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Copper in Rice and in Soils According to Soil Type in Japan, Indonesia, and China: A Baseline Study

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Copper is essential to human life and health because of its important role in various metabolic processes, although as with most heavy metals, excess amounts of copper are toxic. Many studies had been carried out on the effect of copper on the environment and on human health. However, there have been few studies on the copper content of rice and rice field soil (Rivai *et al.*, 1988; Ohmomo and Sumiya, 1981; Suzuki, 1980), and none of these studies have fully reported on the content of copper in rice grown in Indonesia or China or on the copper content of soil in these two countries.

The copper content of rice, as a staple food in most of Asian countries, has been considered a good indicator of daily copper intake. The copper content of brown rice and paddy soil in Japan reported by Iimura (1981) was 2.9 µg/g and 32 µ g/g, respectively, and the copper content of unpolished rice grown in Java, Indonesia, was reported by Suzuki *et al.* (1980) to be 3.41 µg/g. The daily copper intake of Japanese people estimated by multiplying the copper content of rice by daily rice consumption was 660 µg/person (Ohmomo and Sumiya, 1981). Toro *et al.*, (1994) conducted research on toxic heavy metals and other trace elements in foodstuffs from 12 different countries, but no data for Indonesia or China were available. Horiguchi *et al.* (1978) reported daily intake of several metals in foods in thirty countries but there were no data for Indonesia. Because of the existence of differences in food consumption and environmental contamination in different countries, the present study aims: 1) to determine copper content of rice and rice field soils in Japan, Indonesia, and China in order to identify the possibility of copper pollution with special reference on daily copper intake in rice from these three countries; 2) to determine the relationship between copper in rice and in soil.

MATERIALS AND METHODS

A total of 178 pairs of unpolished rice and soil samples were collected from Japan, Indonesia, and China. Soil samples were also collected from rice fields where rice plants were growing. Samples were taken from Hokkaido/Tohoku, Hokuriku, Kanto, Tokai, Chugoku, Shikoku, and Kyushu in Japan (N=111), from the east, northeast, and south portion of China (N=22), and from Java, Sumatra, Kalimantan, and Sulawesi in Indonesia (N=45). Sample sites recorded were usually on the prefecture or city level. An approximately 0.1 gram rice sample was placed in a test tube for pre-treatment, weighed, dried in an oven at 105° C for 48 hours, and then weighed again to assay water content. The dried sample was ashed on a hot plate with 1.0 ml of concentrated nitric acid (metal free) until dry, and

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2.0 ml of 14% nictric acid was then added to dissolve the residue. Two methods were used to pre-treat the soil samples. The first method was extraction by HCl without ashing. Approximately 1 ml of a dried and filtered soil sample was placed in a tube and weighed, 50 ml of 0.1 N HCl was added, and the tube was then shaken in a 30° C water bath for 1 hour. The upper, clear solution was separated and centrifuged at 3,000 rpm for 5 minutes for copper analysis. The second method was extraction by ashing with nitric acid. An appproximately 1 gram dried and filtered soil sample was placed in a test tube and weighed, and then 5.0 ml of concentrated nitric acid (metal free) was added, and the sample was ashed on a hot plate. After adding 10.0 ml of pure water, the clear supernatant was taken for copper analysis. Each sample was analyzed two or three times with an autosampler AAS (Hitachi 2100) at a wavelength of 229 nm for rice samples and 326 nm for soil samples. Standard materials provided by the US National Bureau of Standards were used under the same conditions for reference to confirm accuracy: 0.1 gram of powdered rice (No. 1568) and 0.5 g of orchard leaves (No. 1571) for rice and soil samples. Concentrations of copper were determined with a flameless AAS (Hitachi 2100) under the recommended conditions.

Estimation of daily copper intake based on the amount consumed per day in a usual diet was calculated by the CIC method (copper level in rice multiplied by daily rice consumption). In addition, the ratios of copper level in rice to the level in soil were estimated by dividing the content of copper in rice by copper content in soil. Identification of soil type was based on the Soil Map of the World, Volume VIII (1978) and Volume IX by the FAO (Food and Agricultural Organization). A few samples on a borderline between two soil types were excluded.

RESULTS AND DISCUSSION

The arithmetic means and the standard deviation of the copper content of rice samples from Japan, Indonesia and China were shown in Table 1. Geometric means and the deviations were used when the data were skewed. The copper level of rice in Japan reported by Ohmomo and Sumiya (1981) was 2.81 µg/g, lower than in the present study. The level of copper in Indonesian unpolished rice from Java in a study of cadmium, copper, and zinc in rice produced in Java conducted by Suzuki *et al* (1980) was higher, 3.41 µg/g, than in the present study, 2.69 µg/g. The copper content in Chinese rice (4.21 µg/g) was practically identical to the copper content of rice from Taiwan, 4.4 µg/g in a study by Masironi *et al.* (1977). Compared with other Asian country data reported by Masironi *et al.* (1977) for Philippines (3.9 µg/g), Bangladesh (4.7 µg/g), and Taiwan (4.4 µg/g) the copper content of rice seems to be about the same as that of Chinese and Japanese rice. However, compared with the copper content of rice from the Southern Catalonia, Spain (1.39 µg/g), according to Schuhmacher *et al.* (1994) and 2.49 µg/g for copper content of unpolished rice from Houston, Texas (Suzuki and Iwao, 1982) the copper content in the three countries seemed higher, but was in the same range as the copper content of wild rice from central Canada, 1.6—14.4 µg/g (Pip, 1993).

