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Cadmium, Copper, and Zinc Levels in Rice and Soil of Japan, Indonesia, and China by Soil Type

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The main sources of heavy metals in soil are the parent materials from which the soil was derived, but the influence of parent materials on the total content and form of the metals in soil is modified to varying degrees by pedogenetic processes. Surface contamination of soils with trace metals is most evident in sites with a known history of pollution, and it has been assumed that the behaviour of trace elements in soils, and in consequence their bioavailability, differs according to their origin. Recent findings clearly supported these assumptions (Pendias and Pendias, 1992). The bioavailability of Cd, and to a smaller extent Cu, added to soils in oxide form was significantly higher than the bioavailability of those metals occurring naturally in soils. Thus, it is most likely that, under similar soil conditions, trace metals in parent materials will be less mobile and less bioavailable than trace metals in surface soil. The behaviour and especially the bioavailability of trace metals in soils are also governed predominantly by their specification as well as by several soil properties (pH and redox potential) and soil factors such as cation exchange capacity (CEC), carbonates, Fe and Mn hydrous oxides, and clay minerals.

Japanese agriculture has experienced serious problems of soil contamination by heavy metals (Tsuchiya, 1978; Kondo, 1996). The concentration of Cd in paddy soils of Japan is 0.45 ppm on average (Iimura, 1981), which is well below the maximum allowable limit set for paddy soils, 5 ppm (0.1 N HCl soluble) (Pendias and Pendias, 1992). The levels of Cd, Cu, and Zn in brown rice grown in normal soils were 0.05, 3.3, and 15.5 ppm, respectively, while for rice grown in contaminated soils they stood at 3.7 and 20.5 ppm for Cu and Zn, respectively, but there is no data for Cd level in rice grown in contaminated soils (Chino, 1981). There have been a few studies on the cadmium, copper, and zinc contents of rice and rice field soils in various countries (Rivai, *et al.*, 1990; Suzuki, 1982), but little is known about the level of these metals in the rice and soils of Indonesia or China. The present study attempetd to accurately determine 1) Cd, Cu, and Zn content of soil and rice samples from Japan, Indonesia, and China, and 2) the correlation between Cd, Cu, and Zn in rice and in soils from each country.

MATERIALS AND METHODS

A total of 178 paired unpolished rice and soil samples were collected. Samples were taken from Hokkaido, Tohoku, Hokuriku, Kanto, Tokai, Chugoku, Shikoku, and Kyushu in Japan (n=111); the east, the northeast, and the south of China (n=22); and from Java, Sumatra, Kalimantan, and Sulawesi in Indonesia (n=45). Soil samples at 3 cm depth were also collected from rice fields just where the rice plants

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of the rice samples were growing. Rice samples were pretreated by placing approximately 0.1 g of a rice sample into a test tube and weighing it, drying it in an oven at 105°C for 48 hr, and weighing it again to assess the water content. The completely dried rice sample was ashed on a hot plate (80°C) with 1.0 ml of concentrated nitric acid (metal-free) until dry. Two millilitres of 14% nitric acid were added to dissolve the residue. Two methods were used for pretreatment of a soil sample: 1) Extraction by HCl without ashing. Approximately 1 g of a dried and screened soil sample was put into a tube, weighed, and 5.0 ml of 0.1 N HCl was added, and shaken in a water bath at 30°C for 1 hr. The upper layer of clear solution was separated and centrifuged at 3000 rpm for 5 min for Cd, Cu, and Zn analysis. 2) Extraction by ashing with nitric acid. Approximately 1 g of dried and screened soil sample was put into a test tube, weighed, 5.0 ml of concentrated nitic acid (metal-free) was added, and then ashed over a hot plate (80°C). Next, 10.0 ml of pure water was added and the clear supernatant was removed for Cd, Cu, and Zn analysis. Concentrations of Cd and Cu were analyzed by a flameless atomic absorption spectrophotometer (AAS) under the suggested condition, and Zn in the ashed rice solution was analyzed using the conventional AAS method after five-fold dilution with deionized water, under the recommended conditions. Each sample was analyzed two or three times by an autosampler at a wavelength of 229 nm for rice samples and 326 nm for soil samples. Under the same conditions, standard materials provided by the U.S. National Bureau of Standards were used for reference to confirm accuracy: 0.1 g of powdered rice (No. 1568) and 0.5 g of orchard leaves (No. 1571) for soil samples. Identification of soil type was based on the Soil Map of the World, Volume VIII (1978) and Volume IX (1979), by the Food and Agriculture Organization (FAO). A few samples on the borderline between the two soil types were excluded.

