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Toxic Metals and Metalloids in Dietetic Products

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Aim. To determine the concentrations of cadmium, lead, mercury, and metalloid arsenic in the samples of some dietetic products marketed in Croatia, and to compare the values obtained with maximum allowed amounts (MAA) according to the law.

Methods. Metal and metalloid concentrations were measured in 30 dietetic products from the group of industrial food supplements and food additives. The measurements were performed by the method of atomic absorption spectrometry. The concentrations of cadmium, lead, mercury, and arsenic were compared with the maximum allowed amounts for these substances in corn and corn products, and their estimated daily intake with the recommendations of the World Health Organization.

Results. Two out of 30 samples contained cadmium, 5 samples contained lead, and as many as 16 samples contained mercury in concentrations exceeding maximum allowed amounts. The concentration of arsenic was below maximum allowed amount in all samples. In total, the concentrations of metals exceeding maximum allowed amount were found in 17 out of 30 samples. Extremely high contamination with heavy metals was detected in a sample based on zinc oxide, in which the concentration of cadmium (0.418 mg/kg) was four times higher than the maximum allowed amount, and of lead (6.074 mg/kg) 15 times higher than the maximum allowed amount. The highest concentration of mercury (1.117 mg/kg), 35-fold maximum allowed amount, was found in a ginseng-based sample.

Conclusions. Cadmium, lead, mercury, and arsenic were present in some dietetic products in concentrations exceeding maximum allowed amounts. Dietetic products control should match respective legal provisions of the European Union requirements, and requires continual monitoring.

Key words: *arsenic; cadmium; Croatia; lead; legislation, food; mercury; spectrophotometry, atomic absorption*

Food is the source of essential metals and metalloids but frequently may contain harmful or even noxious metals and metalloids. These are found in relatively small amounts in foodstuffs, either as natural ingredients or as a result of food contamination during the process of manufacture, processing, transportation, or storage (1-3).

Today, when non-medical therapeutic procedures are becoming ever more popular, various herbal teas and mineral products available to the population at large may also be the source of metal and metalloid poisoning (4). Although herbal teas are frequently promoted as natural and thus harmless, various ingredients found in these products may have detrimental effects in humans, such as allergic reactions (5,6), toxic reactions (7), severe nephropathy (8), colitis (9), drug interactions (10), and carcinogenic effects (11,12). Contamination of these products with toxic metals and metalloids, which is mostly due to the lack of legal regulation in the field of herbal medicine, presents a special problem (13).

Toxic activity of metal and metalloids can be manifested in two forms: acute and chronic toxicity. Acute toxicity occurs upon exposure to relatively high doses of some metals and metalloids over a short period of time, whereas prolonged exposure to low doses may lead to gradual development of the symptoms and the chronic form. Acute exposure to high doses of lead can cause severe neurologic symptoms, and acute poisoning with methyl mercury is characterized by toxic effects on the central nervous system. Chronic exposure to many metals is usually associated with renal and hepatic tissue damage and function impairment, probably due to the role of these organs in detoxification and elimination of toxic metals and metalloids. The potential carcinogenic effects in the human body, demonstrated for arsenic, probably for cadmium, and possibly for lead, are of high importance in chronic exposure to these substances (14).

Cases of poisoning with toxic metals and metalloids were repeatedly reported in relation to Ayurveda (15-17) and traditional Chinese medicine (18-

20). However, not only traditional remedies but also other dietetic products can represent a significant source of exposure to toxic metals and metalloids, especially if used without control. Results of the studies performed to date point to the need of an increased surveillance in the manufacture and use of food supplements and herbal medicines (21).

The aim of our study was to determine the level of contamination of dietetic products from the group of industrial food supplements and food additives with cadmium, lead, mercury, and arsenic, and to compare them with maximum allowed amounts in some foodstuffs. Considering that the field of dietetic products has not yet been covered by legal provisions in Croatia, we compared our findings with the maximum allowed amounts for particular metals and metalloids in corn and corn products.

Material and Methods

Concentrations of cadmium, lead, mercury, and toxic metalloid arsenic were determined in 30 samples of dietetic products of different manufacturers from Croatia and abroad. Dietetic products were randomly selected from 393 samples of dietetic products referred during 2001 to the Zagreb Institute of Public Health by the Governmental Sanitation Department for Safety Assessment.

