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Chromium, Copper, and Zinc Concentrations in Edible Vegetables Grown in Tarragona Province, Spain

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Because of the wide distribution of heavy metals throughout the earth's crust and oceans, as well as the remarkable environmental pollution, it is inevitable that trace of these metals can be detected in virtually all plant and animal organisms. Some of these metals (e.g., lead, cadmium, mercury) are contaminants and they have a toxicological significance, whereas other such as chromium, cobalt, copper, manganese, zinc, etc., are essential micronutrients for higher animals and plants (Somers 1974). However, these essential metals can also be dangerous at sufficiently high levels.

Vegetables absorb heavy metals from the soil, as well as from surface deposits on parts of vegetables exposed to polluted air (Buchauer 1973; Haghiri 1973). Moreover, the use of sewage for the irrigation of vegetables and the presence of heavy metals in fertilizers constitute additional sources of metal pollution for vegetables.

Whereas lead and cadmium are well-known environmental pollutants, chromium, copper, zinc, and their compounds play an important role in many fields of modern industry. Substitutes will not be available even in the future or only to a very limited extent (Raithel et al. 1988). In a previous study, we investigated the average content of lead and cadmium in edible vegetables from Tarragona Province (Spain) (Bosque et al. 1990). The objective of the present study was to establish the present levels of chromium, copper and zinc pollution in edible vegetables from Tarragona Province, and to determine the contribution of these vegetables to the tolerable daily intakes of chromium, copper and zinc.

MATERIALS AND METHODS

All samples of edible vegetables were randomly obtained from commercial growers or from retail outlets from several locations in Tarragona Province (NE Spain), which was divided for the study in two areas presumably exposed to different degrees of environmental pollution. The northern area is basically industrial, whereas the southern area is essentially agricultural with an important

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number of vegetable gardens being irrigated with waters from the Ebro river. A more extensive description of the study areas has been given in previous publications (Bosque et al. 1990; Schuhmacher et al. 1991). After delivery to the laboratory, samples were stored at 4°C and processed further as soon as possible. A total of 275 samples (belonging to 16 different species) for each area were analyzed. The species investigated included: radish root (*Raphanus sativus*), celery (*Apium graveolens*), potato (*Solanum tuberosum*), onion (*Allium cepa*), leek (*Allium ampeloprasum*), chard (*Beta vulgaris*), spinach (*Spinacea oleracea*), lettuce (*Lactuca sativa*), endive (*Chichorium endivia*), cauliflower (*Brassica oleracea*), cabbage (*Brassica oleracea*), tomato (*Lycopersicon lycopersicum*), green pepper (*Capsicum anuum*), artichoke (*Cynara scolymus*), green bean (*Phaseolus vulgaris*), and eggplant (*Solanum melongena*). The samples were divided into five groups based on the edible parts according to the Spanish Alimentary Code (Código Alimentario Español 1967).
*Group 1: **Roots and tubercles** (radish root, celery, and potato).
*Group 2: **Bulbs** (onion and leek).
*Group 3: **Leaves and soft stalks** (chard, spinach, lettuce and endive).
*Group 4: **Cabbages** (cauliflower and cabbage).
*Group 5: **Fruits and similar garden produce** (tomato, green pepper, artichoke, green bean, and eggplant).

Vegetables were washed in fresh running water to eliminate dust, dirt, possible parasites or their eggs and then they were again washed with deionized water (Zurera et al. 1987). Non-edible parts were removed according to common household practices. Any water remaining from washing was removed by placing the sample on filter papers. When dry, 1 g of each sample was digested in a teflon bomb with 2 ml of 65% nitric acid (Suprapur Merck, Darmstadt, FRG) heating at 110°C for 18 hr. On completion of the digestion and after adequate cooling, solutions were made up to 10 ml with deionized water and stored in polyethylene bottles. The final chromium solutions were determined using a Perkin-Elmer 5100 Zeeman spectrophotometer and Spectra A-30 graphite furnace. Zinc was determined by atomic absorption spectrometry with flame in a Perkin-Elmer model 4000. Copper concentrations were measured in a computer-controlled sequential inductively coupled plasma spectrometer (Jobin Yvon JY 38 VHR). During the analytical work, together with each series of six samples, always at least one blank was run and analyzed for the appropiate elements. Chromium, copper and zinc recoveries were assessed by analyses of Bovine Liver (National Bureau of Standards SRM 1577). The mean recovery rates obtained were 85.6% for chromium, 95.3% for copper, and 97.2% for zinc. All necessary precautions were adopted to avoid possible contamination of the samples. The limits of determination were respectively 0.001 μg/g for chromium and copper, and 0.002 μg/g for zinc. Moreover, samples were analyzed as blind duplicates. The average difference between the duplicate determinations was 5.1% for chromium, 6.9% for copper, and 3.5% for zinc.

