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Cadmium, Chromium, Copper, and Zinc in Rice and Rice Field Soil from Southern Catalonia, Spain

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Metals are ubiquitous in the modern industrialized environment. Some metals (lead, cadmium, mercury, uranium, etc.) have no beneficial effects in humans and there is no known homeostasis mechanism for them. In contrast, other metals such as chromium, copper, zinc, manganese, cobalt or iron are essential for man. However, these essential trace elements can also be dangerous at high levels.

Many metals are natural constituents of soils, whereas soils may also be contaminated by a number of elements such as lead, cadmium, arsenic, mercury or chromium among others as the results of less-than-ideal disposal practices from past industrial processes (Sheehan et al. 1991). Vegetables absorb metals from the soil (Bosque et al. 1990; Schuhmacher et al. 1993a). When trace elements are transferred from soil to plants to animals and/or humans, there is selectivity for some elements and barriers to others in their movement from lower to higher trophic levels within the human food chain (Welch and House 1984). The availability of a particular element to a crop can vary widely depending on the soil the crop is grown on. Thus, soil properties affecting mineral elements availability are the first determinants of the transfer of elements to higher trophic levels in the soil-plant-animal/human system (Kubota et al. 1992).

Rice plants are annual emergent aquatic macrophytes which are economically important as a cereal crop in Tarragona Province (southern Catalonia, Spain). Macrophytes may absorb metals through both roots and shoots, while aerial deposition may also be an additional source in emergent species (Pip 1993). It has been established that cadmium rich soils generally produce cadmium rich foods (Suzuki et al. 1988). Accumulation of cadmium in the kidney has been found to occur depending on the daily intake of cadmium according to geographical differences (Piscator 1985).

On the other hand, in recent decades it has been demonstrated that a number of metals such as chromium, copper and zinc, which play an important role in many

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fields of modern industry, have a notorious role in various biochemical processes. The beneficial or the toxic effect of an element depends on its concentration in the organism. Consequently, information on the trace elements intake from different sources is useful for the prevention and control of diseases that are caused by mineral imbalance (Schuhmacher et al. 1991, 1992, 1993b).

Although there are many reports in the world on environmental metals, to date no data about the metal contents in spanish rice have been available. The purpose of this study was to examine the concentrations of cadmium, chromium, copper and zinc in rice from the Delta of Ebro river (Tarragona, Spain). These particular metals were chosen because of current interest in either toxicity or potential deficiency in humans. The metal contents in rice were related to rice variety, locality, and soil type. The dietary intake of cadmium, chromium, copper and zinc from rice was also determined.

MATERIALS AND METHODS

Sixty duplicate rice samples were collected during the harvest period in September-October 1992 from five representative rice fields in the Delta of Ebro river: Amposta, Camarles, L'Aldea, La Cava and S. Jaume (Tarragona, southern Catalonia, Spain). An extensive description of the study areas has been given in previous publications (Bosque et al. 1990; Schuhmacher et al. 1991). The samples concerned two rice varieties: *Senia* (short) and *Thaibonet* (long). Each sample was identified according to name of variety, location of rice field and type of soil in field, and kept in a polyethylene bag until analysis. Thirty duplicate superficial soil samples were also collected from the rice fields where rice plants grew. These samples were classified into three categories according to the type of soil in fields: peat, sandy and clay. They were dried at 60 °C and packed in a polyethylene bag until analysis. Samples (30) of waters irrigating the rice fields were also collected.

About 1 g of rice was exactly weighed and ashed with 10 ml of nitric acid (Suprapur, Merck, Darmstadt, Germany) heating at 110 °C for 2 hr. Five ml of perchloric acid were then added and the mixture was heated at 180 °C for 2 hr. After cooling, ashed samples were diluted with 0.1 M HNO_3 and transferred to Teflon vessels. Two ml of HF were added and the samples were heated until ashing was completed. After adequate cooling, solutions were made up to 25 ml with 1% nitric acid.

The dried soil samples without stones and pebbles were well mixed and 1 g of the powdered soil was processed. Samples were put into a test tube and 1 ml of HCl, 4 ml of HNO_3 and 4 ml of H_2SO_4 were added. The mixtures were heated at 100 °C for 5 hr. On completion of the digestion and after cooling, the samples were filtered and solutions were made up to 25 ml with 1% nitric acid.

Water samples were filtered through a 0.45 μm membrane immediately after collection. The first 50 ml were kept and nitric acid was added until pH 1.

