (upland field)	6	0. 28	0, 26-0, 32		
Chūgoku (paddy field)	11	0. 35	0. 30—0. 40		
Shikoku (upland field)	10	0, 42	0, 28—0, 64		
Whole coutry (tea field)	27	0, 55	0. 03—0. 94		

Table 2. Natural background contents of cadmium in plants and soils* (ppm)

* Based on the results obtained by five agricultural experiment stations, Central Agricultural Experiment Station, and Tea Research Station.

cadmium content in lower soil layers, suggesting that cadmium is concentrated in surface soil layer through vegetation in soil formation process⁷⁾. Many data on natural content of cadmium in crop plants, particularly in grains of rice, wheat and barley, were collected throughout the country. As shown in Table 2, cadmium content of brown rice, which can be regarded as non-polluted, averages about 0.06 ppm, and that of wheat and barley grains about 0.05 ppm⁶⁾.

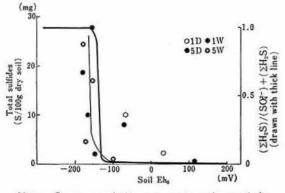
Behavior of cadmium in soil

From the experiments on adsorption to soil

and elution from soil, it was recognized that a considerable part of cadmium is adsorbed by clay and humus as an exchangeable cation, and accordingly cadmium in soil is relatively easy to dissolve; most of it is eluted with dilute hydrochloric acid or ammonium acetate solution⁶.

In the incubation experiments under water submergence a rapid decrease in cadmium elution occurred when the oxidation-reduction potential (Eh) lowered to about -150 mV. This change was found to correspond to the Eh change of a sulfate \Rightarrow sulfide system^{2.4)}. It was also reported that the decrease of solubility of cadmium under a reductive state

was a result of sulfide formation, based on the relationships observed between Eh change and sulfide formation and a decrease in cadmium



Note: Same symbols are commonly used in Figs. 1, 2 and 3 for indicating experimental plots:

- W: Continuous flooding irrigation throughout the whole growing season.
- D: Surface drainage was practiced after the tillering stage.
- ○, ●: Control plot with soil pH 5.6 6.0 and standard rate of application of phosphates.
- ●, ⊚: Soil pH was raised to 7.5 and heavy application of phosphates (equivalent to 20% of phosphorus absorption coefficient).
- Fig. 1. Changes of oxidation-reduction potentials and sulfides formation

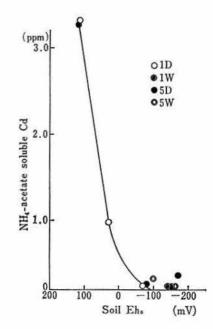


Fig. 2. Sulfides formation in soils and elution of cadmium (N-Ammonium acetate solution, pH 7.0)

Table 3. Cadmium in each soil horizon after three years' successive cultivation of rice plant (ppm, 0.1 N-HCI soluble Cd)

						Kind of s	soil			
			Alluvial soil					Volcanic ash soil		
plot*		0. 01—3	0. 01—10	0.1—3	0.1—10	S-10	Control	0.1-10	S-10	Control
soil horizon (cm)	0-2	2.1	3. 1	11.6	28. 9	4. 3	0.5	14.7	2.6	0.3
	2-5	0.6	0.9	2, 2	8.4	3.6	0.4	3. 3	2.6	0.3
	5-12	0, 4	0.6	1.7	3. 2	3.0	0.3	2.0	2.1	0.3

 0.01—10:
 0.01ppm Cd
 10 ℓ/day.

 0.1 — 3:
 0.1 ppm Cd
 3 ℓ/day.

 0.1 —10:
 0.1 ppm Cd
 10 ℓ/day.

 S —10: 150 mg of cadmium (as cadmium sulfate), equivalent to the amount supplied on the plot (0.1—3) for 3 years, was mixed into surface 10 cm soil at the beginning and irrigated

with water containing no Cd at permeation rate of 10 l/day.

Control : No Cd was supplied; irrigated at permeation rate of 3 l/day.

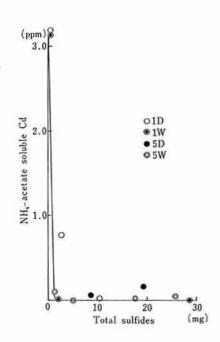


Fig. 3. Oxidation-reduction potentials of soils and elution of cadmium (N-Ammonium acetate solution, pH 7.0)

soluble in ammonium acetate solution (Figs. 1, 2, and 3) in pot experiments^{4,6)}.

Adsorption of heavy metals contained in irrigation water to soil and the balance sheet of heavy metals in soil were studied by using small lysimeters under paddy field condition with results shown in Table 3. More than 95% of cadmium supplied by irrigation water was retained in soil, accumulating in surface 0-2 cm layer of soil¹⁰. In other experiment, it was found that uptake by plants and leaching from soil of cadmium in the polluted soil with rice cropping were very small, and that the natural clean-up can hardly be expected. Therefore, it is suggested that the environmental standard for water quality should be set at a sufficiently low level.