Differences between northern and southern areas were determined by one-way analysis of variance (ANOVA). Statistical significance was evaluated by Kruskal-Wallis test or by Mann-Whitney U test. A probability of 0.05 or less was considered significant. Linear regression analysis (Pearson's correlation coefficient) was applied following a log-transformation of the chromium, copper and zinc concentrations.

RESULTS AND DISCUSSION

The mean values for chromium, copper and zinc concentrations in the edible vegetables included in this study are summarized in Tables 1,2 and 3. The results show that all metals accumulated to a greater or lesser extent by the 16 species investigated. The remarkable standard deviations for most results (especially for chromium) are probably due to that the samples were collected in a relatively high number of different places from Tarragona Province.

Radish root, potato, green bean, spinach, artichok and chard contained the highest mean concentrations of copper and zinc, whereas radish root and spinach contained the highest levels of chromium (Tables 1-3). Most species did not present significant differences between samples collected in both areas, although the concentrations of copper and zinc in the vegetables obtained from the southern area were usually higher than those collected in the northern area, whereas the levels of chromium were very similar for the two areas. The higher levels of copper and zinc found in the southern area are very probably due to irrigation with waters from the Ebro river which contain high concentrations of heavy metals.

On the other hand, a high Pearson's correlation coefficient was found between the levels of copper and zinc in the vegetables evaluated in the present study ($r = 0.651$, $p < 0.001$). However, the correlation coefficient was lower between copper and chromium concentrations ($r = 0.285$, $p < 0.001$) and between chromium and zinc levels ($r = 0.343$, $p < 0.01$).

With regard to the levels of the metals according to the five groups of vegetables established in the Spanish Alimentary Code, the group containing the highest concentrations of chromium, copper and zinc was made up of roots and tubercles, followed by bulbs (Figures 1-3), while the levels of metals in leaves and soft stalks, cabbages and fruits and garden produce were rather similar. Therefore, for environmental contamination of edible vegetables, our results would indicate that the levels of chromium, copper and zinc in soils, and irrigation waters are probably more important than their concentrations in the air.

In an additional investigation, the concentrations of chromium, copper and zinc in different zones of some vegetables were also measured: leek (root, stalk and leaves); spinach, celery and chard (stalk and leaves); and radish root (root and leaves) (Table 4). These results are in agreement with the theory of Haghiri (1973) who considered the root as an important entry point for metals into the vegetables. In a previous study (Davies and White 1981), roots and aerial parts

Table 1. Chromium concentrations (μg/g fresh weight) in edible vegetables from Tarragona Province, Spain[1]

Species	Northern area	Southern area	P[2]
Roots and tubercles			
Radish root	0.18 ± 0.22	0.15 ± 0.19	NS
Potato	0.11 ± 0.18	0.03 ± 0.01	NS
Celery	0.09 ± 0.07	0.10 ± 0.07	NS
Bulbs			
Onion	0.21 ± 0.25	0.02 ± 0.01	NS
Leek	0.02 ± 0.02	0.05 ± 0.05	NS
Leaves and soft stalks			
Chard	0.01 ± 0.01	0.04 ± 0.04	<0.05
Spinach	0.14 ± 0.10	0.22 ± 0.05	NS
Lettuce	0.04 ± 0.02	0.06 ± 0.03	NS
Endive	0.07 ± 0.06	0.03 ± 0.02	NS
Cabbages			
Cabbage	0.07 ± 0.05	0.05 ± 0.07	NS
Cauliflower	0.01 ± 0.01	0.08 ± 0.07	<0.05
Fruits and garden produce			
Tomato	0.12 ± 0.24	0.06 ± 0.12	NS
Green pepper	0.02 ± 0.03	0.03 ± 0.01	NS
Artichoke	0.01 ± 0.01	0.03 ± 0.01	NS
Green bean	0.03 ± 0.03	0.06 ± 0.07	NS
Eggplant	0.05 ± 0.12	0.01 ± 0.01	NS

[1]All values are shown as means ± SD. [2]ANOVA P value; NS, not significant.