RESULTS AND DISCUSSION

The estimated average levels of Cd, Cu, and Zn in rice and rice-field soil samples from Japan, Indonesia, and China are shown in Table 1. Geometric means and geometric deviations were calculated, since the frequency distribution of the data was mostly skewed. In this study, Japanese rice (124.7 ng/g)) had the highest levels of Cd of the three countries studied. The cadmium levels of Japanese rice in this study were higher than those reported by Moritsugu *et al.* (1964) of 90 ng/g dry wt., Masironi *et al.* (1977) of 65 ng/g wet wt., and Nakatsuka *et al.* (1988) of 66 ng/g dry wt. Similar levels were seen in Indonesian rice (66.7 ng/g)) which had higher Cd concentrations than the 41.0 ng/g dry wt. observed by Suzuki et al. (1980) in Javanese rice. China had the lowest Cd levels in rice among the three countries (50.4 ng/g).

Copper levels in rice from Japan (3.71 g/g) were higher than the level reported by Ohmomo and Sumiya (1981), which was 2.81 μ g/g. The level of copper in Indonesian unpolished rice from Java in a study of Cd, Cu, and Zn in rice produced in Java conducted by Suzuki *et al.* (1980) was higher at 3.41 μ g/g than in the present study (2.7 μ g/g). The copper content of Chinese rice (4.2 μ g/g) was equivalent to the 4.4 μ g/g Cu content of rice from Taiwan in a study by Masironi *et al.* (1977).

In this study, Japanese rice seemed to have somewhat higher Zn levels (23.4 μ g/g) than those reported by Ohmomo and Sumiya (1981) of 20.5 μ g/g, and by Masironi *et al.* (1977) of 15.2 μ g/g, for Japanese polished rice. Similar levels were seen in Indonesian rice (23.5 μ g/g), which had higher Zn concentrations than those observed by Suzuki *et al.* (1980) in Javanese rice (19.02 μ g/g), but a little lower than reported by Koyama *et al.* (1988) for Javanese rice (24.9 μ g/g). China had the lowest Zn levels in rice among the three countries (21.5 μ g/g). Statistical analysis showed that the levels of Cd and Cu in rice from Japan, Indonesia, and China were significantly different, but that there were equivalent Zn levels in rice from the three countries.

Table 1. Cd, Cu, and Zn levels in rice and soils of Japan, Indonesia, and China

Cd	in rice samples from:			in soil[a] samples from:			in soil[b] samples from:		
	Japan	Indonesia	China	Japan	Indonesia	China	Japan	Indonesia	China
n	111	45	22	111	45	22	111	45	22
GM	75.9	26.3	11.8	81.4	20.1	33.1	445.8	73.7	99.5
GD	3.0	4.0	4.5	2.2	3.3	2.2	1.6	2.4	2.7
Cu	in rice samples from:			in soil[a] samples from:			in soil[b] samples from:		
	Japan	Indonesia	China	Japan	Indonesia	China	Japan	Indonesia	China
n	111	45	22	111	45	22	111	45	22
GM	3.71	2.26	3.99	6.09	1.24	2.78	19.52	10.26	15.07
GD	1.61	1.97	1.41	1.78	2.69	1.81	1.27	1.75	1.10
Zn	in rice samples from:			in soil[a] samples from:			in soil[b] samples from:		
	Japan	Indonesia	China	Japan	Indonesia	China	Japan	Indonesia	China
n	111	45	22	111	45	22	111	45	22
GM	22.90	22.89	21.19	1.91	1.29	1.47	96.44	64.23	81.24
GD	1.23	1.26	1.18	2.13	2.31	2.55	1.55	1.65	1.73

