

Health risk from heavy metals via consumption of food crops grown on the soils in the vicinity of manganese mine

Senad Murtic^{1*}; Emir Sahinovic¹; Hamdija Civic² and Josip Jurkovic³

¹University of Sarajevo, Faculty of Agriculture and Food Sciences, Department of Plant Physiology, 71 000 Sarajevo, Bosnia and Herzegovina

²University of Sarajevo, Faculty of Agriculture and Food Sciences, Department of Plant Nutrition, 71 000 Sarajevo, Bosnia and Herzegovina

³University of Sarajevo, Faculty of Agriculture and Food Sciences, Department of Chemistry, 71 000 Sarajevo, Bosnia and Herzegovina

*Correspondence author: murticsenad@hotmail.com

Abstract

Murtic, S., Sahinovic, E., Civic, H. & Jurkovic, J. (2020). Health risk from heavy metals via consumption of food crops grown on the soils in the vicinity of manganese mine. *Bulg. J. Agric. Sci.*, 26 (2), 452–456

The objective of this study was to determine the content of heavy metals in the soils as well as in food crops in the vicinity of the manganese mine ‘Buzim’, and to assess the health risks of consumption of these plants on residents. Analyses of the heavy metals (Cr, Cd, Pb, Zn, Cu, Mn) in soils and plant samples was performed using atomic absorption spectrophotometry, and the health risks of food crops consumption was determined using a hazard quotient (HQ). The results of this study showed that the content of Mn and other examined heavy metals in soils and edible parts of onion, cabbage, raspberry and strawberry was lower than the permissible limits established by the legislation in Bosnia and Herzegovina. These results lead to the conclusion that the consumption of food crops grown on soils at the examined area, from the point of view of heavy metals, should not be dangerous to human health.

Keywords: fruits; vegetables; health; environment

Introduction

Heavy metals are generally defined as metals having a specific density of more than 5 g/cm³ and harmful effects on the environment and living organisms. These elements are considered systemic toxicants that are known to cause risks to human health, plants, animals, even at lower levels of exposure (Tchounwou et al., 2012). Although heavy metals are natural components of the Earth’s core, most environmental pollution with heavy metals, results from anthropogenic activities such as mining, foundries and smelters, industrial production, and domestic and agricultural use of heavy metal-containing compounds (Shallari et al., 1998; He et al., 2005).

In recent years, there has been a growing global public health concern associated with environmental pollution by heavy metals. Certainly, the accumulation of toxic heavy metals in edible parts of plants is a potential threat to human and animal health. Therefore, the study on dynamics of heavy metals in soil-plant interactions is very meaningful, especially if agricultural production is carried out near the ore deposits (Hu et al., 2017).

In the area of Buzim municipality, in the north-western Bosnia, there are several deposits of manganese ore, and the biggest among them is active manganese mine in the local community ‘Vrhovska’, located approximately 8 km northeast of the town of Buzim. Also, in this area a lot of people are engaged in agriculture.

Numerous studies have demonstrated the negative impact of mining area on agriculture (Qu et al., 2012; Hang et al., 2013; Galuszka et al., 2015). On the other hand, mining industry argue that mining activity and agriculture are not necessarily incompatible.

The main objective of this study was to determine the content of heavy metals (Cr, Cd, Pb, Zn, Cu, Mn) in the soils as well as in edible parts of plants in the vicinity of the manganese mine 'Buzim', and to assess the health risks of consumption of these plants on residents.

Materials and Methods

Plant material

Food crops that are mostly grown in the study area are onion (*Allium cepa* L.) strawberry (*Fragaria viridis* Weston), cabbage (*Brassica oleracea* L. var. *capitata*) and raspberry (*Rubus idaeus* L.), and therefore these plants were selected as the subject of this study.

Soil sampling

The soil samples used for analysis were taken from three agricultural plots located just three hundred meters from the manganese mine, in Buzim municipality, Bosnia and Herzegovina. The area of each plot was approximately 500 m². According to Soil Taxonomy (FAO, 1998), examined soils were classified as Cambisol. Soil samples (approximately 1 kg) were collected in October 2017 before cultivation at a depth of 0–30 cm using a soil sampler probe. At each plot, four sub-samples were collected and thoroughly mixed to form a soil sample.

The soil samples were air dried at room temperature, crushed and grinded using soil mortar and pestle, passed through sieves (1 mm) and then stored until measurement.

Soil analysis

Total contents of Cr, Cd, Pb, Zn, Cu and Mn in soil was determined by atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan) according to the instructions specified in the ISO 11047 method (ISO, 1998), after aqua regia extraction (ISO, 1995).