Absorption of cadmium by crop plants and growth damage

Rice plants were grown by the water-culture

method, in which culture solution containing 0.01 ppm of cadmium was continuously supplied. Cadmium absorption by plants increased along with the increase of plant dry weight and water absorption, reaching a fairly high level. In the whole top part of plants at the final growth stage, cadmium concentration was as high as 2400 times that of the culture solution, and it was equivalent to 7 times of transpiration coefficient^{3.6}. Cadmium in brown rice was largely influenced by the supply of cadmium during a period from young-ear formation stage to milk ripe stage, and about 10% of cadmium absorbed in the top of rice plants was translocated to brown rice⁶.

When soil was kept to be oxidative at any time of the rice growth duration, absorption of cadmium was increased. Surface drainage at about heading stage was most influential in increasing cadmium content of brown rice⁶⁹.

As to the effect of co-existence of zinc and others, close to cadmium in chemical property, on cadmium absorption, it was found that zinc promoted cadmium translocation to tops⁸', without apparent antagonistic effect in absorption.

Growth inhibition was studied by solution culture method based on the relationship between water absorption and content of heavy metals in seedling tops. When cadmium content exceeded 10 ppm in tops, marked inhibition of water absorption took place: the toxicity of cadmium was highest among all heavy metals used (Fig. 4). In addition,

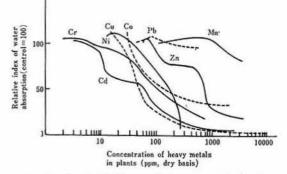


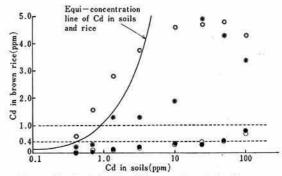
Fig. 4. Concentrations of heavy metals in the tops of rice seedlings and water absorption.

absorption of cadmium and growth inhibition of rice plants were studied in relation to the concentration of cadmium added to culture media by pot experiments with water culture or soil culture. Cadmium content in leaves plus stems apparently increased at the concentrations of cadmium in media beyond a critical level at which the growth inhibition began to occur. Concentration of 10–20 ppm in leaves plus stems, and of 1–2 ppm in brown rice was regarded as critical⁶. Among common upland crops, soybean was highly susceptible: foliage weight and grain weight decreased at 10 ppm of cadmium in soil⁶.

Water culture experiments with barley and corn seedlings indicated that the translocation of cadmium to top parts of plants was not reduced by increased phosphate concentration in plants, and that phosphate was not effective in inhibiting cadmium absorption⁹⁾.

Characteristic results relevant to soil-plant relationships were that the absorption of cadmium was greatly influenced by water management and soil properties. For example, a pot experiment using strong gley, heavy clay soil (Cd 0.39 ppm) and gley, loamy soil (Cd 0.37 ppm) showed that under continuous flooding throughout the whole growing duration cadmium content in brown rice was 0.01 ppm for both kinds of soil, but it increased to 0.19 ppm with the clay soil and to 0.62 ppm with the loamy soil when the surface drainage was practiced after the tillering stage. Cadmium contents of brown rice produced on these soils with cadmium addition are given in Fig. $5^{2.4.6}$. Another example is that cadmium uptake by rice plant is less in volcanic ash soil than in alluvial soil. Therefore, the same level of cadmium content in plants is obtained at higher concentration of cadmium in the former soil6).

As these facts make it difficult to establish a corresponding relationship between cadmium content in brown rice and that in soil, it is impossible at present to formulate the environmental standard which can designate regions of polluted rice (cadmium in brown rice at higher concentration than 1.0 ppm, a



Note: Symbols in the Figure: ○, ④ indicate a strong gley, heavy soil (Hokuriku Agricultural Experiment Station); ●, ③ indicate a gley, loamy soil (Toyama Prefectural Agricultural Experiment Station); ○, ● indicate plots with submerging irrigation throughout a growing season and ● ③ indicate plots with surface drainage after tillering stage.

Fig. 5. Relationship between concentrations of cadmium in soils and those in brown rice under different water management

safety standard of foods determined by Ministry of Welfare) based on cadmium content of soil.

Ameriolating measures for cadmium pollution

Many research works were done to find out effective measures to inhibit cadmium absorption by rice plants. As stated above, continuous flooding irrigation is very effective in preventing cadmium absorption. In addition, effects of application of some materials to soil were also examined. Results are summarized as follows:

Rising of soil pH by the application of liming materials resulted in reduced cadmium absorption in many cases^{6.7,10}. Soil pH increased to about 7.3–8.0 is regarded as effective. There is a case that basal application and additional appliaction at the young-ear formation stage of slaked lime is found to be effective. Many works on heavy application of phosphatic fertilizers were reported, and in many cases fused magnesian phosphate was effective^{6,7)}. Although the increase of available phosphate may exert a synergistic effect, many results suggest the neutralizing effect and the effect of accompanying constituents of the fertilizer on cadmium absorption. Most of these results were those from pot experiments and therefore studies on effective rates of application and continuation of effectiveness in polluted paddy fields are needed.

Future problems

To establish effective countermeasures, basic studies on mechanism of cadmium absorption by plants, effects on plant metabolism, differences in response to cadmium among crop species, and form and behavior of cadmium in soil are more required. By these studies, it is expected that the relation between cadmium concentration in brown rice and that of soils will be made clear and technical guidelines to prevent cadmium absorption will be developed. Furthermore, the fact that many of the cadmium-polluted areas are also polluted by cupper and arsenic, and the behavior of these elements in the soil-plant system is quite characteristic with each other makes it difficult to use countermeasures. Research on such combined pollution is an important subject still remains to be done in future.

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