Note: n, number of samples; GM, geometric mean; GD, geometric deviation; soil[a], metals extracted by hydrochloric acid; soil[b], metals ashed by nitric acid; p, level of significance; ANOVA, $F=26.3$, 36.6 and 120.5 at $p<0.01$, for Cd rice, soil[a] and soil[b], respectively; ANOVA, $F=1.3$, $p>0.05$, for Cu in rice, $F=4.3$ and 12.02, $p<0.01$, for Cu in soil[a] and soil[b], respectively; ANOVA, $F=2.5$, $p>0.05$, for Zn in rice, $F=4.3$ and 12.0, $p<0.01$, for Zn in soil[a] and soil[b], respectively.

The cadmium content in the soil of Japan, 108.3 ng/g extracted by hydrochloric acid (soil[a]) and 537.8 ng/g ashed by nitric acid (soil[b]), seems to be the highest of the three countries. Similar results were seen in Cd levels of rice growing in the soil of Houston, Texas, extracted by nitric acid and by acetic acid 26.9 ng/g and 2.0 ng/g,, respectively (Suzuki and Iwao, 1982). Copper levels in the soil of Japan (7.35 μ g/g in soil[a] and 20.2 μ g/g in soil[b]) were significantly different from Cu levels in soil from Indonesia and China. Soil[a] from Japan, Indonesia, and China contained on average Zn levels of 2.5, 1.9 and 2.4 μ g/g, respectively, while those in soil[b] were 105.6, 72.5, and 98.8 μ g/g, respectively.

The content of Cd, Cu, and Zn in soil[b] was three to five times higher in all three countries compared with that in soil[a], which confirms the results of Suzuki *et al.* (1982) that nitric acid extracts more Cd, Cu, and Zn from soil than acetic acid does. However, extraction by the HCl method is reported to be suitable for detecting the soluble or mobilizable fraction of the element (Nihon Dojo Hiryo Gakkai, 1986).

Table 2 shows the analysis by soil type of the soil samples collected from Japan, Indonesia, and China. Rice grown in *Fluvisols* soil type, all from Japan, had the highest Cd levels (164.0 ng/g) in rice, though the highest level of Cd in soil was in *Cambisols* (148.4 ng/g in soil[a] and 601.8 ng/g in soil[b]). *Fluvisols* developed from recent alluvial deposits and unconsolidated materials (FAO 1978; 1979), and absorption of Cd was high in *Fluvisols* soil, accompanied by higher rice-to-soil ratios of Cd content (Table 4).

Table 2. Number of rice samples collected from Japan, Indonesia, and China analyzed by soil type

Soil type	Japan	Indonesia	China	Total
Andosols	81	4	0	85
Cambisols	8	0	0	8
Fluvisols	11	0	0	11
Gleysols	3	0	12	15
Histosols	0	14	0	14
Luvisols	0	10	0	10
Acrisols	0	17	0	17
Mixed soils*	8	0	10	18
Total	111	45	22	178

*Soils of mixed *Andosols*, *Lithosols*, *Histosols*, and *Acrisols*.

Levels of Cu were high in rice grown in *Gleysols* (organic soils), 12 out of 15 samples of which were from China, even though the highest Cu levels in soil were seen in *Cambisols* soil type (7.5 in soil[a] and 25.3 in soil[b]), all samples of which were from Japan. *Cambisols* (silty and loamy soils) is highly altered soil, having a cambic B horizon, and contains Cu 23 ppm on average, alluvial clay, iron, aluminum, humus accumulation, and is strongly acid (Pendias and Pendias, 1992). As concluded by Gupta (1979), Cu is more strongly bound by clays and humus than other cations, and an aluminum content in soil as low as 0.1 ppm markedly reduces total Cu uptake by plants, although the acidity of the soil has no effect on Cu absorption by plants. Therefore, even though Cu in *Cambisols* soil was high, it was less available for uptake by plants. The existence of Copper mines in Japan may also have a significant impact on agricultural soils, especially on Cu levels in soil. In contrast, *Histosols* soil, all samples of which were from Indonesia, had the lowest Cu content but the highest rice-to-soil ratio of Cu (Table 4) indicating higher absorption of Cu by rice plants from *Histosols* soil. *Acrisols,* or strongly leached soils, had the lowest Cu content (9.6 μ g/g) of all soil types.

