LEAD, CADMIUM, AND MERCURY DIETARY INTAKE IN CROATIA

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This paper gives an overview of published data on levels of lead, cadmium, total and methyl-mercury in various food items, and of a daily dietary intake assessment in Croatia focusing on the last 10 years. It briefly describes the most reliable methods for quantitative analysis of lead, cadmium, and mercury in biological material. Lead and cadmium concentrations in vegetables and in organs of domestic animals refer to non-exposed rural areas. Mercury concentrations in fish and mussels refer to industrially polluted and non-polluted areas of the Adriatic. The daily dietary intake of lead and cadmium was assessed on the basis of duplicate-diet-collection and food-disappearance method. The assessment of the total and methyl-mercury dietary intake was based on dietary surveys of family seafood consumption. Lead and cadmium intake through food in the general population was 6–40% of the Provisional Tolerable Weekly Intake (PTWI), depending on the assessment method. The only Croatian population consuming more mercury through seafood is the one living in Dalmatia, approaching the PTWI defined by WHO.

Key words: atomic absorption spectrometry, duplicate diet, fish, mussel, total and methyl-mercury, vegetable

The major route of exposure of general population to lead, cadmium, and mercury is through air and/or diet. The three metals are very toxic and their absorption and toxicity depends on dose and, among other diet constituents, on intake of essential metals through diet. Few literature data have been reported on the assessment of

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dietary intake of lead, cadmium, or mercury in Croatia (1–4). More documented are the levels of toxic metals in various food items (1, 5–12). Most reports published by the Croatian Public Health Institutes relate to statistical evaluation of compliance of food control of toxicants with the Croatian legislation and not to the assessment of the normal population dietary intake of certain toxic metal pollutants.

This aim of this paper is to review literature data on the levels of lead, cadmium, and mercury measured in food items and on the daily dietary intake assessment in Croatia. Attention will be given to reports published in the last ten years.

METHODS

Most laboratories in Croatia use the atomic absorption spectrometry (AAS) method to analyse lead, cadmium, and mercury in food. The flame (F AAS) or the electrothermal method (ET AAS) are applied to analyse lead and cadmium and the cold vapour method (CV AAS) or the hydride generation method (HG AAS) to analyse mercury. When sampling individual food items to analyse metals (such as a vegetable), it is usually washed under the tap water, and the samples are cut to small pieces. Homogenisation is not necessary. The sampling of the duplicate or the market basket diets, however, requires homogenisation. One sample of duplicate diet contains food and drink consumed over 24 hours and collected from selected individuals. The market basket diet, also called total diet study, has the sample composed of 5–10 cooked or raw food items (13).

The destruction of the organic component of the sample depends on the method of analysis used and on the element analysed. To determine lead and cadmium by ET AAS dry ashing at 450 °C is the procedure of choice for the following reasons; at that temperature the two elements do not evaporate and ashes can be dissolved in a minimum quantity of concentrated HNO₃ and adjusted to a certain volume with deionised water to form the final 1% v/v HNO₃ solution. At this concentration of HNO₃ graphite tubes are lasting longer and the possibility to contaminate samples by large volumes of acid is smaller. Porcelain or glass crucibles should be avoided for dry ashing due to possible contamination with lead from crucibles or adsorption of lead on crucibles (14). Quartz or platinum crucibles are recommended instead.

For mercury analysis, nitric acid is successfully used in wet digestion to destroy biological materials and transform the organically bound mercury to the ionic form. This method involves heating of the sample in concentrated nitric acid up to 80 °C in a closed system. If the sample is heated in an open system, losses of mercury are inevitable (15). Another wet digestion method for mercury analysis involves addition of concentrated nitric acid and the sample treatment in a microwave oven. This method has some limitations when using the Teflon™ tubes, as these can be contaminated with mercury irreversibly. Even quartz tubes show occasional high blank values.

Distilled or suprapur HNO₃ and deionised water of 0.06 µS/cm conductivity should be used throughout the preparation phase. For the internal quality control of analysis during the analytical procedure it is also necessary to use a certified biological material (such as wheat flower, bovine liver, or fish muscle). National or international inter-
laboratory comparisons are recommended for the external quality control. In most references cited in this review the internal or external quality control procedures were not mentioned. The results in this report are expressed either as µg/kg wet weight of food item, µg/m³ of air, µg/g of Hg in the hair or as µg/person of daily diet. All values are presented as mean ± standard deviation.