Chromium, copper and zinc concentrations were determined by inductively coupled plasma atomic emission spectrometry (Jobin Yvon 38 VHR), whereas cadmium levels were determined by Zeeman atomic absorption spectrophotometry using a Varian spectrophotometer and a Spectra A-30 graphite furnace. The standard addition method was used. Three replicate determinations were made for each solution. During the analytical work, together with each series of ten samples always at least one blank was run and analyzed for the appropiate elements. The accuracy and precision of the analytical methods were tested with standard reference materials (NBS-bovine liver, No. 1577).

Statistical differences were evaluated by Kruskal-Wallis test. Statistical significance was evaluated by Mann-Whitney U test. The level of significance was set at $P < 0.05$. Linear regression analysis (Pearson's correlation coefficient) was applied following a log-transformation of the metal concentrations.

RESULTS AND DISCUSSION

The concentrations of cadmium, chromium, copper and zinc in rice, soil and water samples from five localities of the Delta of Ebro river are shown in Table 1. No statistically significant differences between samples of rice and soils collected in the different fields were observed, whereas in waters only the levels of zinc in the samples collected in Amposta were significantly higher than those found for the other areas.

A significant Pearson's correlation coefficient was found between the copper and zinc contents in rice ($r = 0.7065$, $P < 0.0001$) and soil ($r = 0.4546$, $P < 0.05$). Cadmium and chromium concentrations were also significantly correlated in rice ($r = 0.6006$, $P < 0.01$) and soil ($r = 0.6881$, $P < 0.0001$). However, metal levels in rice were not significantly correlated neither with metal concentrations in soil nor with metal levels in waters, which agrees with the results of previous studies (Suzuki and Iwao 1982; Rivai et al. 1990a). The reason is that the pH of soil, oxidation-reduction conditions, content of humus and organisms, formation of insoluble compounds, etc., are interrelated in a very complicated manner with the absorption of the metals by the crops (Suzuki et al. 1980). With regard to cadmium, it was found that if the other conditions are constant, cadmium-rich soil produces cadmium-rich rice (Suzuki et al. 1980). On the other hand, a significant inverse correlation was recently reported for cadmium and copper contents in wild rice from central Canada (Pip 1993).

In the present study, the soil cadmium levels were remarkably lower than those found in Poland (Gzyl 1990) and more similar to those previously reported for other areas of Spain (Alegria et al. 1991). However, the concentrations of cadmium in soils are considerably higher than those reported for a number of asian countries (Rivai et al. 1990a). The cadmium levels found in rice were similar to those reported for Thailand, Philippines and Bangladesh, higher than those found in Brazil, China and Korea, and lower than the levels found in Japan (Rivai et al. 1990b). The mean cadmium and copper concentrations observed in this study were lower than those reported by Pip (1993) in wild rice from Canada, whereas the levels of copper, zinc and cadmium in rice were also lower than those reported for rice from Texas (Suzuki and Iwao 1982).

Table 1. Influence of locality on cadmium, chromium, copper and zinc concentrations in polished rice (μg/g), soil (μg/g) and water (μg/l) samples from the Delta of Ebro river (southern Catalonia, Spain)[1]

Locality	Cadmium	Chromium	Copper	Zinc
Amposta				
Rice	0.022±0.005	0.54±0.33	1.42±0.65	19.82±1.21
Soil	0.37±0.07	5.23±3.19	6.78±0.87	20.37±3.29
Water	0.007±0.006	3.05±0.99	0.24±0.17	99.80±41.68*
Camarles				
Rice	0.023±0.004	0.65±0.13	1.46±0.50	13.52±2.87
Soil	0.51±0.12	6.22±3.50	7.63±1.42	25.84±5.72
Water	0.012±0.005	5.09±0.92	2.44±1.95	51.23±7.23
L'Aldea				
Rice	0.018±0.007	0.31±0.35	2.52±2.28	21.64±9.35
Soil	0.48±0.06	6.40±3.95	7.84±0.76	22.72±1.68
Water	0.016±0.014	6.25±2.98	0.45±0.33	32.45±4.16
La Cava				
Rice	0.020±0.003	0.31±0.29	1.08±0.68	20.64±6.82
Soil	0.46±0.20	7.66±1.23	6.38±0.38	21.66±1.25
Water	0.016±0.014	4.53±1.65	0.50±0.05	35.00±11.35
S. Jaume				
Rice	0.019±0.005	0.45±0.17	0.69±0.24	18.32±6.07
Soil	0.50±0.29	7.04±3.23	7.67±2.30	20.75±2.35
Water	0.006±0.005	6.95±2.41	1.06±0.71	33.33±11.67

[1]Results are means ± SD. An asterisk indicates a significant difference by Kruskal-Wallis test at $P<0.05$.

