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Heavy metal accumulation in vegetable species and health risk assessment in Serbia

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Abstract Continuous monitoring of heavy metal content in vegetables is of high priority for population nutrition control, as well as risk assessment for human health. The chemical composition of plants is a reliable indicator of their contamination by hazardous substances accumulated in the environment as a consequence of inadequately applied agro-technology. The main goal of this study was to examine the quality of vegetables that reach consumer markets as a function of growth location. Samples of 11 of the most common vegetable species used in the human diet were collected during a 4-year survey. Vegetables originated from local farm producers who cultivated them at different locations in Vojvodina Province, Serbia. Many vegetable samples contained disturbingly high levels of the investigated metals: cadmium, lead, nickel, and chromium. The plant species with the highest Cd accumulation was spinach, where Cd leaves exceeded the maximum permissible concentrations (MPCs) in more than half of the analyzed samples from different localities (54%). Pb concentrations in spinach were also higher than MPC values (according to Serbian law 3.0 μg/g) in 46% of all analyzed samples. Results showed that Cr levels in all tested vegetable species were below MPC values recommended by the FAO/WHO organization. The largest chromium accumulator was spinach, with average values of 2.3 μg/g, followed by beetroot and parsnips with an average concentration of 1.4 μg/g. The highest average content of Ni in all analyzed vegetable species was also recorded in spinach leaves, with an average value of 2.2 μg/g, followed by broccoli (1.7 μg/g) and tomatoes (1.5 μg/g).

Keywords Toxic element pollution · Vegetable quality · Green markets · Hazard quotients · Human health

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Introduction

Plants are important for cycling many chemical elements in nature, due to their unique role in primary organic production and the physiological transformation of inorganic into organic compounds. They also play an indispensable role in human nutrition: according to nutritionists, fresh vegetables should make up a large proportion of a "healthy" human diet as essential sources of vitamins, fiber, antioxidants, and minerals (Zhong et al. 2017). Therefore, the specificity, habits, and customs related to local diets have a significant impact on the health of a population. The nutritional value of vegetables used in human diets is significantly dependent on their geographical origin and methods of cultivation, as well as regional specificity in applied agricultural technology (Li et al. 2001; Osaili et al. 2016). The adequate implementation of chemicals, fertilizers, and pesticides significantly contributes to higher crop production. However, inadequate application, exclusively oriented towards increasing yields, leads to soil contamination by very persistent substances such as heavy metals with long-term harmful effects (Li et al. 2006; Arsenov et al. 2017).

Heavy metals are widespread due to natural or anthropogenic activities, which contribute to elevated concentration of toxic elements in the environment (Li et al. 2006). With respect to agro-ecosystem pollution and subsequent food chain contamination, elevated levels of non-essential trace elements such as As, Cd, Hg, and Pb are most important (Chojnacka et al. 2005; Li et al. 2016). Heavy metals, which play an important role in plant metabolism as micronutrients (Cu, Cr, Ni, Zn, etc.), could be very toxic for both plants and animals, if they are present in excessive concentrations in plant tissues (Pajević et al. 2016). Plants import chemical elements and nutrients directly from the soil or water by root absorption, or indirectly via foliar adsorption, resulting in accumulation within different tissues (Galal 2016). The use of sewage sludge in agrotechnical practice enables recycling organic matter and many nutrients like N, P, and K. However, despite the economic benefits which this agro-technical practice could have in crop production, there is also a threat of addition and accumulation of different toxic organic compounds, heavy metals, leachable phosphorous, etc. (Gaskin et al. 2003; Kidd et al. 2007). In addition to the use of commercial fertilizers, there is also the practice of application of municipal waste water as amendments to agricultural soils (Singh and Agrawal 2007).

Larger amounts of heavy metals, particularly lead, nickel, and cadmium also contaminate agricultural soil located in the vicinity of roads, oil refineries, and factories (Li et al. 2001). Cultivation of vegetables and medicinal plants on contaminated soil near industrial sites, highways, or regions with high automotive traffic objects is a common route for metals and other pollutants to enter the food chain and human body (Cui et al. 2004). Soluble metal ions present in excessive concentrations in the soil solution can be easily absorbed by plants together with essential nutrients. Their accumulation in plant roots may cause inhibition or stimulation of the uptake and metabolism of different minerals in plant tissues, affecting plant quality and health (Antisari et al. 2015; Pajević et al. 2016). For example, Pb, Ni, and especially Cd inhibit not only the uptake of Ca, Mg, Fe, Zn, Mn, and Cu by plant roots but affect their transport in aboveground plant parts as well (Borišev et al. 2016). Plants differ in their physiological capacity for heavy metal accumulation, and there are many tolerant species that have high concentrations of heavy metals and toxic chemicals in their tissues with no visible symptoms (Emamverdian et al., 2015). In a number of plant species, there is significantly higher accumulation of heavy metals, and in particular non-essential metals, in the roots compared to aboveground organs (Cao et al. 2016). Lower translocation of some heavy metals to leaves, flowers, and fruits is a form of physiological protection in plants, and effects vegetable quality depending on which plant part is edible (Nikolić et al. 2014).