Dietetic products analyzed in the study belonged to the group of industrial food supplements and food additives, differing in both their form and purpose. They included agents used for vigor enhancement and stress reduction, immune system reinforcement, dietary vitamin and mineral supplementation, body weight regulation, and natural digestives. They were available in the form of a tablet, effervescent tablet, pastille, capsule, liquid, tincture, or powder. According to the composition, the samples were divided into six groups, as follows: 1) honey-based products (2 samples, containing purified propolis extract), 2) products based on medicinal herbs (13 samples, containing *Hypericum perforatum, Garcinia Cambodia,* Siberian ginseng, dandelion, sunflower, *Ginkgo biloba,* natural gelée royale, evening primrose oil, or Korean ginseng), 3) products based on fruit, vegetable, or other nutritive substance extracts (5 samples, containing extracts of various fruits or/and vegetables, and plant oil mixtures), 4) products containing coenzymes and enzymes (3 samples, containing Q10 coenzyme, or papain, mylase, or prolase enzymes), 5) products containing vitamins or minerals (6 samples, containing A, E, C, and B group vitamins, or/and iodine, calcium, iron, magnesium, copper, zinc, chromium, selenium, potassium, or molybdenum); and 6) products of animal origin (a sample containing dried shark cartilage).

The samples of dietetic products were prepared for analysis by the method of microwave digestion (22,23). One gram of a properly homogenized sample was weighed and placed into a cuvette. Five mL of 65% HNO_3 and 0.5 mL of H_2O_2 were added to the sample. The cuvettes were placed into a microwave oven and submitted to digestion for about 20 min, as recommended for this type of samples. Upon the completion of digestion, the cuvettes with samples were cooled in a water bath, and their content was transferred to a volumetric flask and filled up with distilled water to 50 mL. Microwave digestion was performed in a Milestone MLS 1200 Mega Oven (Milestone, Bergamo, Italy) for microwave sample incineration.

The concentrations of cadmium, lead, mercury, and arsenic in the samples of dietetic products were determined by atomic absorption spectrometry on a Perkin-Elmer 4100 Zeeman ZL.FIMS-400 atomic absorption spectrometer (Perkin-Elmer, Überlingen, Germany). The graphite cuvette technique was used to determine the concentrations of cadmium and lead, cold vapor technique to determine mercury, and hydride technique to determine arsenic (24-26). The absorbance was measured at a wavelength of 228.8 nm for cadmium, 283.3 nm for lead, 253.7 nm for mercury, and 193.7 nm for arsenic.

The accuracy of atomic absorption spectrometry, after the samples had been prepared by the method of microwave digestion, was 96.8% for cadmium, 92.7% for lead, 98.8% for mercury, and 95.7% for arsenic (27). The limits of atomic absorption spectrometry detection were 0.2 g/L for cadmium, 2.0 g/L for lead, 0.1 g/L for mercury, and 0.5 g/L for arsenic (28).

The values were expressed in milligrams of metals or metalloid per kilogram of a dietetic product and compared with maximum allowed amount for the particular metal or metalloid. The maximum allowed amounts for metals and metalloids in various foodstuffs are regulated by law (29,30). However, not all groups of foodstuffs, including dietetic products, are covered by the by-law regulating these values. Therefore, maximum allowed amounts for the study metals and metalloid in corn and corn products, which, like dietetic products, are daily used in human diet, were chosen for comparison.

Results

The analysis of dietetic products for the presence of cadmium showed that the mean cadmium concentration was below the maximum allowed amount in all groups of dietetic products. Cadmium concentrations exceeding the maximum allowed amount were recorded in 2 of 30 samples, 1 from the group of products based on herbal medicines, and 1 from the group of products containing vitamins and minerals (Table 1, Fig. 1).

The mean lead concentration was below the maximum allowed amount in 5 of the 6 dietetic product groups. Lead concentrations exceeding maximum allowed amount were detected in 5 out of 30 samples.