The differences in metal contents in rice and soil samples according to the soil type are shown in Table 2. The cadmium and chromium levels in soil were significantly higher in peat and clay soils than in sandy soils. In contrast, copper and zinc concentrations in rice were lower for samples from sandy soils, which suggests that this kind of soils would not be adequate to grow rice.

The metal contents in unpolished and polished rice of the same variety and location of rice field were also compared (Table 3). No significant differences were observed in cadmium, chromium, copper or zinc concentrations. It would indicate that from the nutritional point of view there are no differences in the consumption of polished or unpolished rice from the Delta of Ebro river. Masironi et al. (1977) found 109% cadmium, 75% copper and 84% zinc in polished rice samples compared to unpolished ones.

Table 2. Influence of soil type on metal concentrations ($\mu g/g$) in unpolished rice and soil samples from the Delta of Ebro river[1]

Type of soil	Cadmium	Chromium	Copper	Zinc
Peat				
Rice	0.020±0.004	0.32±0.12	1.64±0.88[a]	17.59±7.75
Soil	0.60±0.10[a]	7.91±1.29[a]	7.21±1.92	19.96±2.35
Sandy				
Rice	0.020±0.004	0.30±0.11	0.49±0.12[b]	12.67±2.77
Soil	0.30±0.13[b]	3.45±3.36[b]	7.69±2.70	24.46±4.84
Clay				
Rice	0.018±0.004	0.29±0.10	1.32±0.44[a]	19.67±7.14
Soil	0.54±0.10[a]	7.75±2.23[a]	7.04±0.78	22.13±2.33
P^2 (rice)	NS	NS	<0.001	NS
P^3 (soil)	<0.001	<0.01	NS	NS

[1]Results are means ± SD. [2,3]Statistical significance. NS denotes not significant. For each metal and variable, results not showing a common superscript are significantly different according Mann-Whitney U test at the indicated level.

Table 3. Cadmium, chromium, copper and zinc levels ($\mu g/g$) in unpolished and polished rice samples from the Delta of Ebro river (Catalonia, Spain)[1]

Rice	Cadmium	Chromium	Copper	Zinc
Unpolished	0.019±0.003	0.31±0.11	1.16±0.72	16.93±6.88
Polished	0.020±0.004	0.45±0.28	1.43±1.21	19.07±6.01
P^2	NS	NS	NS	NS

[1]Results are means ± SD. [2]Statistical significance. NS denotes not significant.

Table 4. Influence of variety of rice on cadmium, chromium, copper and zinc concentrations ($\mu g/g$) in rice samples from the Delta of Ebro river (southern Catalonia, Spain)[1]

Variety of rice	Cadmium	Chromium	Copper	Zinc
Senia (short)	0.020±0.005	0.45±0.28	1.43±1.26	19.07±6.01
Thaibonet (long)	0.027±0.005	0.31±0.22	1.74±1.47	18.68±3.57
P^2	<0.01	NS	NS	NS

[1]Results are means ± SD. [2]Statistical significance according to Kruskal-Wallis test. NS denotes not significant.

Table 4 shows the influence of variety of rice on metal concentrations in rice samples. Cadmium levels are significantly lower ($P<0.01$) in the *Senia* variety, whereas rice variety made no distinct differences in chromium, copper or zinc contents. These results agree with those reported by Suzuki et al. (1980). Table 5 summarizes a toxicological (cadmium) and nutritional (chromium, copper and zinc) estimation of the metal content in rice from the Delta of Ebro river.

Table 5. Estimation of daily cadmium, chromium, copper and zinc intake from rice in Tarragona Province (southern Catalonia, Spain)

	Cadmium	Chromium	Copper	Zinc
Metal content (μg/g rice)	0.020	0.44	1.39	19.07
Daily metal intake from rice (μg/person)	0.27	6.03	19.04	261.26
Total daily intake[1] of metals (μg/person)	56	125	1156	7523
Percentage of metal intake from rice	0.48	4.82	1.65	3.47

[1]From Schuhmacher et al. 1991, 1993b.

Although the absolute amounts of cadmium and chromium ingested from rice by the population of Tarragona Province are relatively high compared to those ingested in other countries (Suzuki et al. 1980; Rivai et al. 1990b), the total amount of these metals coming from the diet would not mean a health hazard.

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