The nutritional value of vegetable plant species and their impact on human consumption depends not only on the chemical composition of agricultural lands but also on the bioaccumulation capacity of specific vegetable species and the distribution of accumulated heavy metals in different plant parts (Pajević et al. 2016; Gan et al. 2017). A large number of studies revealed that vegetables consumption is one of the primary pathways of human exposure to heavy metals (Chang et al. 2014; Li et al. 2016). Approximately 90% of total metal intake is provided by consumption of vegetables contaminated with heavy metals (Martorell et al. 2011). Therefore, investigation of the chemical composition, nutritional value, and medicinal properties of vegetable plant species are issues of great significance. Continual monitoring of the chemical composition of plants important in human nutrition and the quality of the soil on which they are grown is of high priority. Reliable assessment of the quality of growing practices and applied agricultural technology could be provided based on the chemical composition of the plant tissue.

Although desirable, it is not always possible to perform quality control on vegetables from the farm to the final product, because of the large number of individual manufacturers. Therefore, the basic idea and goal of this study was to examine the quality of vegetable foods that reach consumers as a function of cultivation site. Furthermore, the aim of the present study was to analyze the potential human risks of heavy metal pollution through consumption of vegetables. Based on these results, suggestions for vegetable producers on how to implement (and reduce) fertilization, the application of pesticides and herbicides, and location of agricultural lands are provided.

Material and methods

Study area

Samples of 11 the most abundant vegetable species used in the local human diet were collected during September and October in a 4-year survey. Vegetable species were grown during spring and summer period and harvested in their full maturity phase during autumn, when their highest yield as well as nutritive quality were obtained. Vegetables originated from local farm producers who cultivated them at different locations in Vojvodina Province (Fig. 1). Vojvodina Province is located in the southern Pannonian plane, in the northern part of Serbia. This part of Serbia is covered by agricultural land, encompassing about 84% of the total area of Vojvodina. The climate zone is continental with an average annual precipitation of 617 mm and average annual temperature of 11.3 °C (Seremesić et al. 2016), which is favorable for cultivation of most vegetable species. Samples were taken from different localities where the latitudes range from 44° 87′ to 46° 05′ N, and longitudes from 19° 01′ to 20° 39′ E, varying in distance from the main roads and highways (Fig. 1, Electronic Supplementary Material 1).

Sampling, preparation, and chemical analysis

Vegetables were grown at different sites in Vojvodina Province and were supplied to local markets. Samples of the same species from different localities were taken as presented in Table 1.

The edible parts of vegetables were collected and prepared for chemical analysis by standard procedures (Arsenov et al. 2017). Plant material was dried at room temperature and then at 105 °C for 48 h. Dry plant material was powdered, and 1 g of each sample was measured and burned at 450 °C for 4 h followed by addition of 33% H_2O_2 to complete mineralization, and then 10 mL of 25% HCl was added for making an acidic solution. The solution was filtered through Whatman filter paper, and the filtrate was diluted to 50 mL with distilled water. Heavy metal determination was conducted on the edible parts of vegetables by atomic absorption spectrophotometry (Varian, AAS240FS), and their concentrations in plant tissue were expressed in μg/g dry mass. Analyses of each sample were performed in three independent replicates.

The level of vegetable pollution has been determined and compared to the "Regulations for pesticides, metals and metalloids and other toxic substances, chemotherapeutics, anabolic steroids and other substances which can

Fig. 1 Map of Vojvodina Province with the main growing sites of analyzed vegetable samples

Table 1 Edible plant organs of analyzed vegetables with MPC (maximum permissible concentrations) values according to FAO/WHO (2001)

Vegetable species	Plant organ	Cd [μg/g]*	Pb [μg/g]*
Tomato (*Lycopersicon esculentum* Mill.)	Fruit	0.05	0.05
Potato (*Solanum tuberosum* L.)	Tuber	0.1	0.1
Onion (*Allium cepa* L.)	Bulb	0.05	0.1
Spinach (*Spinacia oleracea* L.)	Leaves	0.2	0.3
Beetroot (*Beta vulgaris* L.)	Root	0.1	0.1
Parsley (*Petroselinum crispum* (Mill.) Fuss)	Root	0.1	0.1
Parsnip (*Pastinaca sativa* L.)	Root	0.1	0.1
Carrot (*Daucus carota* L.)	Root	0.1	0.1
Cauliflower (*Brassica oleracea* L. var. *botrytis* L.)	Inflorescence	0.05	0.1
Broccoli (*Brassica oleracea* var. *sylvestris* L.)	Inflorescence	0.05	0.1
Pepper (*Capsicum annuum* L.)	Fruit	0.05	0.05

* Concentration in plant tissue were expressed in μg/g dry mass

be found in food (Sl. list SRJ", br. 5/92, 11/92 - 32/2002 and Sl. glasnik RS", br. 25/2010 and 28/2011) where the maximum permissible concentrations (MPC) of cadmium (Cd) and lead (Pb) in dry vegetables have been set to 0.3 and 3.0 μg/g, respectively. For chromium (Cr) and nickel (Ni) the limits are not defined. Similarly, MPC values recommended by FAO/WHO organization (Food additives and contaminants. Joint Codex Alimentarius Commission, FAO/WHO Food Standards Programme, ALINORM 01 12A. 2001) are 0.2 μg/g for Cd, 2.3 μg/g for Cr, and 0.3 μg/g for Pb, respectively.

Metal pollution index (MPI)

The combined effects of different heavy metals in the edible part of plants can be quantitatively measured using the following equation according to Sharma et al. (2016):

$$\text{MPI}\ (\mu g/g) = (C1 \times C2 \times \ldots .Cn)\ 1/n$$

where C1, C2, C3…up to C*n* are the concentration of metal "*n*" in the plant sample.