The arithmetic mean of copper content in the soil from Japan, Indonesia, and China was 7.35 ± 5.94, 1.98 ± 2.09, and 3.35 ± 2.37 µg/g, respectively, by the hydrochloric acid extraction method, and 20.20±6.28, 11.57±4.64, and 15.14± 1.44 µg/g, respectively, by the nitric acid ashing method. The level of copper content in soil from Japan, Indonesia, and China seemed much lower than in the paddy soils of Alcacer do Sal, Portugal, 49.4 µg/g (Fernandes *et al.*, 1990).

Table 2 shows number of soil samples collected from Japan, Indonesia, and China. The geometric means and geometric deviations of copper contents in 7 soil types are shown in Table 3. The content of copper in rice was highest in *Gleysols* (5.14 µg/g). However, although 12 of the 15 Gleysols samples were from China, using t-test, the rice grown in *Gleysols* in Japan had a significantly higher copper content than the rice grown in *Gleysols* in China ($t=2.92$, $p<0.05$). The copper in the *Gleysols* of China may be less soluble and less available to the rice plants. Rice grown on the *Acrisols,* all of which were from Indonesia, had the lowest copper content (1.71 µg/g). *Cambisols,* all of the samples of which were from Japan,

Table 1. Arithmetic and geometric mean of copper level in rice and soil samples from Japan, Indonesia and China (µg/g)

	Rice samples from:			Soil[a] samples from:			Soil[b] samples from:		
	Japan	Indonesia	China	Japan	Indonesia	China	Japan	Indonesia	China
N	111	45	22	111	45	22	111	45	22
Min	0.34	0.22	1.61	1.56	0.25	1.02	13.10	1.73	12.00
Max	14.06	5.85	7.32	47.77	10.15	9.89	49.27	17.04	16.85
Mean	4.09	2.69	4.21	7.35	1.98	3.35	20.20	11.57	15.14
SD	1.84	1.39	1.37	5.94	2.09	2.37	6.28	4.64	1.44
CV, %	45.00	51.20	32.50	80.90	105.50	70.80	31.10	40.10	9.50
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

Note: N, number of samples; Cu, copper; Min, minimum; Max, maximum; Mean, arithmetic mean; SD, standard deviation; CV, coefficient of variation; GM, geometric mean; GD, geometric deviation; soil[a], metals extracted with hydrochloric acid; soil[b], ashed with nitric acid; ANOVA, $F=16.21$, 82.55, and 56.95 at $p<0.01$, for rice samples from Japan, Indonesia and China, for soil[a], and for soil[b], respectively.

Table 2. Numbers of rice samples collected from Japan, Indonesia and China broken down into seven soil types

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 soil*	8	0	10	18
Total	111	45	22	178

*, mixtures of *Andosols, Lithosols, Histosols,* and *Acrisols.*

Table 3. Differences in the copper content of rice and soil by soil type

Soil type	N	Cu in rice (μg/g) GM	GD	Cu in soil[a] (μg/g) GM	GD	Cu in soil[b] (μg/g) GM	GD
Andosols	85	3.38	0.21	5.50	0.26	18.33	0.09
Cambisols	8	4.42	0.28	7.47	0.39	25.3	0.16
Fluvisols	11	4.33	0.10	3.94	0.18	17.83	0.09
Gleysols	15	5.14	0.11	4.25	0.26	16.91	0.13
Histosols	14	3.28	0.18	0.91	0.34	9.98	0.21
Luvisols	10	1.95	0.43	1.29	0.57	10.79	0.21
Acrisols	17	1.71	0.25	1.51	0.40	9.63	0.29
Mixed soils*	18	3.28	0.14	4.39	0.47	18.59	0.15

Abreviations and marks: see the footnote of Table 1 and Table 2; ANOVA, F=7.36, 5.48, and 11.21 at $p<0.01$, for copper in rice, soil[a], and soil[b], respectively.

seemed to have the highest copper in soil whether extracted with hydrochloric acid or ashed with nitric acid, 7.47 and 25.30 μg/g, respectively. The high copper level of the *Cambisols* is probably caused by the stucture of the soil, which contains alluvial clay, iron, aluminum, humus accumulation, and is strongly acid. As concluded by Gupta (1979), copper is more strongly bound by clays and humus than other cations, and high aluminum content in soil, as low as 0.1 ppm markedly reduces total copper uptake by plants, although the acidity of the soil has no effect on copper absorption by plants. Therefore, the copper in *Cambisols* was less available for uptake by the plants. The existence of copper mines in Japan may also have a significant impact on agricultural soils, especially copper levels in soil. In contrast, *Histosols*, all of the samples of which were from Indonesia, have the lowest copper content but seemed to have the highest ratio of copper in rice to copper in soil (Table 4) indicating higher absorption of copper by rice plants on *Histosols*. The amount of organic material in which *Histosols* was formed probably made it more porous and open. *Acrisols* had the lowest copper content, 9.63 μ g/g, of all soil types.

