

HEAVY METALS IN SOME IMPORTED FOOD PRODUCTS AND THEIR POTENTIAL TOXIC IMPLICATIONS

Biljana Vitosević¹, Svetomir Samardžić², Vuko Antonijević³, Vladimir Jakovljević⁴

¹Department of Medical Subjects, Faculty of Physical Education, University of Kosovska Mitrovica, ²Department of Hygiene, Faculty of Medicine, University of Kosovska Mitrovica, ³Public Health Institute, Kosovska Mitrovica, ⁴Department of Physiology, Faculty of Medicine, University of Kragujevac, Serbia

TEŠKI METALI U ŽIVOTNIM NAMIRNICAMA UVOZNOG POREKLA I NJIHOVE EVENTUALNE TOKSIKOLOŠKE IMPLIKACIJE

Biljana Vitošević¹, Svetomir Samardžić², Vuko Antonijević³, Vladimir Jakovljević⁴

¹Katedra za medicinske predmete, Fakultet za fizičku kulturu, Univerzitet u Kosovskoj Mitrovici, ²Institut za higijenu, Medicinski fakultet, Univerzitet u Kosovskoj Mitrovici, ³Zavod za zaštitu zdravlja, Kosovska Mitrovica, ⁴Katedra za fiziologiju, Medicinski fakultet, Univerzitet u Kragujevcu, Srbija

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ABSTRACT

Heavy metal pollution is a result of increased industrialization throughout the world, which has penetrated into all sectors of the food industry. Because of that the World Health Organization (WHO) classifies heavy metals too as one of the risks to whom people are exposed through food. With this work we wished to examine the content of heavy metals in imported food products. We divided the samples into the following groups of food products: fish and canned fish products, milk and dairy products, vegetable and vegetable products, fruit and fruit products, cocoa and its products and infant foods. Our results show that the content of heavy metals in analyzed samples is quite below maximum limits allowed in some food products, except in three samples which have the values that are close to maximum limits allowed, because of improper processing. Our results can provide a contribution to health safety of imported food products.

Key words: food contamination, heavy metals

INTRODUCTION

Heavy metal pollution is a result of increasing industrialization throughout the world which is accompanied by the extraction and distribution of mineral substances from their natural deposits. Taking into consideration that they are transported both as gases or adsorbed on hard particles, heavy metals are able to pass great distances before being deposited on ground or water. In different chemical and biological processes, as the reaction of hydrolyses, chelation, complexation, biometylation, precipitation and adsorption, heavy metals change their chemical form, distribution and bioavailability. In that way and through plants, heavy metals are included in the food chain and come to a man.

The most important sources of food contamination are:

- soil (medium) where food is grown,
- fertilisers and other chemicals used for agriculture,
- water used for food processing or cooking,
- equipment used for food processing and
- conditions for food storage and for food transportation (1).

Considering theoretically, every 1000 kg of „normal“ soil contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium. It means that even foodstuffs produced in completely unpolluted areas, they are not completely free of heavy metal presence and the absorption of very small amounts of metals is always present (2).

SAŽETAK

Zagađenje teškim metalima je rezultat povećane industrijalizacije širom sveta, koja je prodrila i u sve okvire prehrambene industrije, pa Svetska Zdravstvena Organizacija (WHO) klasifikuje i teške metale kao jedan od rizika kojima su ljudi izloženi preko hrane. Ovim radom želeli smo da ispitamo sadržaj teških metala u namirnicama uvoznog porekla. Uzorke smo podelili u sledeće grupe životnih namirnica: ribe i proizvodi od ribe (u limenci), mleko i proizvodi od mleka, povrće i proizvodi od povrća, voće i proizvodi od voća, kakao i njegovi proizvodi i dečja hrana. Naši rezultati pokazuju da je sadržaj teških metala u analiziranim uzorcima znatno ispod maksimalno dozvoljenih koncentracija (MDK), a samo mali broj uzoraka (svega 3 uzorka) ima vrednosti koje su približne maksimalno dozvoljenim koncentracijama, što se pripisuje propustima u procesu proizvodnje. Naši rezultati mogu da pruže doprinos zdravstvenoj bezbednosti namirnica uvoznog porekla.