Hazard quotients (HQs)

The level of HQ was calculated using the equation established by US Environmental Protection Agency (US EPA) 1989):

$$\text{HQ} = \frac{(\text{D})^*(\text{Cmetal})}{(\text{RfD})^*\text{BO}}$$

Hazard quotients were calculated separately for females (HQf) and males (HQm). D = is the daily intake of vegetables (kg/day), Cmetal = is the concentration of metal (μg/g), Rf D = is a reference oral dose of metal (μg/g of body weight/day) and BO = is the average body weight (kg). According to Harmanescu et al. (2011), average body weight in this part of Europe is set as 67 kg for women and 81 kg for men, respectively. Reference oral dose (Rf D) was set for Cd at 0.001 mg/kg/day (Harmanescu et al. 2011), and for Pb at 0.004 mg/kg/day (Sharma et al. 2016).

Statistical analysis

The obtained data were expressed as the mean ± standard deviation of three replicates. Results were processed statistically by the method of variance analysis (ANOVA). The significance of differences in the heavy metal content among all analyzed vegetables was established using Duncan's test ($p \leq 0.05$) (supplement material). Statistical analyses were performed using Microsoft Office Excel® and STATISTICA® ver. 13.2 software (Dell Inc. 2016). It is of crucial importance that vegetables used in the human diet in fresh or processed form are of high or satisfactory quality in terms of nutritional characteristics and safety.

Results

It is of crucial importance that vegetables used in the human diet in fresh or processed form are of high or satisfactory quality in terms of nutritional characteristics and safety.

Heavy metal contamination in vegetable species

Heavy metal content for the tested contaminants in vegetables varied considerably as a function of plant species and plant edible organs, as well as growth location. Many vegetable samples contained disturbingly high levels of the investigated metals. Four years of investigation and monitoring resulted in the statistically confirmed fact that vegetable species have a specific accumulation capacity and chemical composition. The obtained results indicate that heavy metal accumulation significantly depends not only on soil quality, but also on plant species and in accordance, translocation of heavy metal ions from roots to aboveground plant parts. In order to determine plant-specific heavy metal accumulation capacities and their potential contamination, the percentage of samples from different localities with the obtained elevated metals in edible organs was determined. The total concentrations of Cd, Pb, Cr, and Ni varied considerably in the edible parts of vegetables grown in different localities in Vojvodina Province.

Cadmium (Cd) content in vegetables

The average concentrations of Cd among the analyzed vegetables are shown as Supplemental Data (Electronic Supplementary Material 2). It can be seen that each species has a specific capacity for Cd accumulation. The level of Cd exceeded the MPC values in 16.8% of the total number of samples analyzed. The plant species with the highest accumulation of Cd was spinach, with an average Cd content in leaves of 0.5 μg/g (in the first year of investigation), 0.30 μg/g (the second year), 0.89 μg/g (the third year), and 0.23 μg/g in the fourth year (supplement material). As shown in Fig. 2, measured Cd concentrations in spinach leaves exceeded the allowable concentration in more than half of the analyzed samples from different localities (in 13 samples out of 24, or 54%). In addition to spinach leaves, which had the highest concentration of cadmium, carrot roots and tomato fruits also had very high Cd concentrations. We detected Cd concentrations up to, or near national MPC values in almost 30% of investigated samples from different localities (Fig. 2). The lowest average Cd concentration was detected in cauliflower blooms (0.12 μg/g), and the highest in spinach leaves (0.48 μg/g), which is above the MPC. High average Cd values were detected in carrot roots (0.29 μg/g) and tomato fruits (0.27 μg/g).

Lead (Pb) content in vegetables

The highest content of lead was measured in spinach leaves. In 46% of all analyzed samples of spinach, Pb concentrations were higher than MPC values, according to Serbian law (Fig. 3). The highest average concentration was found in spinach leaves (3.56 μg/g), while the lowest average concentration of lead was detected in parsnips (1.11 μg/g), followed by potatoes (1.13 μg/g), which was above MPC values according to Serbian legislative, but over 10-fold higher than values set by the FAO/WHO (2001). Summarizing all 4 years of research, it has been established that 46% of analyzed samples of spinach leaves had Pb content higher than 3 μg/g, 38% of carrots, 25% of tomatoes, 23% of broccoli, 17% of parsley and beetroots, 13% of pepper and cauliflower, 8% of onion, and 4% of potatoes, respectively (Fig. 3).

Chromium (Cr) content in vegetables

Study results show that the levels of accumulated Cr in all tested vegetable species was below MPC values recommended by the FAO/WHO organization. The largest chromium accumulator was spinach with an average value of 2.3 μg/g, followed by beetroots and parsnips, with an average concentration of 1.4 μg/g. Tomatoes, onions, potatoes, carrots, broccoli, and cauliflower did not differ significantly, with an average value of 1.2 μg/g dry mass. The lowest chromium content was recorded in parsley and carrots with an average value of 1.1 μg/g dry mass, respectively. Further, the highest levels of Cr were recorded in spinach in the third year of research (7.13 μg/g), which is 3-fold higher than the permissible level set by the FAO/WHO (Fig. 4).