Aqua regia extraction of heavy metals from the soil was prepared as follows: 3 g of air-dried soil (fraction smaller than 1 mm) was placed in 250 ml round bottom flask, 28 ml of aqua regia was added (21 ml HCl and 7 ml HNO₃), the flask was covered with a watch glass and then allowed to stand 16 h (overnight) at room temperature. Afterwards, the solution was heated on hotplate under reflux for two hours, cooled down to room temperature, filtered through quantitative filter paper into 100 ml Erlenmeyer flasks and diluted to the mark with deionized water.

Plant sampling

Edible parts of plants from the examined plots were collected at the stage of commercial maturity in an quantity of approximately 200 g for each food crops.

Plant analysis

The edible parts of plants were dried in a well-ventilated place at room temperature, and then grinded. The content of heavy metals in the plant samples was also determined by atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan) according to the instructions specified in the ISO 11047 method, after HNO₃-H₂SO₄ extraction (Lisjak et al., 2009).

Extraction of heavy metals from the plant material was performed as follows: 1 g of dry matter was placed in 100 ml round bottom flask, and 10 ml HNO₃ and 4 ml H₂SO₄ were added. The flask was left for few hours at room temperature and then heated gently on a hot plate for thirty minutes. After cooling to room temperature, the solution was filtered through quantitative filter paper in 50 ml flask and diluted with deionized water to the mark.

Calculation of risk to human health by the consumption of food crops

The health risks of consumption of edible parts of plants was determined using a hazard quotient (*HQ*) (US EPA, 1989) by the following equation:

$$HQ = \frac{(Div)(C)}{RfD Bo},$$

where (*Div*) is the daily intake of vegetables or fruits (kg per day), (*C*) is the average content of heavy metal in the edible parts of plants (mg/kg), *RfD* is the oral reference dose for the heavy metal (mg/kg per day) and *Bo* is the human body weight (kg).

The *HQ* are calculated by considering that adult person (70 kg of body weight) consumes 301 g (WHO, 1998) of vegetables or fruits per day and children (32.7 kg of body weight) consumes 231.5 g/person/day (Wang et al., 2005). The oral reference dose (*RfD*) prescribed by EPA is as follows: 0.3 mg/kg per day for Zn, 0.001 mg/kg per day for Cd, 0.003 mg/kg per day for Cr, 0.04 mg/kg per day for Cu, 0.0035 mg/kg per day for Pb, and 0.14 mg/kg per day for Mn (US EPA, 2010).

HQ value higher than one indicates the potential health risk, while less than one suggests acceptable risks of food crops consumption.

Statistical analysis

All experimental measurements with plant material were performed in triplicate and the results were presented as mean

± standard deviation. Statistical analysis was performed using Microsoft Excel software and differences between means were tested using the least significance difference (LSD) test at $P < 0.05$.

Results

The content of heavy metals (Cr, Cd, Pb, Zn, Cu, Mn) in examined soil plots are presented in Table 1.

The content of toxic heavy metal Cr, Cd and Pb in soil plots was lower than the permissible value in agricultural soils established by the legislation in Bosnia and Herzegovina (Official Gazette of FBiH, 2009). Also, the content of potential toxic element Zn and Cu did not exceed the limit values prescribed by the same legislation. The soils had only the high presence of Mn, and that was expected, since the soils were located near the manganese mine.

The content of heavy metals (Cr, Cd, Pb, Zn, Cu, Mn) in edible parts of food crops that have been grown in soil plots are presented in Table 2.

The results of this part of the research have shown that the content of all tested heavy metals in the examined plants was relatively low in comparison with the maximum permissible

value of heavy metals in food crops reported by FAO/WHO (2001). Accordingly, the maximum permissible value for Cr content is 2.3 mg/kg, for Cd 0.2 mg/kg, for Pb 0.3 mg/kg, for Zn 99.4 mg/kg, for Cu 73.3 mg/kg, and for Mn 500 mg/kg.

The HQ values of Cr, Cd, Pb, Zn, Cu, and Mn through food crops consumption for residents (adults and children) of the study area are listed in Table 3.

HQ value of all heavy metals except Mn and Cu in examined food crops were below one, regardless of the population type. HQ values of Cu in onion for adults and children were 1.089 and 1.793, respectively. Also, the HQ values of Mn for children in all examined food crops were higher than one, suggesting the potential health risks by Mn through consumption of food crops grown on study area. The sequence of HQ for adults and children followed the decrescent order $Mn > Cu > Zn > Cd > Pb > Cr$. The sequence was the same for both; however the HQ for children was higher than that for adults.