Table 1. Concentrations (mg/kg) of cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As) in 30 dietetic products analyzed at the Zagreb Institute of Public Health*

	Cd		Pb		Hg		As	
Group of dietetic products	No./Total†	Conc.‡	No./Total	Conc.	No./Total	Conc.	No./Total	Conc.
Honey-based products	0/2	0.009 (0.007-0.011)	0/2	0.235 (0.007-0.349)	2/2	0.047 (0.036-0.058)	0/2	0.072 (0.068-0.075)
Medicinal herb-based products	1/13	0.007 (0.006-0.124)	3/13	0.146 (0.065-1.061)	5/13	0.022 (0.007-0.076)	0/13	0.044 (0.017-0.128)
Products based on fruit, vegetable, and other nutritive substance extracts	1/6	0.007 (0.006-0.418)	1/6	0.115 (0.066-6.074)	3/6	0.041 (0.006-0.049)	0/6	0.112 (0.016-0.121)
Products containing coenzymes and enzymes	0/3	0.0052 (0.006-0.052)	0/3	0.219 (0.109-0.230)	2/3	0.032 (0.014-0.039)	0/3	0.052 (0.027-0.063)
Products containing vitamins and minerals	0/5	0.006 (0.006-0.036)	1/5	0.087 (0.007-0.606)	3/5	0.031 (0.003-0.060)	0/5	0.040 (0.016-0.130)
Products of animal origin	0/1	0.0097	0/1	0.315	0/1	0.072	0/1	0.044
Total	2/30	0.009 (0.006-0.418)	5/30	0.149 (0.007-6.074)	16/30	0.032 (0.003-0.076)	0/30	0.040 (0.016-0.130)

*Maximum allowed amount (MAA) of metals in corn and corn products are as follows: Cd = 0.1 mg/kg; Pb = 0.4 mg/kg; Hg = 0.03 mg/kg; As = 0.5 mg/kg (29,30).
†No. – number of samples with metal concentration exceeding MAA/number of analyzed samples.
‡Concentration; median (range).

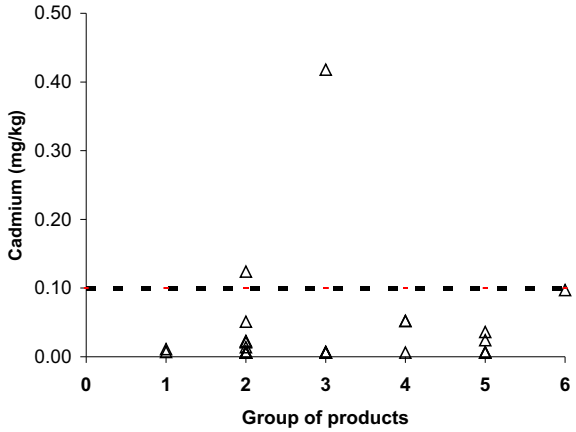

Figure 1. Cadmium concentrations (mg/kg) in 30 dietetic products analyzed at the Zagreb Institute of Public Health in relation to maximum allowed amount (MAA) (broken line). Groups of dietetic products: 1. honey-based products; 2. medicinal herb-based products; 3. products based on fruit, vegetable, and other nutritive substance extracts; 4. products containing coenzymes and enzymes; 5. products containing vitamins and minerals; 6. products of animal origin.

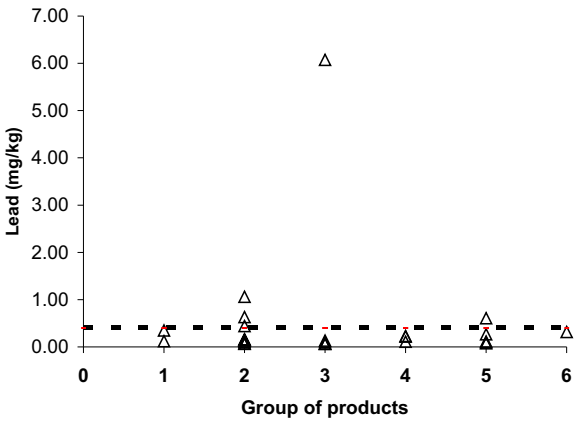

Figure 2. Lead concentrations (mg/kg) in 30 dietetic products analyzed at the Zagreb Institute of Public Health in relation with maximum allowed amount (MAA) (broken line). Groups of dietetic products: 1. honey-based products; 2. medicinal herb-based products; 3. products based on fruit, vegetable, and other nutritive substance extracts; 4. products containing coenzymes and enzymes; 5. products containing vitamins and minerals; 6. products of animal origin.