Table 2. Copper concentrations (μg/g fresh weight) in edible vegetables from Tarragona Province, Spain[1]

Species	Northern area	Southern area	P[2]
Roots and tubercles			
Radish root	0.94 ± 0.83	2.26 ± 1.45	<0.05
Potato	1.38 ± 0.73	1.69 ± 0.62	NS
Celery	0.87 ± 0.56	0.82 ± 0.52	NS
Bulbs			
Onion	0.36 ± 0.13	0.99 ± 0.42	<0.01
Leek	0.98 ± 0.41	1.54 ± 0.72	<0.05
Leaves and soft stalks			
Chard	0.88 ± 0.48	1.16 ± 0.83	NS
Spinach	1.26 ± 0.82	0.95 ± 0.57	NS
Lettuce	0.48 ± 0.28	0.36 ± 0.23	NS
Endive	0.67 ± 0.26	0.94 ± 0.17	NS
Cabbages			
Cabbage	0.75 ± 0.48	0.61 ± 0.32	NS
Cauliflower	0.42 ± 0.08	0.33 ± 0.21	NS
Fruits and garden produce			
Tomato	0.61 ± 0.23	0.61 ± 0.32	NS
Green pepper	0.69 ± 0.28	0.87 ± 0.32	NS
Artichoke	1.23 ± 0.09	1.10 ± 0.23	<0.05
Green bean	1.51 ± 0.67	0.76 ± 0.27	<0.05
Eggplant	0.57 ± 0.32	0.67 ± 0.10	NS

[1]All values are shown as means ± SD. [2]ANOVA P value; NS, not significant.

Table 3. Zinc concentrations (μg/g fresh weight) in edible vegetables from Tarragona Province, Spain[1]

Species	Northern area	Southern area	P[2]
Roots and tubercles			
Radish root	3.17 ± 1.90	4.10 ± 2.02	NS
Potato	2.81 ± 1.03	3.47 ± 0.81	NS
Celery	3.28 ± 2.41	4.30 ± 3.90	NS
Bulbs			
Onion	1.45 ± 0.48	2.95 ± 1.03	<0.05
Leek	4.50 ± 3.08	4.30 ± 2.50	NS
Leaves and soft stalks			
Chard	1.53 ± 1.53	2.93 ± 0.91	NS
Spinach	4.11 ± 2.13	3.73 ± 1.26	NS
Lettuce	1.02 ± 0.65	1.52 ± 1.07	NS
Endive	1.60 ± 0.33	2.90 ± 0.58	<0.01
Cabbages			
Cabbage	2.95 ± 0.71	2.42 ± 0.86	NS
Cauliflower	2.83 ± 1.09	2.41 ± 1.06	NS
Fruits and garden produce			
Tomato	1.57 ± 0.73	1.76 ± 0.46	NS
Green pepper	0.87 ± 0.72	1.09 ± 0.50	NS
Artichoke	4.07 ± 0.63	5.75 ± 0.82	NS
Green bean	5.59 ± 3.10	2.70 ± 0.51	<0.05
Eggplant	1.29 ± 0.55	1.81 ± 0.44	NS

[1]All values are shown as means ± SD. [2]ANOVA P value; NS, not significant.

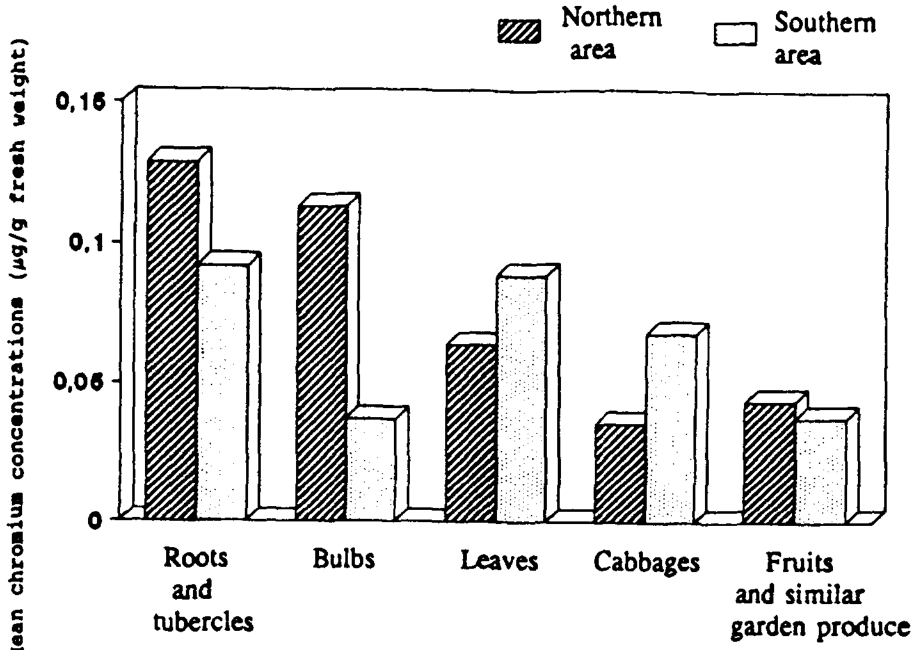

Figure 1. Mean chromium concentrations of the five groups of vegetables.