Discussion

The soils in the vicinity of the mining area have the potential to contaminate the agricultural crops by heavy metals and therefore the agricultural production in that area is very questionable

Table 1. The content of heavy metals in examined soil plots

Soil plot	Heavy metals, mg kg ⁻¹ dry matter					
	Cr	Cd	Pb	Zn	Cu	Mn
1	22.82	0.54	43.67	57.54	18.59	1072.11
2	23.11	0.42	57.11	60.11	23.05	1133.13
3	22.05	0.57	55.23	64.05	24.05	1203.64
Limit value	100 ¹	1.5 ¹	100 ¹	200 ¹	80 ¹	1000 ²

¹limit value prescribed by legislation in BIH ; ²toxic value by Kastori

Table 2. The content of heavy metals in edible parts of food crops

Food crops	Heavy metals, mg kg ⁻¹ dry weight					
	Cr	Cd	Pb	Zn	Cu	Mn
Strawberry	n.d.	0.03±0.02	0.08±0.03	11.43±2.55 ^d	7.32±0.83 ^b	26.23±2.02 ^a
Raspberry	n.d.	0.06±0.03	0.07±0.05	17.43±3.02 ^{bc}	5.63±0.48 ^c	24.22±2.11 ^{ab}
Cabbage	n.d.	0.03±0.05	0.07±0.07	19.32±6.55 ^b	4.11±1.19 ^d	23.78±2.66 ^b
Onion	n.d.	0.02±0.03	0.06±0.03	26.03±3.31 ^a	10.13±1.36 ^a	19.21±2.34 ^c
LSD _{0.05}	–	–	–	4.093	0.958	2.289

The values marked with different letters in the same column indicate significantly differences at $P \leq 0.05$

Table 3. Values of Hazard Quotient (HQ)

Plant species	Adults						Children					
	Cr	Cd	Pb	Zn	Cu	Mn	Cr	Cd	Pb	Zn	Cu	Mn
Strawberry	–	0.129	0.098	0.164	0.787	0.806	–	0.212	0.162	0.27	1.296	1.326
Raspberry	–	0.258	0.086	0.25	0.605	0.744	–	0.425	0.142	0.411	0.996	1.225
Cabbage	–	0.129	0.086	0.285	0.442	0.73	–	0.212	0.142	0.456	0.727	1.203
Onion	–	0.086	0.074	0.373	1.089	0.59	–	0.142	0.121	0.614	1.793	0.971

to human health (Li et al., 2014). The toxicity of heavy metals and their tendency to accumulate in the edible parts of plants make them a significant health hazard.

Although numerous studies have shown that mining and milling operation provide obvious sources of heavy metals contamination (Cao et al., 2010; Borgese et al., 2013), the obtained results did not confirm this observation. In this study, the content of Cr, Cd, Pb, Zn, and Cu in the soil plots did not exceed the permissible limit value in agricultural soils established by the legislation in Bosnia and Herzegovina. Only the results of Mn content in examined soil plots were relatively high in comparison with average value of Mn in soil, as expected, since the examined soils located near the manganese mine.

There are few possible explanations for relatively low content of heavy metals in soils of the study area: slightly disintegration (physical) and decomposition (chemical) of rocks and minerals into soils, anthropogenic influence or insufficient examined area. Namely, the area of each of the three agricultural plots in this research was approximately 500 m², and that is relatively small area of research. Furthermore, the plots were located quite close – practically next to each other, and therefore the results in this study are not entirely reliable. Regardless of that, it is indisputable that the examined soil plots from the point of view of heavy metals are not polluted by heavy metals and that the production of health food on these plots is possible and achievable. This fact is also confirmed by the results of the heavy metal content in the edible parts of plants grown on the study area. Namely, the content of all tested heavy metals in all examined plants was significantly lower compared to the toxic value of heavy metals in plants reported by Kabata-Pendias (2004).

The heavy metal contents of the studied food crops varied in different samples, suggesting that variations in heavy metal contents among different plant species reflect the difference in their uptake capabilities and further translocation to the edible parts of the plants. The lowest content of hazardous heavy metals Cd and Pb was determined in edible parts of onion. Also, in other examined plants the values of Cd and Pb content in edible parts were very low. The maximum permissible level of Cd and Pb in food crops recommended by FAO/WHO (2001) is 0.2 and 0.3 mg kg⁻¹, respectively.