Cljučne reči: kontaminacija namirnica, teški metali

Increasing of metal concentration in food over the allowed limits (either concerning not essential metals or essential metals in surplus), may cause toxic effects for these products consumers. The gravity of toxic effects depends on nature, quantity and chemical form of metals and synergetic or antagonistic effects of other chemical contaminants. Children and old people are more sensitive to the toxic effects of metals than middle aged people. Children are mostly exposed to the toxic metal effects through food, concerning their more taking food according to their physical weight. Metals, especially lead, are also better resorbed in children digestive tract. Metal genotoxic effects are more often in children because their organism grows faster, the metabolism is more intensive and the cells are divided more quickly (3, 4).

Lead is one of the most significant and the oldest metals with damage effects on humans health. There is even an information that the fall of the Roman Empire was hastened by the chronic lead poisoning of the rule class who drank water and wine from goblets which had lead-alloy composition (5). In food production, lead is used for milk pottery, for the metal covers of wine bottles, for lead water pipes, and even for wine sweetener in the form of acetate („lead sugar“) (6).

The main source of cadmium exposition is contaminated food, cereals and rice which come from contaminated soil areas. In contrast to lead, it cannot be removed from plants by washing them, because it is distributed

within the plant through root. There is the most cadmium in sea food, shells and some mushrooms. The increased cadmium content in Central American cocoa is probably the result of its specific local constituency of the soil. As opposed to African cocoa kernels which contain 0.08–0.14 mg/kg, values from 0.18–1.5 mg/kg are found in the fine cocoa varieties from Venezuela and Ecuador, for example. There is a high level of cadmium in cacao in the Far East too (7).

Mercury gets into water current by rinsing out the soil that was treated with pesticides which contain it. In that way, it is included in food chain and gets into various plants, algae and fish where is deposited in their muscles. By using the contaminated fish, shells and crayfish in the nutrition, mercury gets into human organism in the form of toxic methylmercury. The presence of mercury in the vegetable, for example, is very low, except if it grew near industrial factories. Arsenic in the form of inorganic and organic trivalent and pentavalent chemical compound, is used in industry as pesticide and for some color making (well known arsenic green colours „scheel green“, „schweinfurt green“ etc.) (8). It is also known as an additive for poultry and domestic animals (especially swine) in parasitic disease test. It is used for fattening up, faster grow and for better pigmentation, so it is often present in chicken and turkey meat. It is not that much present in vegetable, and the concentration is sometimes higher a little bit in fruit because it is used as fungicide in the fruit production (9).

Essential elements are also present in the industrial processes and agrotechnical operations, so disregarding their nutritive essence, their contents should be checked because they can often reach toxic level. A copper intoxication can be made by its many chemical compounds which are used as fungicide in agriculture and veterinary practice and by using vegetable and fruit that grew on the copper high level soil (near smelters, industrial factories). Zinc and iron are used in the form of alloys in industry. They are even some inorganic fertilizer components.

According to these facts, the aim of our investigation was to determine the heavy metal level in imported food products in order to estimate their quality. The nature of the food we consume and our total diet greatly influences our health and well being. The safety of our food supply is a shared responsibility, from farm to fork, of the food producing industry, regulatory authorities and consumers. As part of this responsibility it is essential to assess the potential risks posed by food and food ingredients.

