CONTROL OF HEAVY METAL CONTENT IN DIFFERENT TYPES OF VEGETABLES PRODUCED IN THE AREA OF ZENICA

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: In this study, concentrations of lead Pb, cadmium Cd and arsenic As were tested in 177 samples of fresh vegetables produced in the area of Zenica. This locality is exposed to the strong influence of high emissions of various pollutants primarily originating from metallurgical and thermal power plants, but also from local heating plants. The accumulation of heavy metals is followed by the types of vegetables: tuber and root, bulb, leaf, fruiting and legume from the group of fruiting vegetables. Preparation of samples was done with microwave digestion. The concentration of the selected metals in solutions after digestion was determined on Induced coupled plasma mass spectrometry (ICP-MS). The percentage participation of contents Pb, Cd and As, either higher or lower than the maximum allowable amount prescribed by the applicable law, was calculated in all 177 samples. The results showed that different groups of vegetables have different ability to adopt and accumulate heavy metals. The largest number of samples containing Pb content above the maximum level (ML) was in the group of leaf vegetables, then in the roots and finally in bulb groups. Cd was at the very limit with the maximum level in the parsley sample, while all other tested samples were in compliance with the applicable regulations. Two of the tested samples of the parsley leaves group had an increased content of As according to the legal regulations.

KEYWORDS: heavy metals, vegetables, maximum level (ML)

INTRODUCTION

The development of technology has brought to progress and serious damage of the eco-system. The area of Zenica municipality is under a strong influence of high emissions of different pollutants which are primarily derived from metallurgical and thermal power plants as well as from local boilers and other smaller environmental pollutants. Emission of different gases and solid particles results in contamination of soil, water and plants. Particularly threatened is the quality of agricultural crops that are constantly exposed to unfavourable impacts, leading to the accumulation of certain toxicants in plants. That is why this aspect of the research devotes great importance to determination of accumulation and effects of toxic substances in the diet chain. The term "heavy metals" is often used for a group of metals and metalloids that are related to toxicity, potential toxicity and ecotoxicity[1]. According to toxicity, metals and metalloid ions can be divided into three groups[2].

The first group includes metals (metalloids) which are toxic regardless of their concentration (lead, cadmium, mercury). Metals of the second group (arsenic, bismuth, indium, antimony and thallium) are less toxic, i.e. they are toxic only at higher concentrations. In the third group are metals (metalloids) of essential importance, such as copper, zinc, cobalt, selenium and iron, which are necessary for various biochemical and physiological processes in the body, and are toxic only above the certain concentration.

Concentration of essential and toxic heavy metals in ecosystems is continually increasing due to anthropogenic processes of urbanization, industrialization, transport, agricultural production and military activities. Production and industrial processes and road traffic are the most important for the deposition of zinc, copper, lead, cadmium and nickel and thermal power plants for arsenic[3].

As it is related to toxic substances which in a very low concentrations have a harmful effect on human health (mutagenic, teratogenic and carcinogenic effects), regular control of their presence in vegetables is gaining ever greater significance, especially given the fact that vegetables are consumed on a daily basis. In order to protect the health of the consumer, in the world and even in our country, the maximum level (ML) of metals in vegetables is regulated by normative regulations.

Plant adopts heavy metals from the soil through the root system, but also through the shoot system. Heavy metals that are deposited on the surface can often be eliminated by the washing, while bioaccumulated are difficult to remove[4].

Depending on the fact which plant organ is used in the diet, the following groups of vegetable crops are distinguished: bulb, fruiting, leafy, root vegetables. The categorization of the ability to accumulate heavy metals in important cultivated plants has a practical value because it provides the choice of species in relation to the level of loading of soil by heavy metals. So on land that is contaminated with heavy metals, it is not desirable to grow salad, spinach and so on.

MATERIALS AND METHODS

177 vegetable samples (fruits, leaves, tubers and bulbs) were collected at a phase of useable value. The vegetables were sampled from the locations which were from 0.1 up to 18 km far from a steel plant in Zenica. All samples were analyzed on lead, cadmium and arsenic. They were grouped into the following types of vegetables:

- tuberous and rooted vegetables (potatoes, carrots, parsley),
- bulb vegetables (red onion, white onion, young onions, leek),
- leafy vegetables (chard, lettuce),
- fruiting vegetables (tomato, pepper, cucumber, eggplant),
- legume from the group of fruiting vegetables (beans, peas, green beans).