Nickel (Ni) content in vegetables

The highest average content of Ni in all analyzed vegetable species was recorded in spinach leaves, with an

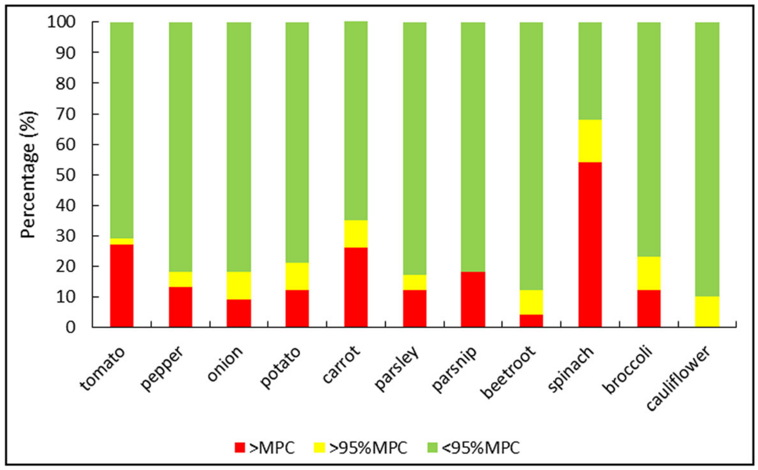

Fig. 2 Percentage of samples from different localities with obtained cadmium (Cd) concentrations in edible vegetable organs according to Serbian legislative. Red color indicates values > MPC, yellow indicates values > 95% MPC, green indicates values < MPC

average value of 2.2 μg/g, followed by broccoli (1.7 μg/g), tomatoes (1.5 μg/g), potatoes, carrots (1.3 μg/g), parsnips (1.3 μg/g), cauliflower (1.2 μg/g), peppers (1.1 μg/g), parsley and onion (0.9 μg/g), and the lowest content of Ni was recorded in beetroot 0.7 μg/g dry mass. Meanwhile, the highest level of Ni was recorded in broccoli in the first year of research (6.93 μg/g), while during years the Ni level was in decreasing order (Fig. 5).

Potential health risk through consummation of vegetables

The potential health risk associated with consummation of vegetables potentially contaminated with heavy metals was assessed through calculation of hazard quotient of Cd and Pb for both, female and male (HQCdf, HQCdm, HQPbf, HQPbm) and metal pollution index (MPI) according to the mean metal content observed in vegetables at each growing site. The value of HQ < 1 indicates that the level of heavy metal content in vegetables is below the safe limit. Values of 1 < HQ < 5 indicate that the population is exposed to a concerning level of contamination. The HQ for Cd was higher than 1 for spinach, tomatoes, carrots, and broccoli; with HQ values for spinach<tomato<carrot<broccoli. Other tested species showed an HQ index for Cd below the safe limit. Simultaneously, HQ values for Pb exceeded safe limits in most analyzed species. An exception was the HQ for Pb for men with respect to potatoes and tomatoes (Fig. 6a, b). Thus, consumption of vegetables grown in this region presents a potential risk because of lead pollution. In agreement with their high heavy metal accumulation, spinach showed very high hazard quotients for both Cd and Pb. Further, although hazard quotients are not defined for Cr and Ni, levels of these metals in plant tissue can influence total metal pollution. Metal pollution index

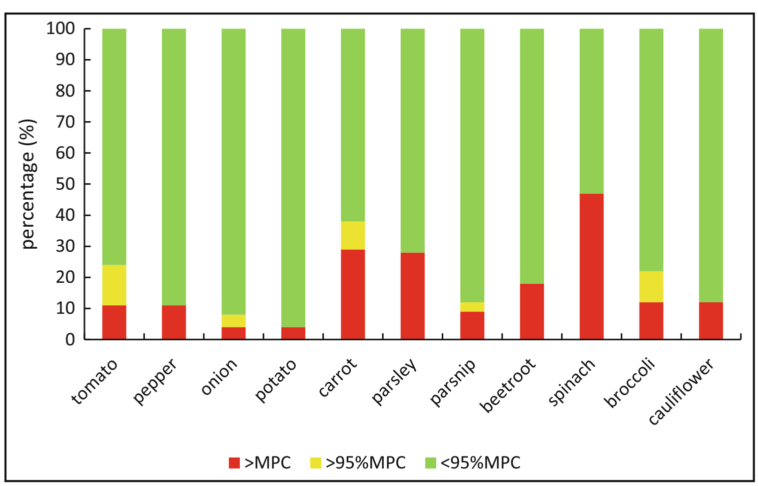

Fig. 3 Percentage of samples from different localities with obtained lead (Pb) concentrations in edible vegetable organs according to Serbian legislative. Red color indicates values > MPC, yellow indicates values > 95% MPC, green indicates values < MPC