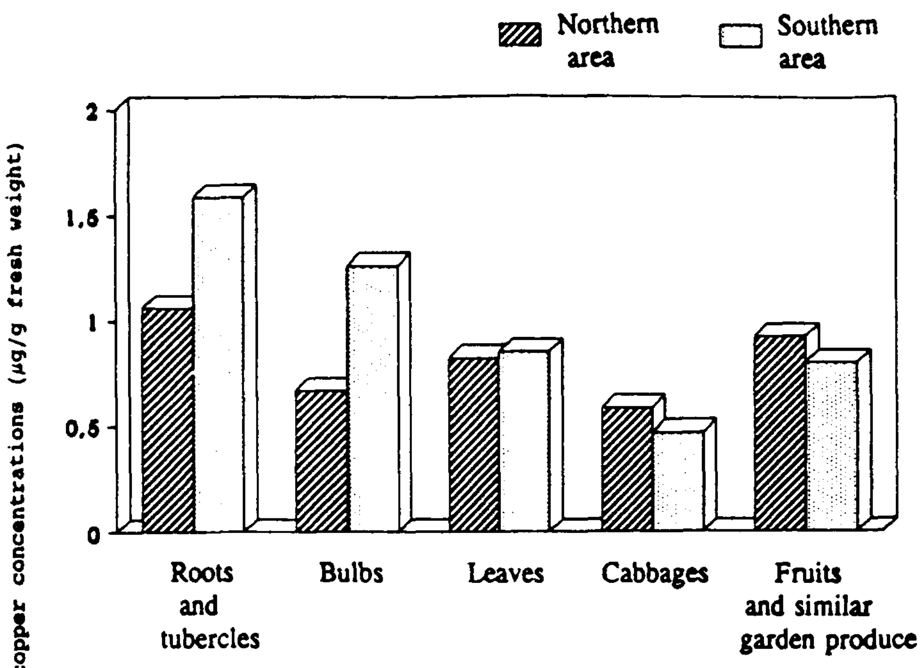

Figure 2. Mean copper concentrations of the five groups of vegetables.

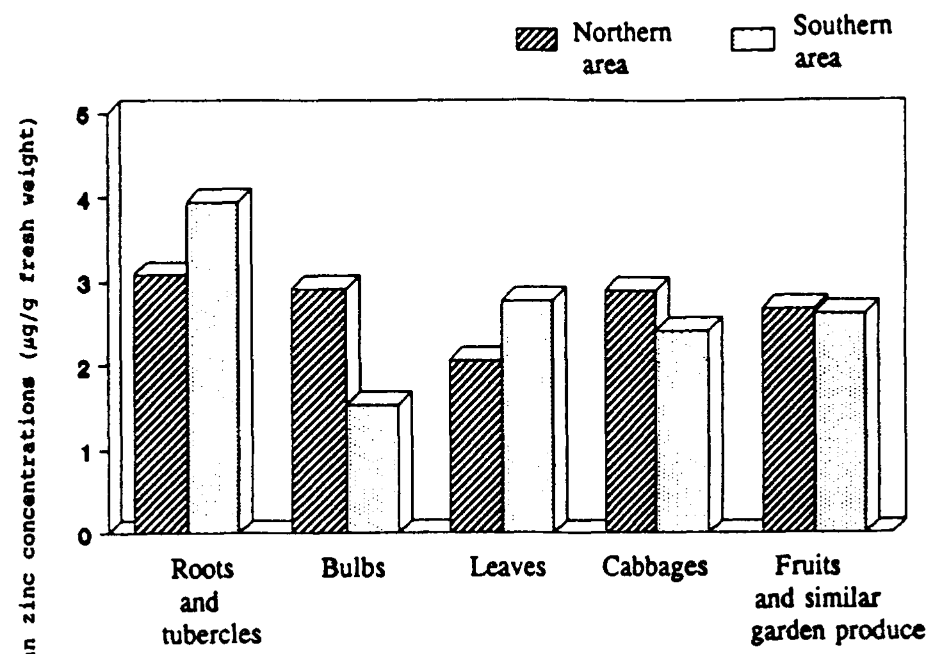

Figure 3. Mean zinc concentrations of the five groups of vegetables.

of lettuce, onion, carrots and Brussels sprouts were analyzed for lead, zinc, copper and chromium concentrations. It was concluded (with the exception of the lettuce) that the root seems to be a barrier to the translocation of metals. In contrast, in other studies on lead and cadmium contamination levels in edible vegetables, it was considered that the aerial vegetable zones are the most important entry point for these metals (Havre and Underdal 1976; Zurera et al. 1987; Bosque et al. 1990).