In the group of dietetic products containing vitamins and minerals, the lead concentration was almost 3-fold maximum allowed amount (Table 1, Fig. 2) or 15-fold maximum allowed amount, mainly due to the high lead amount (6.074 mg/kg) in a zinc oxide-based sample (Table 2).

Thpe mean mercury concentration exceeded maximum allowed amount in 4 of 6 dietetic product groups analyzed, in as many as 16 of 30 samples (Table 1, Fig. 3). Very high mercury concentration of 1.117 mg/kg, (35-fold maximum allowed amount), was found in a sample based on Korean ginseng (Table 2).

The mean arsenic concentration was below maximum allowed amount in all groups of dietetic products and all samples (Table 1, Fig. 4).

Increased metal concentrations (Cd, Pb, and Hg) were detected in 17 out of 30 samples (Table 2). Increased concentrations of all three metals were recorded in a single sample, of 2 metals in 4 samples, and of 1 metal in 12 samples. Extremely high metal concentrations were found in the sample based on Korean ginseng and in a sample based on zinc oxide (Table 2).

Discussion

Because dietetic products have been regularly referred to the Department of Safety Control, we investigated the concentrations of toxic metals and metalloids to provide basis for legal regulation of these products. Maximum allowed amounts for metals and metalloids in corn and corn products were used as reference values, because maximum allowed amounts for metals and metalloids in dietetic products in Croatia still do not exist. Because dietetic products are products ingested regularly on a daily basis, more than half of study samples proved unacceptable. The major weakness to this selection of food-

Table 2. Dietetic products with metal concentrations exceeding maximum allowed amounts (MAA)*

Sample No. audit specification	Metal concentration (mg/kg)		
	cadmium (Cd)	lead (Pb)	mercury (Hg)
1. Honey based product			0.058
2. Product based on medicinal herb extracts		0.442	0.044
3. Honey based product			0.036
4. Product containing coenzymes and enzymes			0.032
5. Product containing coenzymes and enzymes			0.039
6. Product of animal origin			0.072
7. Product based on fruit, vegetable and other nutritive substance extracts			0.052
8. Product based on fruit, vegetable and other nutritive substance extracts		0.606	0.060
10. Product based on fruit, vegetable and other nutritive substance extracts			0.041
11. Product containing vitamins and minerals			0.031
15. Product based on medicinal herb extracts			0.031
19. Product based on medicinal herb extracts			0.044
21. Product containing vitamins and minerals			0.034
23. Product containing vitamins and minerals	0.418	6.074	
24. Product containing vitamins and minerals			0.049
27. Product containing vitamins and minerals		0.630	0.076
29. Product containing vitamins and minerals	0.124	1.061	1.117
MAA	0.100	0.400	0.030

*Analyzed products were compared with maximum allowed amounts (MAA) of metals and metalloid in corn and corn products as most similar to dietetic products, because there are no special legal provisions on dietetic products in the Republic of Croatia or other European countries.

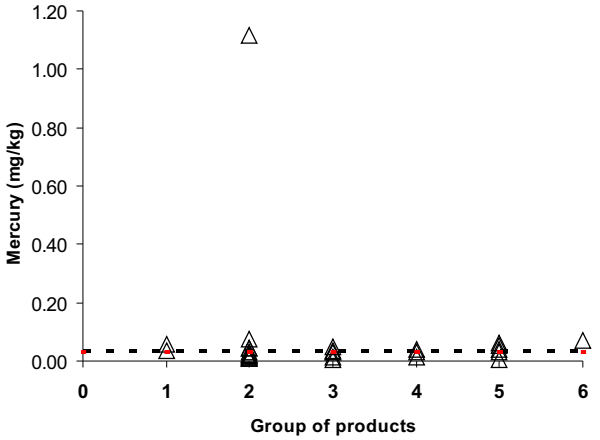

Figure 3. Mercury concentrations (mg/kg) in 30 dietetic products analyzed at the Zagreb Institute of Public Health in relation with maximum allowed amount (MAA) (broken line). Groups of dietetic products: 1. honey-based products; 2. medicinal herb-based products; 3. products based on fruit, vegetable, and other nutritive substance extracts; 4. products containing coenzymes and enzymes; 5. products containing vitamins and minerals; 6. products of animal origin.