LEAD

The general population is exposed to lead through food, water, and air. Exposure to lead from the air is higher in urban population. Hazards from these sources have gradually diminished in Croatia due to removal of lead from gasoline. Measured concentrations of lead in the Zagreb air show a great decrease in average values over the last 10 years. Values dropped from 0.8 in 1990 to 0.09 µg/m³ in 2000 (16, 17). The future population exposure to air lead is expected to fall further. However, concentrations of lead in different food items including vegetables are expected to remain at the present level if produced/grown in contaminated areas. Lead concentrations were measured in 81 samples of different kinds of brassicas collected in Zagreb household gardens in 1995–1996. A wide range of values was obtained from 19 to 1,871 µg Pb/kg wet weight with median value of 454 µg/kg (10). Vegetable samples (14 samples of carrot, 17 of parsley, 10 of lettuce, and 18 of potato) collected outside the Croatian capital and far from any possible pollution gave lead concentration values of 11.1±8.7 to 73.8±66.9 µg/kg (Figure 1, unpublished results obtained in our laboratory). Twen-
ty-nine samples of the most commonly consumed Adriatic fish (Figure 2) were collected at the Zagreb market during 2000. Lead concentrations obtained in the fish muscle ranged from 9.6 to 44.1 µg/kg wet weight (12). The concentration in the mussel tissue, however, was about 10 times higher, that is 121 to 150 µg/kg.

![Graph showing lead, cadmium, and mercury in fish and mussels](image)

Figure 2  Lead, cadmium and mercury in common fish and mussels from Adriatic Sea (unpublished data; see text for details)

A study of daily dietary lead intake was performed during the 80s on a small group of women in Zagreb. The study was a part of a global-scale UNEP/WHO project (2, 18). After the international quality control of the analytical procedures, the results were compared between the participating countries. The method of duplicate diet collection and analysis of 119 samples showed that the daily dietary intake of lead in Zagreb was 15±7.2 µg/person (mean±SD). The findings in other countries varied between 26±7.9 µg/person in Stockholm and 46±18 µg/person in Beijing. Another study of daily dietary lead intake assessment in Croatia relied on lead levels in 19–22 foodstuffs. The composition of the diet and the consumption of the foodstuffs was calculated using the food-disappearance method, which relied on data published in the Statistical Yearbook of the Republic of Croatia. The daily dietary lead intake obtained by this method was 100 µg/person (4).

Absorption of lead from ingested food and water greatly depends on levels of other element present in the diet such as calcium, iron, and zinc. It has been shown that dietary deficiencies in these essential elements enhance lead absorption (19). Therefore, when assessing toxic element daily intake of a certain population it is always useful to analyse the intake of other essential elements as well. During the UNEP/WHO project, zinc, copper, iron, manganese, and calcium were analysed in duplicate
diets collected in Zagreb and compared to Swedish diets (Figure 3). All analysed elements in the Zagreb duplicate diets were lower than the Recommended Dietary Allowances (20) and significantly lower than in the Stockholm diets (21). The lower blood lead values found in the same study in the Stockholm population, as compared to Zagreb (18), might be partly associated with that difference in the daily intake of essential elements.

**Figure 3** Daily dietary intake of metals estimated by duplicate diet method (mg/person).

*Statistical significant difference between Stockholm and Zagreb data tested by the Student’s t-test. RDA= recommended daily allowance (adapted from ref. 21)*

Compared to the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (22), the daily dietary intake of lead found in the Croatian population of 232 µg/day and adult person makes only about 6–40% of PTWI, depending on the method applied.

**CADMIUM**

Cadmium is a nonessential, toxic metal to which humans are exposed through a variety of pathways including food, particularly leafy vegetables, grains, and cereals. The tobacco, itself a leafy plant, contains substantial amounts of cadmium, and its uptake is doubled in heavy smokers (19). Cadmium, which is in general lower in vegetables, muscle-meat, and fish, concentrates in shells and internal organs of different organisms. During the 80s cadmium was measured and reported in muscles, kidneys, and liver of several hundred samples taken from domestic animals (7). The range of cadmium concentrations in the muscles of cattle, pigs, lambs, fattened chicks, turkeys, and freshwater fish ranged from 17 to 102 µg/kg fresh weight. Cadmi-
um in the liver of domestic animals was between 70 and 300 µg/kg and in the kidney from 150 to 650 µg/kg. The level of cadmium in common fish muscle from the Adriatic Sea was 5.1–49.1 µg/kg and in mussels from 130 to 142 µg/kg (Figure 2) (12). Vegetables (carrots, lettuces, and potatoes, 20 samples of each, unpublished results) collected in an non-polluted rural area in 1993–1995. contained 14.9±11.6 to 42.3±16.5 µg/kg wet weight of cadmium (Figure 1).