The content of Cr was not determined in any of the examined plants. This data is highly desirable, since the Cr is extremely dangerous to human health even in small quantities. An explanation for low level of Cr in edible parts of food crops is that the Cr mostly accumulates in the root and its translocation to other parts of the plant is not very pronounced (Sundaramoorthy et al., 2010).

The ranges of Zn and Cu contents in edible parts of plants were 11.43–26.03 mg/kg and 4.11–10.13 mg/kg (dry weight),

respectively. Zn contents above 150 mg/kg in plants are generally toxic, while the toxicity of Cu on the plant may occur only if the content of Cu in plant exceeds 15 mg/kg (Kastori et al., 1997). Although Zn and Cu can exert an adverse effect on the plants, their presence in plants are very important for the maintenance of certain physiological processes. Zn is important for cell division and plant growth, while Cu plays an important role in metabolism of carbohydrates and proteins. Also, both elements are constituent of many enzymes in plant antioxidant defense system (Hashimoto and Kambe, 2015).

Manganese is a heavy metal that can have a harmful effect on the plant, but also it is essential for plant growth and development. Mn takes part in chlorophyll synthesis and in the activity of more than 35 enzymes (Malavolta et al., 1997). The ranges of Mn content in edible parts of examined food crops were 19.21 - 26.23 mg/kg, expressed on a dry weight. The lowest Mn content was determined in onion bulbs, and the highest in fruits of strawberry. Average value of Mn content in plants range from 30 to 500 mg/kg, but due to the high impact of soil reaction and other environment factors on the Mn availability, values are often encountered outside this range (Clarkson, 1988). Toxic value of Mn in plants is 1000 mg/kg and more (Fageria, 1984). It is very important to emphasize that the average and permissible values of Mn mentioned above, relate to the leaves of plants, while the other parts of plants especially bulbs and fruits contain much lower amounts of Mn (Horiguchi et al., 1987; Bedassa et al., 2017). This was probably one of the reasons why the values of Mn in edible parts of plants obtained in this research were significantly lower than the permissible value of Mn in the leaves.

Generally, the results of this study showed that the accumulation of Mn and other examined heavy metals in edible parts of onion, cabbage, raspberry and strawberry was within normal ranges, and therefore the consumption of these food crops grown on the examined soils should not be dangerous to human health. The analysis of hazard quotient (HQ) confirmed this observation.

HQ values of toxic heavy metals Cr, Cd, Pb and Zn due to food crops consumption for residents (adults and children) of the study were less than one, indicating no significant potential health risk associated with the consumption of food crops from the examined area.

Only HQ values of Cu in onion for all residents, and the HQ values of Mn in all examined food crops for children were higher than one, suggesting that the residents face with health risk caused by Mn and Cu through consumption of food crops grown in the study area. This data should not be identified as being of very high concern since the HQ slightly exceeds the value of one.

Conclusions

The analysis of heavy metals in food crops grown on soils near manganese mine indicates that the examined soils are not polluted by heavy metals, and that from the point of view of heavy metals there is no significant potential health risk associated with the consumption of food crops from this area. Such soils are therefore suitable for agricultural production.