Table 4. Chromium, copper and zinc concentrations (μg/g fresh weight) in some edible vegetables from Tarragona Province according to the different parts of the vegetables[1]

	Roots	Stalks	Leaves
Chromium	0.34 ± 0.25^a	0.06 ± 0.09^b	0.10 ± 0.08^c
Copper	2.60 ± 1.59^a	0.80 ± 0.53^b	1.21 ± 0.80^c
Zinc	6.05 ± 2.32^a	2.30 ± 1.79^b	4.13 ± 2.37^c

[1]All values are shown as means ± SD. Means with different superscipts (a,b,c) are significantly different from each other at $P < 0.05$.

The reported values of chromium, copper and zinc concentrations in edible vegetables of other areas and countries are very variable, depending on a great number of factors. The copper and zinc levels found in this study agree well in general with published values, while the concentrations of chromium were relatively higher than some previously reported values (Davies and White 1981; Pennington et al. 1986; Alegria et al. 1990; Ellen et al. 1990). Taken into account the average consumption of vegetable foodstuffs in Tarragona Province (Salas et al. 1985), as well as the recommended daily intake of these metals (chromium, 50-200 μg/day; copper, 2000-3000 μg/day, and zinc, 15000 μg/day) (Orten and Neuhaus 1984), the results of this study indicate that the daily intake of chromium, copper and zinc through edible vegetables from Tarragona Province would not mean a health hazard for consumers.

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REFERENCES

Alegria A, Barbera R, Farre R, Lagarda MJ (1990) Lead, cadmium and chromium content of edible vegetables grown in three different agricultural areas. Food Addit Contam 7 (suppl 1): S22-S25

Bosque MA, Schuhmacher M, Domingo JL, Llobet JM (1990) Concentrations of lead and cadmium in edible vegetables from Tarragona Province, Spain. Sci Total Environ 95: 61-67

Buchauer MJ (1973) Contamination of soil and vegetation near a zinc smelter by

zinc, cadmium, copper and lead. Environ Sci Technol 7: 131-135
Código Alimentario Español (1967) Separatas del Boletín Oficial del Estado. Gaceta de Madrid
Davies BE, White HM (1981) Trace elements in vegetables grown on soils contaminated by base metal mining. J Plant Nutr 3: 387-396
Ellen G, Van Loon JW, Tolsma K (1990) Heavy metals in vegetables grown in the Netherlands and in domestic and imported fruits. Z Lebensm Unters Forsch 190: 34-39
Haghiri F (1973) Cadmium uptake by plants. J Environ Qual 2: 93-96
Havre GN, Underdal B (1976) Lead contamination of vegetation grown close to roads. Acta Agric Scan 26: 18-24
Orten JM, Neuhaus OW (1984) *Human Biochemistry*, pp 743-750, Ed. Panamericana, Buenos Aires
Pennington JAT, Young BE, Wilson DB, Johnson RD, Vanderveen JE (1986) Mineral content of foods and total diets: the selected minerals in foods survey, 1982 to 1984. J Am Diet Assoc 86: 876-891
Raithel HJ, Schaller KH, Reith A, Svenes KB, Valentin H (1988) Investigations on the quantitative determination of nickel and chromium in human lung tissue. Int Arch Occup Environ Health 60: 55-66
Salas J, Font I, Canals J, Guinovart L, Sospedra C, Marti-Hennenberg C (1985) Consumo, hábitos alimentarios y estado nutricional de la población de Reus. III. Distribución por edad y sexo del consumo de leche, derivados de la leche, grasas, vegetales y verduras. Med Clin 84: 470-475
Schuhmacher M, Bosque MA, Domingo JL, Corbella J (1991) Dietary intake of lead and cadmium from foods in Tarragona Province, Spain. Bull Environ Contam Toxicol 46: 320-328
Somers E (1974) The toxic potential of trace metals in foods. A review. J Food Sci 39: 215-217
Zurera G, Estrada B, Rincon F, Pozo R (1987) Lead and cadmium contamination levels in edible vegetables. Bull Environ Contam Toxicol 38: 805-812

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