MATERIAL AND METHODS

In our research we analyzed about 200 samples (three samples of every kind foodstuffs are analyzed) of food imported from abroad (Denmark, Portugal, Italy, Germany, Croatia, Holland, Bosnia and Hercegovina, Bulgaria, Romania, Turkey etc.) during the previous year. All foodstuffs were collected in the local supermarkets. The samples are divided into the following groups of food products: fish and canned fish products, milk and dairy products, vegetables and vegetable products, fruit and

fruit products, cocoa and its products and infant food. Samples placed in plastic bags were taken by sanitary inspector by method of an accidental sample. Heavy metal examination in food products was done by using atomic absorption spectrometry (sample preparation by wet burning) in Public Health Institute in Kosovska Mitrovica which is accredited by the European Consortium for Accreditation for the determination of heavy metals in food. All chemicals used were of analytical grade from Merck. Work standard solutions were prepared immediately before the determination of these elements in the samples. All samples were processed for analysis on the day of purchase. Weighted 1–3 g of sample was put into a 100 ml Kjeldahl flask and 10 ml of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) (1:3) were added to the flask. After thermolysis and heating until discoloration (with hydrogen peroxide) to oxidize all the easily oxidizable material, the solution was cooled and added deionized water, filtered and diluted to 50 ml with deionized water (10). This solution is analyzed using atomic absorption spectrometer with graphite furnace, auto-sampler and background correction. There was necessary to remove organic matter present in the sample by mineral acids in order to determine mercury and arsenic and then they are transformed into volatile hydride (11). Metal content is expressed in mg/kg and determination was done on atomic absorption spectrometry type AI-1200 (Aurora Instruments-Vancouver, Canada) under the recommended conditions. Individual metal concentrations in the samples were read at specified absorbencies for each metal. MAL (maximum allowed limits) are from the rule book about content of pesticide, metal and metalloid, chemotherapeutics, anabolics and other toxic substances which can be found in food products (12). All values are expressed as mean \pm standard deviation (SD) and statistical evaluation was performed by Student's t-test

RESULTS

Our results showed that the heavy metal content was considerably below maximum allowed limits (table 1), what was also a case with milk, dairy products, vegetable and fruit (tables 2, 3 and 4). On the other hand, we noted higher content of cadmium content in cocoa products imported from Turkey (table 5), while in infant food all values were bellow MAL (table 6).

Table 1. Fish and canned fish products.

	Hg	Pb	Cd	Fe	Zn	As	Cu
min	0.0010	0.0100	0.0050	10.0000	75.0000	0.0010	7.0000
max	0.0050	0.0600	0.1500	30.0000	100.0000	0.0500	15.0000
\bar{X}	0.0029	0.0373	0.0409	21.3636	87.2727	0.0165	9.4545
SD	0.0012	0.0176	0.0543	7.2019	9.1363	0.0173	2.0611
SE	0.0004	0.0056	0.0172	2.2774	2.8891	0.0055	0.6518
CV%	42.6193	47.2944	132.8060	33.7112	10.4686	105.3700	21.7996
MAL mg/kg	0.6	0.15	0.8	30	100	2	30

MAL – maximum allowed limits

Table 2. Milk and dairy products.

	Hg	Pb	Cd	As	Cu
min	0.0010	0.1600	0.0070	0.0010	0.0010
max	0.0025	5.0000	0.0900	0.0250	0.0250
\bar{X}	0.0015	2.8360	0.0164	0.0062	0.0171
SD	0.0006	1.9400	0.0246	0.0067	0.0073
SE	0.0002	0.6467	0.0082	0.0022	0.0024
CV%	42.1637	68.4068	149.7122	108.6288	42.4491
MAL mg/kg	0.01-0.03	0.1-0.4	0.01-0.02	0.1	0.1

MAL – maximum allowed limits

Table 3. Vegetable and vegetable products.

	Hg	Pb	Cd	Fe	Zn	As	Cu
min	0.0005	0.0400	0.0070	0.4500	0.0010	0.0010	0.0250
max	0.0100	0.9000	0.0500	10.0000	10.0000	0.3000	5.0000
\bar{X}	0.0027	0.2282	0.0165	4.7227	3.7274	0.0508	1.3732
SD	0.0026	0.2600	0.0150	3.3589	3.3531	0.0813	1.3572
SE	0.0008	0.0822	0.0048	1.0622	1.0603	0.0257	0.4292
CV%	95.8587	113.9414	91.4494	71.1228	89.9584	160.0053	98.8366
MAL mg/kg	0.02	1	0.05	20	20	0.3	5

MAL – maximum allowed limits

Table 4. Fruit and fruit products.