Zinc concentrations in rice grown in *Histosols* soil, all samples of which were from Indonesia, had the highest level (27.4 μ g/g), while rice grown in *Acrisols* soil type, also all from Indonesia, had the lowest Zn content (21.0 μ g/g). On the other hand, Zn levels were low in *Histosols* soil type, when extracted by either the hydrochloric acid or the nitric acid ashing method. *Histosols* soil type is high in organic materials, and total soil Zn content has been related more strongly to the level in parent materials than to any other pedogenetic factor (Shuman, 1980). In addition, organic matter in soil can make mineral Zinc soluble, facilitating its uptake by plants. Therefore, even though *Histosols* soil type contains a lower level of Zn, the Zn is more readily available for uptake.

Table 3. Geometric means of cadmium, copper, and zinc content in rice and in soil by soil type

		in rice			in soil[a]			in soil[b]		
		Cd (ng/g)	Cu (μ g/g)	Zn (μ g/g)	Cd (ng/g)	Cu (μ g/g)	Zn (μ g/g)	Cd (ng/g)	Cu (μ g/g)	Zn (μ g/g)
Soil type	n	GM	GM	GM	GM	GM	GM	GM	GM	GM
Andosols	85	66.7	3.4	22.5	60.3	5.5	1.6	403.4	18.3	92.9
Cambisols	8	49.4	4.4	24.9	148.4	7.5	2.0	601.8	25.3	83.2
Fluvisols	11	164.0	4.3	22.9	73.7	3.9	1.4	403.7	17.8	96.1
Gleysols	15	12.2	5.1	22.5	44.7	4.2	2.0	99.5	16.9	75.7
Histosols	14	18.2	3.3	27.1	12.2	0.9	1.8	36.6	9.9	57.9
Luvisols	10	24.5	1.9	21.2	27.1	1.3	0.9	90.0	10.8	52.4
Acrisols	17	40.4	1.7	20.6	30.0	1.5	1.5	148.4	9.6	78.2
Mixed soils*	18	36.6	3.3	22.4	81.4	4.4	2.4	403.4	18.6	112.3

Abreviations and marks: see notes of Tables 1 and 2; ANOVA, F=6.2, 8.6, and 25.7 at $p<0.01$ for Cd in rice, soila, and soilb, respectively; ANOVA, F=7.36, 5.48, and 11.21 at $p<0.01$ for Cu in rice, soil[a], and soil[b], respectively; ANOVA, F=2.5, $p<0.05$ for Zn in rice; 1.65, $p>0.05$ for Zn in soil[a] and 4.54 at $p<0.01$ for Zn in soil[b].

Table 4. Ratios of metals in rice and metals in soil by soil type

		rice/soil[a]			rice/soil[b]			soil[a]/soil[b]		
Soil Type	n	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn
Andosols	85	1.04	0.61	13.74	0.17	0.18	0.24	0.16	0.30	0.02
Cambisols	8	0.34	0.59	12.26	0.87	0.17	0.29	0.26	0.29	0.02
Fluvisols	11	2.32	1.09	16.10	0.42	0.24	0.24	0.18	0.22	0.02
Gleysols	15	0.26	1.21	22.84	0.12	0.30	0.40	0.47	0.25	0.02
Histosols	14	1.55	3.58	14.14	0.53	0.33	0.26	0.33	0.09	0.02
Luvisols	10	0.93	1.49	14.69	0.26	0.18	0.47	0.29	0.12	0.03
Acrisols	17	1.34	1.13	11.10	0.30	0.18	0.29	0.23	0.16	0.03
Mixed soils	18	0.48	0.87	9.37	0.10	0.21	0.19	0.20	0.23	0.02
Total	178	0.89	0.89	2.25	0.19	0.21	1.71	0.21	0.23	2.08