The UNEP/WHO study with duplicate diet collection showed a daily intake of 8.5±3.8 µg/person of cadmium (2). The other study performed using the food-disappearance method (4) reported the daily intake of 17.3 µg/person. These dietary daily cadmium intake assessments make about 20% of the PTWI (22) which is 65 µg/day and person.

**MERCURY**

Mercury in the form of methyl-mercury has the highest concentrations in seafood. It is concentrated from the sea with a concentration factor $10^4$ to $10^5$ (23). It is also considered methylated by micro-organisms in sediments and in marine organisms. Mercury accumulated in the tissues of fish usually takes the form of methyl-mercury (24). It is more toxic than the inorganic form and the population living near the coast and on the islands runs a greater risk of ingesting this highly toxic substance. However, the toxicity of methyl-mercury is moderated by the presence of selenium in fish (19). It has been found that the molar ratio between methyl-mercury and selenium in fish is 0.2–0.4 (25). Due to higher consumption of seafood, mercury monitoring of the Adriatic fish was of special interest for Croatia, as well as the mercury exposure assessment of general population in Dalmatia. Particular attention was paid to the central part of the Adriatic coast which was contaminated by mercury by a chlor-alkali plant. The earliest report on methyl-mercury concentrations in the sediment, mussel, and fish in the polluted area of the Kaštela Bay in the Central Adriatic was given by Mikac and Picer (26). They found 2–20 µg/kg of methyl-mercury in the sediment, 10–110 µg/kg in mussels (*Mytilus galloprovincialis*), and 102–1,448 µg/kg in various species of fish. The same area polluted with mercury by a chlor-alkali plant was further studied by scientists from the Institute of Oceanography and Fisheries in Split (8, 9, 25, 27, 28). The values of total mercury mass fractions in the contaminated area ranged from 162±5 to 1,230±70 and in the non-contaminated area from 83±6 to 380±8 µg/kg. Methyl-mercury participated with 70–97% of total mercury in fish (9). Mussels and oysters from the North Adriatic (*Mytilus galloprovincialis Lam.* and *Ostrea edulis L.*) were studied for methyl and total mercury content in different seasons by Najdek and Sapunar (6). Methyl-mercury varied from 36.5 to 298.9 µg/kg and total mercury from 58.3–766 µg/kg. The total and methyl-mercury content increased in correlation with the body mass. The mercury content in mussels and the most commonly consumed fish from different uncontaminated areas of the North and Middle Adriatic Sea purchased at the Zagreb market ranged from 142 to 252 µg/kg (Figure 2) (12).
The only report of mean weekly mercury intake of general population in Croatia calculated on the basis of mean annual fish consumption was evaluated by Bošnir and co-workers (11). Their calculation gave 19 µg of total mercury and 16 µg of methyl-mercury consumed per person and a week. It amounts to only 6–7% of PTWI (22) for the total and methyl-mercury. However, the population of the Adriatic coast and islands consuming 4–5 times more fish a week is likely to have a much higher total and methyl-mercury intake. Buzina and co-workers compared the total and methyl-mercury content of seafood and dietary intake in polluted and control areas of the Adriatic (1). The daily intake was evaluated on the basis of dietary surveys of family seafood consumption. The results were compared with PTWI for the total mercury (300 µg Hg per person) and for methyl-mercury (200 µg Hg per person). The respective percentages of subjects from the industrially polluted area whose dietary intake exceeded PTWI was about 20% for the total mercury and 16% for methyl-mercury. In the control area, about 5% of adult male population consumed more than the total mercury PTWI and about 13% above the methyl-mercury PTWI. These values were compared to the values of total and methyl-mercury in hair (3). The concentration of the total mercury found in hair was 1.3–12.9 µg/g and of methyl-mercury 1.1–10.8 µg/g. It was concluded that it did not reach the critical level at which the toxic effect of mercury could be expected.

CONCLUSIONS

The daily lead and cadmium diet intake of general population in Croatia is much lower than the PTWI values proposed by WHO. Population living on the Adriatic coast and islands consumes more total and methyl-mercury through seafood than the inland population and its daily intake of mercury is closer to PTWI.

REFERENCES


Sažetak

UNOS OLOVA, KADMIJA I ŽIVE HRANOM U HRVATSKOJ


Ključne riječi:
atomska apsorpcijska spektrometria, dvostruki dnevni obrok, metil-živa, povrće, ribe, školjke

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