	Hg	Pb	Cd	Fe	Zn	As	Cu
min	0.0010	0.0500	0.0050	0.0450	1.0000	0.0010	0.1600
max	0.0050	0.5000	0.0500	10.0000	20.0000	0.5000	5.0000
\bar{X}	0.0024	0.1440	0.0138	2.6145	7.3000	0.1086	2.8360
SD	0.0015	0.1281	0.0139	2.8922	6.7831	0.1729	1.9400
SE	0.0005	0.0427	0.0046	0.9641	2.2610	0.0576	0.6467
CV%	62.3610	88.9431	100.8158	110.6233	92.9187	159.2460	68.4068
MAL mg/kg	0.02	1	0.05	30	20	0.5-1	10

MAL – maximum allowed limits

Table 5. Cocoa and its products.

	Pb	Cd	As	Cu
min	0.0010	0.0070	0.0010	2.0000
max	1.0000	0.5000	0.5000	15.0000
\bar{X}	0.2801	0.1494	0.1157	6.0000
SD	0.3849	0.1549	0.1933	4.0743
SE	0.1283	0.0516	0.0644	1.3581
CV%	137.4227	103.6707	167.0694	67.9052
MAL mg/kg	2	0.2	1	20

MAL – maximum allowed limits

Table 6. Infant food.

	Hg	Pb	Cd	Zn	As	Cu
min	0.0010	0.0100	0.0050	0.0700	0.0010	0.1000
max	0.0025	0.0600	0.0090	7.0000	0.0050	2.5000
\bar{X}	0.0017	0.0450	0.0070	3.0730	0.0030	1.2900
SD	0.0007	0.0157	0.0015	2.8255	0.0015	0.7609
SE	0.0002	0.0052	0.0005	0.9418	0.0005	0.2536
CV%	42.0084	34.7833	22.1313	91.9459	51.6398	58.9810
MAL mg/kg	0.005	0.08	0.02	7-8	0.08	1.5-2.5

MAL – maximum allowed limits

DISCUSSION

Liquid and solid materials are considered to be food. They are energetic substrate for mechanical and metabolic process, growth and reproduction. Good health pictures, a high level of physical, mental and spiritual welfare, and the key for good health and welfare is just a high quality and well balanced food. The contemporary industrialization and the use of chemical products have entered the complete food industry, from the use of chemical fertilizer and chemical pesticides to the genetic modified food. Underdeveloped countries and developing countries have the problems how to fulfill the nutritive necessities in energetic value of the population, while at the same time highly developed countries have a problem in the field of rational consumption and healthy safety food. World Health Organization (WHO) includes the content of heavy metals in food as risks for people who consume such food (13). There are numerous data in literature on heavy metal analyses in food products. Wojciechowska et al. (14) examined the content of Pb, Cd, Cu and Zn in cereals, flour and powdered milk. Their conclusion was that metal level in these samples was considerably below MAL, but heavy metal analyses in fruit showed their rather big content in the samples originated from polluted areas (15). In Finland, for example, these researches are often done, because the previous study showed worrying results. More recent data show the heavy metal contents clearly decreased, what corresponds to pollution reduction in Finland as in other Nordic countries. The continuation of this reduction is predicted on condition that the consuming food is of domestic origin (16, 17). Yurico et al. examined Cd concentration in usual Japanese food and beverages and found out its much higher concentration in spinach, mushrooms, shellfish and soybean sauce (18). Cd concentration in rice depends on Cd content in soil and it is present mainly in the outer parts of grain which was removed in the milling process (19). Muntean et al. (20) examined heavy metal content in some food products in Romania. Their results showed lower level in relation to MAL (maximum allowed limits), excepting the samples taken from the polluted area. Lead mostly runs in bio-circle: atmosphere-water-ground-plants-animals-man. Pb alkyls have the biggest part in the atmosphere pollution, which are given to petrol as additives. They are component part of exhaust gases which appear as a result of petrol combustion in engines. Because of that, the plants on pastures and fields near roads, and through them animals are permanently exposed to lead pollution. In that way, for example, increased lead contents are registered in milk and dairy products of the cows grazed on such fields (21). Because of its characteristics bio-circle mercury is a dangerous pollutant. Heavy intoxication in Japan with mercury is notorious (Minimata disease) what was the result consuming of fish and shell contaminated by methyl-mercury. In New Mexico the children being consumed swine contaminated meat, had brain damage. In 1972 in Iraq there was an epidemic of mercury intoxica-