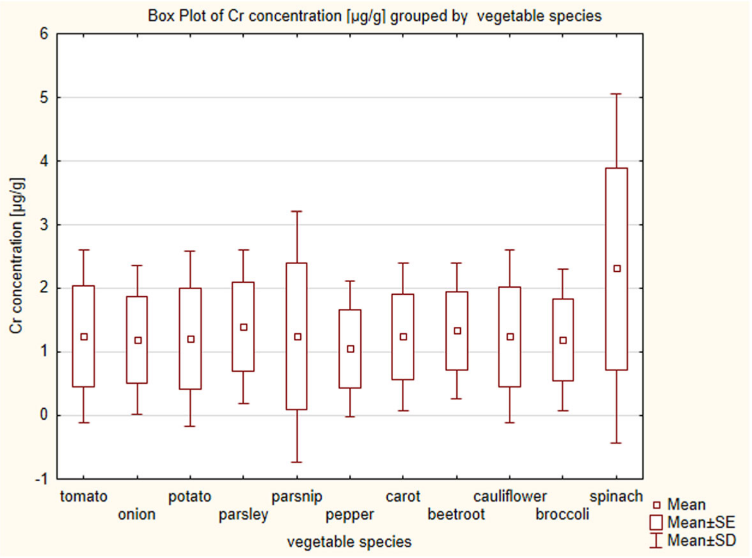

Fig. 4 Average chromium (Cr) content per plant species for period of 4-year survey. Values are expressed as mean ± standard error (SE); mean ± standard deviation (SD)

showed different patterns of metal pollution in the selected vegetables. The highest MPI was recorded in spinach (2.12), followed by tomatoes (1.24), potatoes (1.10), cauliflower (1.01), parsley (0.99), peppers (0.96), beetroots (0.95), parsnips (0.92), onions (0.83), and carrots (0.80), while the lowest metal pollution index was recorded in broccoli (0.40) (Fig. 6a, b).

Discussion

In general, total heavy metal content varied among the analyzed vegetables, which might be attributed to the different accumulation capacities of different elements among vegetable species. Various vegetables have different abilities to uptake and accumulate toxic elements in plant tissues (Singh et al. 2010; Li et al. 2016). Generally, the highest level of heavy metals was recorded in spinach leaves. Similarly to our findings, other studies confirmed that leafy vegetables appear to have a high capacity to uptake heavy metals (Arora et al. 2008; Chang et al. 2014; Li et al. 2016; Zhong et al. 2017). Furthermore, leafy vegetables have higher metal translocation rates in comparison with root and fruit vegetables (Yang et al. 2014). Additionally, the mass and area of the edible parts

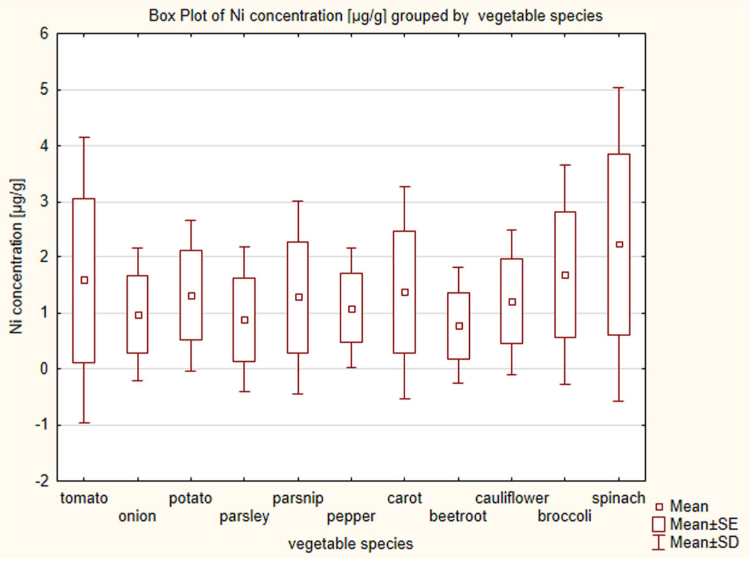

Fig. 5 Average nickel (Ni) content per plant species for period of 4-year survey. Values are expressed as mean ± standard error (SE); mean ± standard deviation (SD)