Table 5 shows the correlation between the levels of Cd, Cu, and Zn in the rice and soil samples of each country. The amounts of Cd, Cu, and Zn in rice do not seem to be correlated with the three metals, content in soil. Similar results were also reported by Suzuki and Iwao (1982), Rivai *et al.* (1990) and Schumacher *et al.* (1994), whose reports all indicated a nonsignificant relationship between metals in rice and metal concentrations in these types of soils. The reason for this is the very complicated interrelation between soil texture, humus in soil, soil pH, etc., on the one hand and metal absorption and assimilation by growing plants on the other hand (Suzuki *et al.,* 1980; Gupta, 1979). Howevers, Cd, Cu, and Zn in soil were correlated with each other. This result was supported by Fasset (1980), who reported that Cd and Zn are always found together in nature. The same argument was also given for Cu in soils, which in both deficient and excess amounts must always be considered in relation to other major and minor elements present (Thornton, 1979).

Table 5. Correlations of Cd, Cu, and Zn in rice and in soils of Japan, Indonesia, and China

	n	Cd in rice	Cu in rice	Zn in rice	Cd in soil[a]	Cu in soil[a]	Zn in soil[a]	Cd in soil[b]	Cu in soil[b]	Zn in soil[b]
JAPAN	111									
Cd in rice		1.00								
Cu in rice		-0.09	1.00							
Zn in rice		-0.12	0.54**	1.00						
Cd in soil[a]		-0.05	0.21*	-0.01	1.00					
Cu in soil[a]		-0.26**	0.15	0.19*	0.54**	1.00				
Zn in soil[a]		0.00	0.14	0.14	0.44**	0.53**	1.00			
Cd in soil[b]		-0.10	0.18	0.09	0.68**	0.53**	0.49**	1.00		
Cu in soil[b]		-0.29**	0.15	0.11	0.46**	0.71**	0.40**	0.45**	1.00	
Zn in soil[b]		0.14	0.15	-0.02	0.29**	0.25**	0.41**	0.42**	0.11	1.00
INDONESIA	45									
Cd in rice		1.00								
Cu in rice		0.34*	1.00							
Zn in rice		-0.15	0.40**	1.00						
Cd in soil[a]		0.32*	0.02	0.06	1.00					
Cu in soil[a]		0.00	-0.06	0.06	0.42**	1.00				
Zn in soil[a]		-0.04	-0.03	0.08	0.13	0.13	1.00			
Cd in soil[b]		0.24	-0.35*	-0.26	0.53**	0.28	0.13	1.00		
Cu in soil[b]		-0.02	0.04	0.15	0.21	0.75**	-0.07	0.21	1.00	
Zn in soil[b]		0.14	-0.16	0.08	0.46**	0.59**	0.46**	0.54**	0.39**	1.00
CHINA	22									
Cd in rice		1.00								
Cu in rice		0.12	1.00							
Zn in rice		0.06	0.35	1.00						
Cd in soil[a]		-0.27	-0.06	0.27	1.00					
Cu in soil[a]		-0.11	0.37	0.27	0.70**	1.00				
Zn in soil[a]		-0.22	0.25	0.28	0.62**	0.73**	1.00			
Cd in soil[b]		0.30	-0.29	-0.02	0.35	0.04	-0.04	1.00		
Cu in soil[b]		0.37	0.33	0.24	0.17	0.37	0.15	0.59**	1.00	
Zn in soil[b]		0.27	0.11	0.24	0.39	0.44*	0.40	0.71**	0.73**	1.00
TOTAL	178									
Cd in rice		1.00								
Cu in rice		0.15*	1.00							
Zn in rice		-0.05	0.41**	1.00						
Cd in soil[a]		0.25**	0.26**	0.06	1.00					
Cu in soil[a]		0.17*	0.29**	0.12	0.68**	1.00				
Zn in soil[a]		0.04	0.14	0.14	0.41**	0.42**	1.00			
Cd in soil[b]		0.39**	0.16*	0.00	0.71**	0.69**	0.32**	1.00		
Cu in soil[b]		0.14	0.29**	0.10	0.52**	0.83**	0.24**	0.59**	1.00	
Zn in soil[b]		0.26**	0.15*	0.04	0.47**	0.51**	0.46**	0.56**	0.40**	1.00

Note: Correlations significant at $p < 0.01$ (**) and $p < 0.05$ (*); see also note at Table 1.

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