Table 4. Ratios of copper content of rice to copper content of soil extracted with hydrochloric acid (a) and ashed with nitric acid (b) according to soil type

Soil type	N	Rice/(a) GM	GD	Rice/(b) GM	GD	(a)/(b) GM	GD
Andosols	85	0.61	0.29	0.18	0.21	0.30	0.21
Cambisols	8	0.59	0.58	0.17	0.37	0.29	0.26
Fluvisols	11	1.09	0.22	0.24	0.17	0.22	0.14
Gleysols	15	1.21	0.28	0.30	0.13	0.25	0.18
Histosols	14	3.58	0.31	0.33	0.25	0.09	0.19
Luvisols	10	1.49	0.69	0.18	0.49	0.12	0.39
Acrisols	17	1.13	0.52	0.18	0.39	0.16	0.27
Mixed soil*	18	0.87	0.37	0.21	0.12	0.23	0.36
Total	178	0.89	0.43	0.21	0.26	0.23	0.29

Abbreviations and marks: see the footnote of Table 1; *, see footnote of Table 3; (a), soil[a]; (b), soil[b]; ANOVA, F=8.39, 3.15, and 11.52 at $p<0.01$, for rice/(a), rice/(b), and (a)/(b), respectively.

Table 5. Correlation coefficients between copper content in rice and in soil samples by country

	N	Cu in rice	Cu in soil[a]	Cu in soil[b]
JAPAN	111			
Cu in rice		1.00	0.15	0.15
Cu in soil[a]			1.00	0.80**
Cu in soil[b]				1.00
INDONESIA	45			
Cu in rice		1.00	-.06	0.04
Cu in soil[a]			1.00	0.75**
Cu in soil[b]				1.00
CHINA	22			
Cu in rice		1.00	0.36	0.33
Cu in soil[a]			1.00	0.37
Cu in soil[b]				1.00
Total	178			
Cu in rice		1.00	0.29**	0.29**
Cu in soil[a]			1.00	0.83**
Cu in soil[b]				1.00

Note: Cu, copper, a and b, see footnote Table 1, * & **, significant correlation at p, 0.05 & p< 0.01, respectively;

A positive Pearson's correlation coefficient was found between copper in rice and in soil extracted with hydrochloric acid (soil[a]) in Japan and China but a negative relationship was found for the samples from Indonesia ($r=-0.06$, $p>0.05$). None of the correlation coefficients for copper in rice and in soil ashed with nitric acid (soil[b]) from Japan, Indonesia, and China were significant. The correlation coefficient for copper level in soil[a] and in soil[b] was significant both for the samples from Japan and Indonesia ($r=0.80$ and $r=0.75$, $p<0.01$, respectively). When samples from the three countries were combined, there was a high correlation between copper content in rice and soil[a] ($r=0.29$, $p<0.01$) and between rice and soil[b] ($r=0.29$, $p<0.01$). The highest correlation was seen between copper in soil[a] to soil[b] ($r=0.83$, $p<0.01$). The amounts of copper in rice did not seem to be correlated with copper in soil. Similar results were also reported by Rivai *et al.* (1990), Suzuki and Iwao (1982), and Scuhmacher *et al.* (1994) whose reports all indicated no significant relationship between metals in rice and metal concentrations in soils. The reason for this is the very complicated interrelation between soil texture, humus content of soil, soil pH, etc., and metal absorption and assimilation by growing plants (Suzuki *et al.,* 1980; Gupta, 1979).

Daily copper intake from rice in the three countries is shown in Table 6. Daily copper intake in rice in China was 1.4 mg/person. The daily intake of copper by Indonesians was 1.1 mg/person, almost the same as the daily copper intake in rice in West Java, 0.9 mg/day for women and 1.3 mg/day for men, previously reported by Rivai *et al.* (1988). The daily copper intake in Japan was 1.1 mg/person, considerably higher than in the 0.66 mg/person reported by Ohmomo and Sumiya (1981). In addition, the daily copper intake in rice in the three countries seemed higher than the daily copper intake in rice of people in Southern Catalonia, Spain,

Table 6. Daily copper intake in rice by country (μg/person)

Country	N	Cu in rice (μg/g)	Daily Cu intake from rice (mg/person)
Japan (300.2)*	111	3.71	1.1
Indonesia (507.3)*	45	2.26	1.1
China (350.8)*	22	3.99	1.4

*, Average daily rice consumption (g/person) of 1979--1981 from the data of Food Balance Sheets by FAO (1984)

and than the daily copper intake in cereals (rice, noodles, sphagetti) of people in Tarragona Province, Spain, 19.04 and 346.4 μg/person, respectively, according to Schuhmacher *et al.* (1994; 1993). Daily copper intake in rice seemed to depend on copper content in rice and daily rice consumption in each country.

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