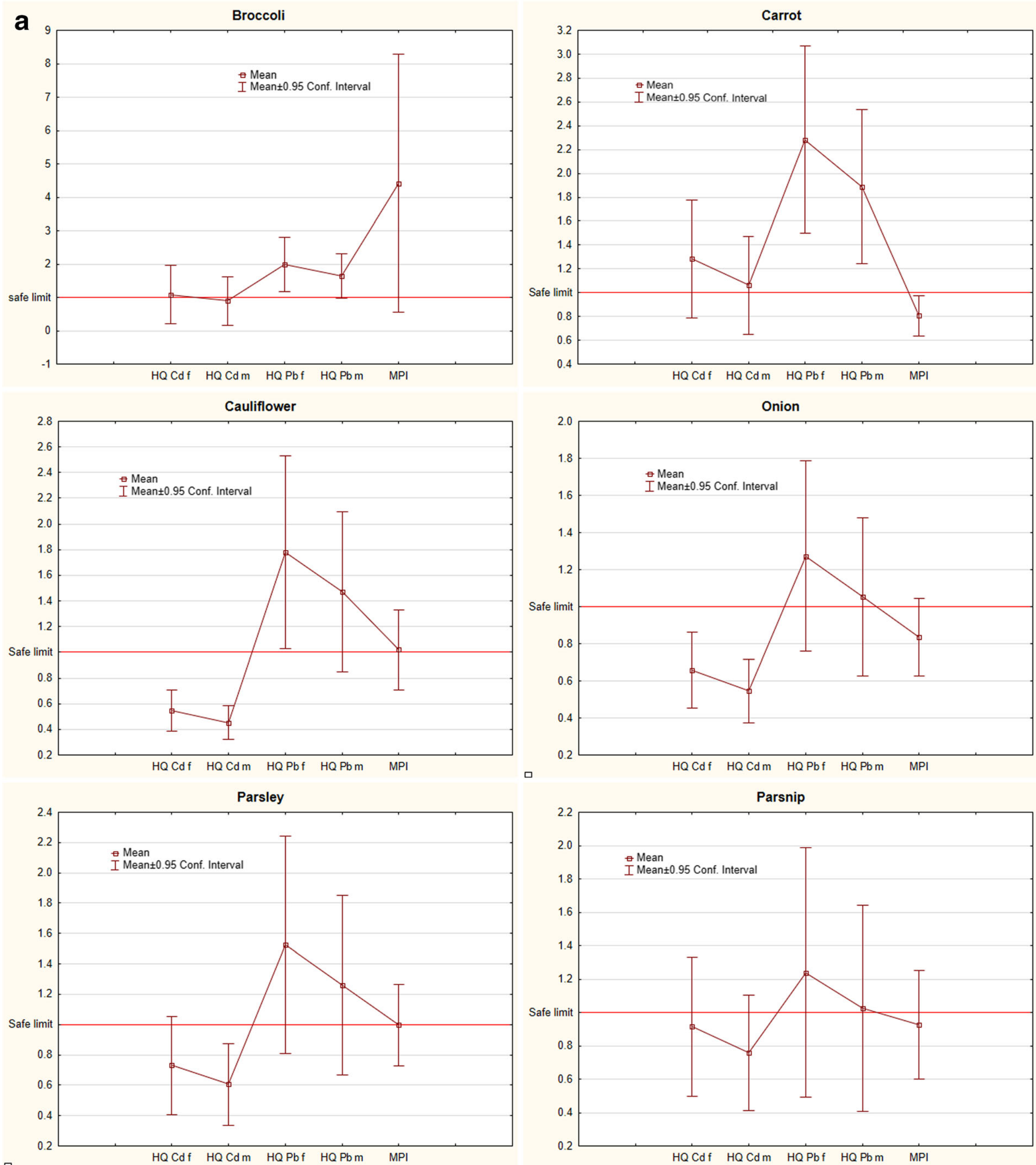

Fig. 6 **a**, **b** Hazard quotients (HQ) of lead (Pb) and cadmium (Cd), and metal pollution index (MPI) for females (f) and males (m) of different vegetables

of leafy vegetables, in combination with the high density of stomata on leaves and large evaporation might be a possible reason for heavy metal accumulation in leafy vegetables (Gan et al. 2017). Nevertheless, spinach as a leafy vegetable, also represents a good source of magnesium, potassium and calcium (Nikolic et al. 2014).

Vegetables as a source of vitamins, minerals and antioxidants are highly recommended in nutrition due to their role in food quality. However, vegetables