The reason for the isolation of vegetable crops of legume vegetables in a special group belonging to the fruiting vegetable group is the separation within the regulation according to which the maximum level of heavy metal is determined[5].

Analyzes were done according to the accredited method "Determination of Trace Elements - Lead, Cadmium and Arsenic in Fruit and Vegetable by ICP-MS Method, after microwave digestion"[8]. For this method, the quantification limits (LOQ) for lead is 0.020 mg/kg and for cadmium and arsenic 0.004 mg/kg.

Sample preparation was performed in a microwave oven for digestion (MDS-8, Sineo). Microwave sample preparation technology is widely used in modern laboratories worldwide, due to their high speed, high efficiency, with the necessary characteristics related to protection of the environment, etc.

Microwave digestion involves rapid heating by direct absorption of microwave energy. This technology applies the closed digestion vessels to achieve a high temperature and high pressure.

The sample for analysis was prepared by removing inedible parts such as claws, leaves, seeds and so on, and washing with water. Then, the complete homogenization of the sample was carried out, by milling in a mixer or a mill. The sample mass used for the analysis was 1 g of wet mass.

Exposition (disquisition) of samples was done in concentration of minimum 65% HNO_3 (suprapur) and H_2O_2 (suprapur) minimum 30%.
The presence of elements in samples was read on the Induced coupled plasma mass spectrometry (ICP-MS), Agilent Technologies 7700x.

For calibration of instruments, at least three different concentrations of calibration solutions were prepared and used. The concentration range was selected in relation to the expected concentration of the analyte in the investigated sample. For these analyses, Multi-Element Calibration Standard concentration of 10 mg/l and internal standard Mix 100 mg/l concentration were used.

Concentrations of heavy metals were monitored according to the current regulation "Ordinance on maximum permissible quantities for certain contaminants in food, BiH Official Gazette No. 68/2014"[5]. According to this Ordinance for vegetables, it is necessary to determine lead, cadmium and arsenic.

RESULTS AND DISCUSSION

Developments of the industry, agriculture, transport and urbanization have resulted in excessive emissions of heavy metals into the environment, which due to their bio-accumulative properties have their negative impacts on the environment and living organisms as a whole. In this paper, the presence of lead, cadmium and arsenic in grown vegetables in the area of Zenica is presented. All 177 samples were classified by vegetable groups and the percentage of samples with lead, cadmium, arsenic content higher and lower than the maximum level (ML) were calculated.

From 59 examined samples in the group of tuberous and rooted vegetables, 41 had content of lead below the limit of quantification. 14 samples ranged from 0.035 to 0.096 mg/kg, as permitted by the Regulations[5,6,7]. Four samples had lead content higher than allowed. The cadmium content in 16 samples was within the range of 0.019 to 0.050 mg/kg. Only one sample had higher concentration than ML, while 42 samples were below the limit of quantification. There were no samples with arsenic content higher than allowed in tuberous and rooted vegetables. 51 samples had the amount of arsenic below the detection limit, while eight samples varied from 0.020 to 0.083 mg/kg.

42 samples were analyzed in the group of bulb vegetables. The content of lead was below the limit of the quantification method in 36 samples. Four

samples had the concentration within the permissible limits of 0.043 to 0.064 mg/kg, while two samples had higher concentration than ML (0.523 and 1.296 mg/kg). According to the Regulations in this group of vegetables, the content of lead should not be higher than 0.10 mg/kg. The cadmium content in 37 samples was below the limit of quantification. Five samples had the concentration within the permissible limits (0.031 to 0.041 mg/kg). The samples with cadmium content higher than allowed did not exist. 36 samples had the arsenic content below the limit of quantification. In six samples the content was within the permissible limits and ranged from 0.018 to 0.234 mg/kg. The samples with high content of arsenic were not in bulb vegetables.