tion because of consuming the cereals contaminated by fungicides having mercury in themselves (22). There is mercury in fish, crayfish, shells and sometimes in grain, too. Mushrooms are big mercury accumulation as well. A bigger quantity of fish from Eastern European and Asian countries has been imported in recent years. Thus, for example a higher level of heavy metals than allowed was found in imported tuna from Japan and imported white and blue sea fish, squid and crayfish in Croatia (23). Fish and other aquatic organisms are generally known as contaminant bioaccumulators in water environment. Thus the examination of accumulated metal concentration in aquatic organisms and the potential endangered human health through contaminated fish consuming arouses a big attention. Although the most recent data of a great number of authors point out to heavy metal low accumulation in fish muscles and that the target organs are liver and kidneys, this fact by no means reduces the significance of its accumulation monitoring especially concerning human health (24).

Our analyses of fish and fish products showed that the heavy metal content was considerably below maximum allowed limits. Somewhat bigger heavy metal content, which came nearer MAL values, was found in two samples of the mussels and shells, imported from Denmark.

Analyses of heavy metal content in the samples of milk, fruit, vegetables and their products also pointed out considerably lower level from the maximum allowed.

Cocoa products were according to heavy metal content below MAL, but a sample of cocoa sugar table imported from Turkey, had some lead and cadmium content close to MAL. Literature data point out the varying quantity of Pb and Cd in cocoa products and chocolate, so they can be considerably bigger than allowed (25, 26). In 2002, American Environmental Safety Institute brought

an accusation against several chocolate manufacturers, including Hershey, Nestle, Kraft and Sees Candies, because the chocolates had lead and cadmium in such quantities which need warning. That level was bigger than allowed daily quantity for food (27). The U.S. Environmental Protection Agency has determined that for every microgram of lead that a child consumes, his blood lead level is increased by 0.16 microgr/dl, and that a sustained 1 microgr/dl increase in blood-lead concentration results in a loss of 0.257 IQ points in an average child (28).

Our results of heavy metal analyses in infant food point out the considerably lower content than MAL, although there are data in literature about bigger concentration than allowed one. There is a difference between an infantile and adult organism concerning toxic aspect in clinical manifestation of heavy metal intoxication. Thus symptoms appear after a shorter period and at a lower grade of exposing (29). Prenatal exposure to heavy metals was measured in a population of pregnant women and showed the negative effects on a childhood development, cognitive ability, behavioral and emotional characteristics, visual ability etc. (30, 31). Heavy metals in food can be problematic even for the child immunity system and they often show immune suppression action. Because of that a special attention is directed to child food check and its quality, because „children constitute 30% of the world's population but they are 100% of our future“ (United Nations, 1998).

Regarding all presented results, we can conclude that heavy metal content in analyzed foodstuffs of imported origin is considerably below maximum allowed limits (MAL) with just few samples close to MAL, what can be a result of production process mistakes. Our results can be a contribution to health safety food of imported origin with an aim of having back the consumer trust.

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