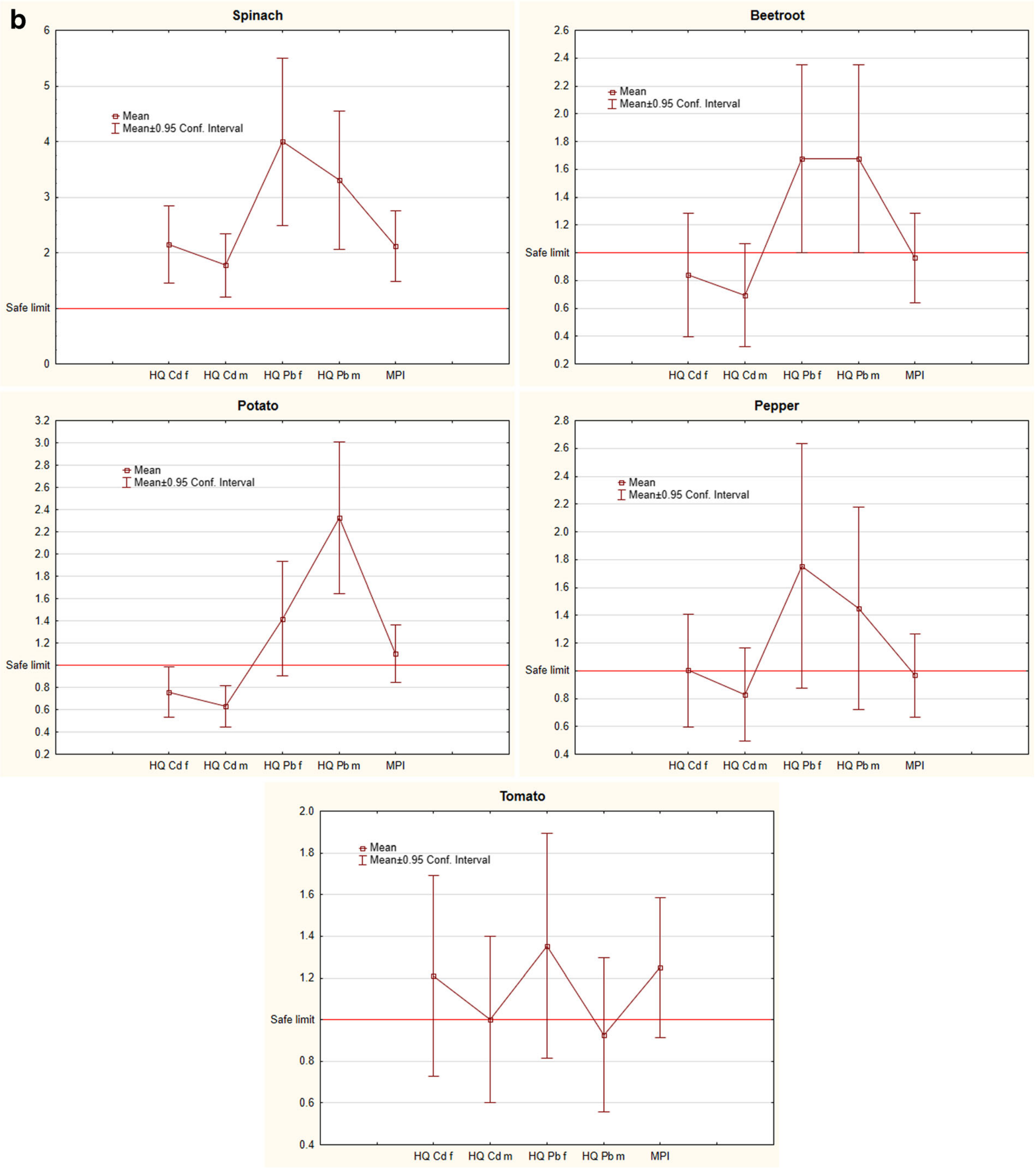

Fig. 6 (continued)

exposed to environmental pollution have the potential to accumulate heavy metals in quantities which can cause adverse effects to human health (Arora et al. 2008). Dietary intake of vegetables contaminated with elevated heavy metal content can lead to serial chronic diseases. Prolonged exposure to Cd can lead to pulmonary changes, such as bronchiolitis and alveolitis, as well as kidney dysfunction (Singh et al. 2010; Osaili et al. 2016). Similarly to our findings, Li et al. (2016) found that 60% of vegetable species grown in greenhouses near a smelter exceeded permissible levels of Cd. Additionally, these authors concluded that fruit vegetables (tomatoes, cauliflower) had lower Cd content in comparison to leafy and root vegetables. Our results confirmed the above findings: during 4 years of monitoring heavy metal content in vegetables, the lowest content of Cd was detected in cauliflower. Further, hazard quotients for Cd, for both men and women, were below the safe limit. Otherwise, tomatoes as fruit vegetables showed good potential to accumulate Cd in edible parts, with HQs higher than the threshold value of 1. Results observed in this survey showed a similar pattern of Cd content among the vegetables, with the exception of cauliflower and parsley, were a decrease of Cd content was detected. Thus, it can be concluded that a good strategy for agricultural practice should be applied in order to assure food quality.

Besides cadmium, lead (Pb) is one of the most abundant toxic elements (Radwan and Salama 2006). Elevated levels of Pb can lead to major human health problems, causing a decrease in hemoglobin synthesis, disturbances in the reproductive and cardiovascular systems, and chronic damage to the nervous system (Singh et al. 2010). Serious health problems caused by Pb toxicity emphasize the need for lowering the maximum permitted levels (MPC) of Pb in vegetables, which are in Serbian legislative 10-fold higher than those set by the FAO/WHO. Pb content exceeding MPC values was estimated in lettuce, cabbage, cauliflower, spinach, rockets, parsley, carrots, onions, and potatoes grown in Brazil (0.44, 1.66, 0.36, 1.05, 0.76, 1.02, 0.38, 0.49, and 0.99 μg/g, respectively) by Guerra et al. (2012). High lead contamination in different fruits and vegetables could be attributed to the vicinity of road traffic (Bakirdere and Yaman, 2008). Additionally, Harmanescu et al. (2011) also found high levels of lead contamination among vegetables, especially parsley, cabbage, lettuce, and carrots (1.97, 0.9, 0.62, and 0.2 mg/kg, respectively). Further, Gan et al. (2017) revealed no significant correlation between Pb content in soil in comparison to lead content in vegetables, indicating that the soil is not the only source of contamination. It is well known that dust particles in the atmosphere contain lead for a very short period, and its deposition on soil surfaces can lead to higher lead content and accumulation in vegetables. Otherwise, recent studies of lead content in plants related to traffic exposure confirmed that Pb content in plants was reduced by using unleaded gasoline (Antisari et al. 2015). Although unleaded fuel has been adopted in our country, the results from the present study do not confirm a reduction of lead content in vegetables. On the contrary, very high Pb content was observed among plant species during each year of research.

Although chromium and nickel are essential elements for plant metabolism, taken in high concentrations they can be toxic for both, plants and humans (Li et al. 2016). Chromium is a widely distributed metal in the environment: occurring in rocks, soil, volcanic dust, and gases. It has a positive effect in the human diet, especially in carbohydrate metabolism; however, its toxic effects at elevated levels suggest the need for setting up maximum permitted levels in food (Arsenov et al. 2016). Additional problems occur because Cr can exist in a variety of oxidation states, including trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. Chromium in the trivalent state is a dietary constituent often present in a variety of foods and dietary supplements, while the hexavalent form is a toxic anthropogenic contaminant, mostly released into the environment by industrial processes (EFSA CONTAM Panel 2014). Intensive agricultural practice, especially in greenhouse growth systems, can significantly increase heavy metal content, particularly for Cr and Zn (Fan et al. 2013). The chromium content in the present study is comparable with those previously reported by Osaili et al. (2016), who found Cr content in the range of 0.105–3.51 mg/kg in leafy vegetables from markets in Jordan. Comparable to other analyzed heavy metals, the highest level of Cr was detected in spinach. This is in accordance with previous studies of Naser et al. (2011) who found a high level of Cr in spinach (6.20 μg/g). Bakkali et al. (2012) recorded Cr contents ranged from 2.0–5.2 μg/g in the same vegetable species. Further, there is a lack of data of Cr (VI) form in vegetables; thus, it is necessary to provide scientific data and correlations between the chromium content in food and human health risk (EFSA CONTAM Panel 2014).