References

- Bedassa, M., Abebaw, A. & Desalegn, T.** (2017). Assessment of selected heavy metals in onion bulb and onion leaf (*Allium cepa* L.), in selected areas of Central Rift Valley of Oromia Region Ethiopia. *J. Hortic.*, 4, 217.
- Borgese, L., Federici, S., Zacco, A., Gianoncelli, A., Rizzo, L., Smith, D. R., Donna, F., Lucchini, R., Depero, L. E. & Bontempì, E.** (2013). Metal fractionation in soils and assessment of environmental contamination in Vallecarnonica, Italy. *Environ. Sci. Pollut. Res.*, 20, 5067-5075.
- Cao, H. B., Chen, J. J., Zhang, J., Zhang, H., Qiao, L. & Men, Y.** (2010). Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. *J. Environ. Sci.*, 22, 1792-1799.
- Clarkson, D. T.** (1988). The uptake and translocation of manganese by plant roots. In: R.D. Graham, R.J. Hannam, N. J. Uren. (eds). *Manganese in soil and plants*. Kluwer Academic Publishers, Dordrecht, 101-111.
- Fageria, N. K.** (1984). Response of rice cultivars to liming in Certoado. *Soil. Pesq. Agropec. Bras.*, 19, 883-889.
- FAO** (1998). World Reference Base for Soil Resources. Food and Agriculture Organization of the United Nations, Rome, Italy.
- FAO/WHO** (2001). Codex Alimentarius Commission Food Additives and Contaminants. Rome, Italy, 1-289.
- Galuszka, A., Migaszewski, Z. M., Dolegowska, S., Michalik, A. & Duczmal-Czernikiewicz, A.** (2015). Geochemical background of potentially toxic trace elements in soils of the historic copper mining area: A case study from Miedzianka Mt., Holy Cross Mountains, south-central Poland. *Environ. Earth Sci.*, 74 (6), 4589-4605.
- Hang, X. S., Wang, H. Y. & Zhou, J. M.** (2013). Prevention and regulation countermeasures of soil heavy metal contamination in Yangtze River Delta. *Chin. J. Soil Sci.*, 44, 245-251.
- Hashimoto, A. & Kambe, T.** (2015). Mg, Zn and Cu transport proteins: A brief overview from physiological and molecular perspectives. *J. Nutr. Sci. Vitaminol. (Tokyo)*, 61, S116-8.
- He, Z.L., Yang, X. E. & Stoffella, P. J.** (2005). Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.*, 19 (2-3), 125-140.
- Horiguchi, T.** (1987). Mechanism of manganese toxicity and tolerance of plants. *Soil Sci. Plant Nutr.*, 33 (4), 595-606.
- Hu, B. F., Wang, J. Y., Jin, B., Li, Y. & Shi, Z.** (2017). Assessment of the potential health risks of heavy metals in soils in a coastal industrial region of the Yangtze River Delta. *Environ. Sci. Pollut. Res. Int.*, 24, 19816-19826.
- ISO** (1995). Soil quality – Extraction of trace elements soluble in aqua regia, International Standards ISO 11466:1995, Geneva, Switzerland.
- ISO** (1998). Soil quality, Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc – Flame and electrothermal atomic absorption spectrometric methods, International standard ISO 11047:1998, Geneva, Switzerland.
- Kabata-Pendias, A.** (2004). Soil-plant transfer of trace elements an environmental issues. *Geoderma*, 122, 143-149.
- Kastori, R., Petrović, N. & Arsenijević-Maksimović, I.** (1997). Heavy metals and plants. In: Kastori, R. (ed.) Heavy metals in the environment. Research Institute of Field and Vegetable Crops, Novi Sad, 195-258.
- Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z. & Huang, L.** (2014). A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Sci. Total Environ.*, 468, 843-853.
- Lisjak, M., Špoljarević, M., Agić, D. & Andrić, L.** (2009). Manual of plant physiology. University of J. J. Strossmayer, Faculty of Agriculture, Osijek, 25.
- Malavolta, E., Vitti, G. C. & Oliveira, S. A.** (1997). Assessment of Nutritional Status of Plants: Principles and Applications. 2nd Edition, POTAFOS, Piracicaba, 308.
- Official Gazette of FBiH** (2009). Rulebook on determination of allowable quantities of harmful and hazardous substances in soils of Federation of Bosnia and Herzegovina and methods for their testing. Sarajevo, BiH, No 72/09.
- Qu, C. S., Ma, Z. W., Yang, J., Liu, Y., Bi, J. & Huang, L.** (2012). Human exposure pathways of heavy metals in a lead-zinc mining area, Jiangsu Province, China. *PLoS ONE*, 7, 1-11.
- Shallari, S., Schwartz, C., Hasko, A. & Morel, J. L.** (1998). Heavy metals in soils and plants of serpentine and industrial sites of Albania. *Sci. Total Environ.*, 209 (2-3), 133-142.
- Sundaramoorthy, P., Chidambaram, A., Ganesh, K. S., Unnikannan, P. & Baskaran, L.** (2010). Chromium stress in paddy: (i) nutrient status of paddy under chromium stress; (ii) phytoremediation of chromium by aquatic and terrestrial weeds. *C. R. Biol.*, 333 (8), 597-607.
- Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. & Sutton, D. J.** (2012). Heavy metal toxicity and the environment. *EXS*, 101, 133-64.
- US EPA** (1989). Risk Assessment Guidance for Superfund: Human Health Evaluation Manual [Part A]: Interim Final. U.S. Environmental Protection Agency, (EPA/540/1-89/002), Washington, DC, USA, 20-121.
- US EPA** (2010). Risk-based Concentration Table. United State Environmental Protection Agency, Washington, DC.
- Wang, X. L., Sato, T., Xing, B. S. & Tao, S.** (2005). Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *Sci. Total Environ.*, 350, 28-37.
- WHO** (1998). Quality Control Methods for Medicinal Plant Materials, World Health Organization, Geneva, Switzerland.

Received: December, 15, 2018; Accepted: September, 24, 2019; Published: April, 30, 2020