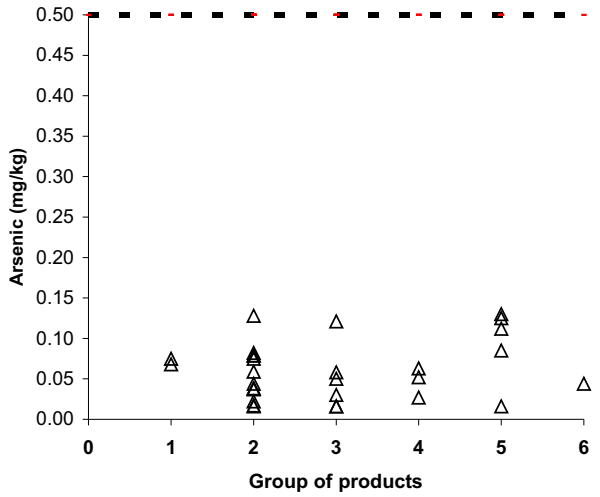

Figure 4. Arsenic concentrations (mg/kg) in 30 dietetic products analyzed at the Zagreb Public Health Institute in relation with maximum allowed amount (MAA) (broken line). Groups of dietetic products: 1. honey-based products; 2. medicinal herb-based products; 3. products based on fruit, vegetable, and other nutritive substance extracts; 4. products containing coenzymes and enzymes; 5. products containing vitamins and minerals; 6. products of animal origin.

stuffs was that the rate of use of dietetic products was rather low in the general population, with the exception of some special products intended for particular population groups (e.g., diabetics, hypertensives, or individuals requiring special dietary regimens). On the other hand, even if the criteria for spice were applied, which allow for 10-fold amounts of all harmful ingredients, including metals, there would be at least 2 samples containing unacceptably high concentrations of these substances.

By definition, dietetic products are foodstuffs intended for special dietary requirements, which differ from the foodstuffs of usual composition by their specific composition or process of manufacture. These special foodstuffs are intended for alimentary needs of (a) infants and children; (b) individuals with digestive or metabolic disturbances; and (c) individuals with specific physiologic conditions requiring special effects by controlled ingestion of particular foodstuff ingredients (33). In addition to the regular and special baby foods and formulas, there are 15 groups of various special-purpose dietetic products. These include products intended for strictly defined users, such as gluten-free foodstuffs, sugar substitutes, low-sodium products, but also food supplements, food additives, and other dietetic products (33).

The use of dietetic products is on a steady increase in Croatia. Although no target studies have been conducted, this trend is definitely stimulated by repetitive restrictions in the rights from health insurance (34), continuous deterioration of the standard of living, and increasing stress and social uncertainty.

Although the decision on purchase and use of these products is a private matter of each individual, the government is obliged to protect the citizens' health by legal regulations and prevent any harm or even development of disease due to the use of these products. The existing confusion in the field has obviously favored uncontrolled and frequently very low-tech manufacture of these products. A large number of such products have been imported, especially exotic miraculous products of traditional oriental medicines. There was even a case of poisoning with one of these products in Croatia (15).

Finally, taking an impartial position between the two extremes, ie, those tending to permit maximum concentrations of metals in dietetic products as in case of spice, and those asking for the respective criteria to be the same as those valid for the foodstuffs widely used on a daily basis, we want to draw attention to the complete confusion in the field at the expense of the health and quality of life of the Croatian population. The similar situation is in other countries in transition as well as the countries in the European Union. Therefore, the forthcoming legal provisions should regulate more precisely the conditions to be met by both manufacturers and importers of dietetic products in the Republic of Croatia, in line with the respective regulations in industrialized countries.

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