Table 1. Lead, cadmium and arsenic content in different vegetable groups (%)

Types of vegetables	Lead		Cadmium		Arsenic	
	n	%	N	%	n	%
Tuber and root	**59**					
<LOQ	41	69.49	42	71.19	51	86.44
Below ML	14	23.73	16	27.12	8	13.56
Above ML	4	6.78	1	1.69	0	0.00
Bulb	**42**					
<LOQ	36	85.71	37	88.10	36	85.71
Below ML	4	9.53	5	11.90	6	14.29
Above ML	2	4.76	0	0.00	0	0.00
Leaf	**28**					
<LOQ	5	17.86	7	25.00	8	28.57
Below ML	16	57.14	21	75.00	18	64.29
Above ML	7	25.00	0	0.00	2	7.14
Fruiting	**31**					
<LOQ	31	100	31	96.77	31	96.77
Below ML	0	0.00	1	3.23	1	3.23
Above ML	0	0.00	0	0.00	0	0.00
Fruiting - legume	**17**					
<LOQ	16	94.12	17	100.00	17	100.00
Below ML	0	0.00	0	0.00	0	0.00
Above ML	1	5.88	0	0.00	0	0.00

28 samples of leafy vegetables were collected and analyzed. Lead content in five samples was below the limit of quantification. In 16 samples lead content ranged from 0.040 to 0.209 mg/kg, and in seven samples it was higher than ML. The highest lead content was found in parsley leaves - 2,385 mg/kg, which is eight times more than the maximum permitted quantity in this type of vegetable and is 0.3 mg/kg. The lead content was increased in salad samples in the amount of 0.767 mg/kg and 0.618 mg/kg, in chard 0.345 mg/kg.

The cadmium in the seven samples was below the detection limit, while in others it ranged from 0.020 mg/kg to 0.156 mg/kg, which is permitted under the Regulations. There were no samples with cadmium content over ML. The amount of arsenic in two samples of parsley leaves was above ML in amounts of 0.563 mg/kg and 0.416 mg/kg. According to the current regulation, the permitted amount is 0.3 mg/kg. Eight samples were below the limit of quantification, and in 18 samples it ranged from 0.020 to 0.191 mg/kg.

Based on the data presented in Table 1, it can be concluded that the content of lead, cadmium and arsenic in fruit crops did not exceed the limit prescribed by the Regulations. In almost all samples the content of the examined elements was even below the limit of the quantification method.

According to the results of the analysis for the content of lead, cadmium and arsenic in legume vegetables from the group of fruiting vegetables it can be concluded that an increased amount of lead was found in only one sample. The content of lead in the pea sample was 0.472 mg/kg and ML was 0.20 mg/kg. All other samples of the legume vegetables from all three locations had the content of lead, cadmium and arsenic below the limit of quantification.

From the results shown, different types of vegetables have different ability to adopt and accumulate heavy metals. The intensity of adoption is primarily influenced by the concentration of heavy metals in the external environment, especially the concentration of dissolved (active) forms of metal, the pH value of the soil, the carbonate content and organic matter in the soil, the degree of soil moisture and so on.

CONCLUSIONS

The development of technology and industry has led to undoubted progress, but also to serious damage of the eco-system. Soil, water, plants, and then animals and humans are contaminated due to the emission of various gases and solid particles. Dominant polluters are spatially and ecologically strongly linked to the city and surrounding settlements and their emissions cause multiple ecological consequences in all components of the ecosystem of Zenica region (air, water, soil, vegetation).

The concentration of lead, cadmium and arsenic in different types of vegetables was as follows:

– In 4 out of 59 samples of tuber and root vegetables or in 6.78% of samples the lead content was above ML. The cadmium content in one sample (1.69%) was higher than allowed, while the arsenic content of all samples was below ML.

- In 2 of 42 bulb samples or in 2.76% of samples, cadmium content was above ML. Cadmium and arsenic content was in all samples below the maximum permitted limit.
- In 7 of 28 leafy samples, or 25.00% of samples had the lead content higher than allowable. The cadmium content in all samples was below ML, while the arsenic content in two samples (7.14%) was above the maximum allowable amount.
- In 31 samples of fruiting crops, the content of lead, cadmium and arsenic did not exceed the limit prescribed by the Ordinance. In almost all samples, the content of the examined elements was even below the detection limit.
- In 17 samples of legume vegetables from the group of fruiting vegetables only one sample had the lead content above ML, while in other 16 samples the content of lead, cadmium and arsenic was below the detection limit.

From the results of the paper it can be seen that different types of vegetables have different ability to adopt and accumulate heavy metals. The largest number of samples with lead content above the maximum level was in the group of leafy vegetables (salad, leaf of parsley, chard) then in root (parsley, cabbage tail) and bulbous (leek). (Cadmium was at the limit of ML only in sample of root vegetable, while arsenic was above ML in two samples of leafy vegetables). The results of the study show that some cultures should be avoided near the emission centre. Special attention must be paid to the choice of cultures to be cultivated in this area because individual plants have a different affinity for heavy metals.

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