Nickel is a widespread essential trace element with important roles in metabolism as a cofactor in enzyme function (Nikolic et al. 2014). Although MPC levels for Ni were not set, EFSA CONTAM Panel (2015) reported that Ni intake in human vegetarian populations is higher than those in the general population. Ni content in the present study ranged from 0.01–6.93 μg/g, which was estimated in broccoli samples. In a previous study of 88 fruits and vegetable samples collected from local markets in Pakistan, Ni content ranged from undetectable to 9.05 μg/g (Parveen et al. 2003). According to the EFSA

CONTAM Panel, (2015), vegetables as well as vegetable products had relatively low Ni content, below 100 μg/g. Our results regarding Ni content in the investigated vegetables are in accordance with the abovementioned studies. In addition, Ni concentrations measured in plant tissues in the present study appear to be a marker of overall metal pollution.

Numerous studies of agro-ecosystem heavy metal contamination have been conducted (He et al. 2005; Muñoz et al. 2009; Fatta-Kassinos et al. 2011). The most important source of heavy metal contamination is due to extensive application of mineral fertilizers and pesticides, as well as the use of poor quality water for irrigation, saturated with urban and industrial pollutants (Candeias et al. 2014). Published results in annual reports issued by Agency for environmental protection of Republic of Serbia referring to 3-year survey (Agency for Environmental Protection, (2011/2012/2013) indicated that average annual concentrations of dissolved heavy metals Cd, Ni, Pb, and Cr in surface waters (rivers and lakes) usually used for irrigation did not exceed limits defined as environmental quality standards for maximum permitted concentrations (MPC) prescribed by the national legislation (regulation on limit values of priority hazardous substances that pollute surface waters and deadlines for their reaching, Official Gazette of Republic of Serbia, 2010). The MPC values for metals in surface waters set up by Official Gazette, are as follows: for Cd, 0.01 mg/l; Pb, 0.1 mg/l; Cr, 0.5 mg/l; and Ni < 0.1 mg/l. Pivic et al. (2017) reported that the content of dissolved heavy metals in surface water of Velika Morava River, which is used for irrigation of agricultural land, is within the MPC values. Authors stated that a number of environmental factors such as municipal and industrial wastewater, agricultural and industrial activities have an influence on the distribution of metals in natural water and consequently lead to overall water pollution. Further, Pajevic et al. (2008) reported data which indicated significant increase of Cd content in water, as well as in sediment of Danube and Sava River, pointing to the need for continuous monitoring of water quality.

As a consequence, soil pollution is a serious environmental concern. The excessive use of mineral fertilizers, especially phosphorus and nitrogen, is a significant source of soil pollution by heavy metals, due to their frequent use correlated with positive effects on yield. Contrary to the beneficial effects of fertilizers, inadequate fertilization in terms of applied concentrations and application time has led to serious environmental contamination, including accumulation of phosphates, nitrates, nitrites, and heavy metals in soil, ground and surface waters, plants, animals, and humans. Intensive urbanization, industrialization, and demographic expansion led to disturbance of the ecosystem balance and elevation of heavy metals and metalloids in the soil. One of the main pathways by which heavy metals enter the food chains is soil contamination and subsequent transfer to plants (Cui et al. 2004). On the other hand, the presence of toxic elements in the soil does not necessarily mean that these elements are available for plants (Chojnacka et al. 2005). The bioavailability of elements in soil is dependent on the pH of the soil, plant species, root system specificity, redox status of the elements, etc. (Pajević et al., 2016). Industrial and urban waste dumps and landfills, as well as the use of sewage sludge and wastewater in agriculture, represent the greatest risks for environmental contamination. According to the Agency of Environmental Protection (2015), the largest sources of pollution for agricultural land are municipal landfills and industrial sites (oil, chemical, and metal). Data obtained by monitoring the total heavy metal content at a soil depth of 30 cm in 2012 in Vojvodina revealed soil surface pollution exceeding MPC values for certain heavy metals. According to the annual report for 2012, issued by the Agency for Environmental Protection, concentrations of Cd exceeding MPC values were detected in 40% of samples (the concentrations were in range of 0.8 up to 28.8 mg/mg dry soil) while Ni contents were higher than MPC values in 85% of soil samples (the concentrations were in range of 35 up to 100 mg/kg dry soil). The heavy metal contaminations had been detected mostly in soil samples taken from agricultural land and land near roads with frequent traffic. In most soil samples taken from agricultural areas near roads, increased concentrations of Cr were not detected. The mean value of total Cr concentration in soil samples was 71.56 mg/kg, which was below the MPC (100 mg/kg dry soil). Heavy metal contamination is most often associated with the utilization of inappropriate agro-technical measures as well as with increased industrial activity. According to data published by the Agency for Environmental Protection for 2013, the concentrations of heavy metals varied in ranges as follows: Cd 0.20–0.73 mg/kg dry soil, Pb 2.12–110.2 mg/kg dry soil, Ni 23.40–311.40 mg/kg dry soil, and Cr 18.43–147.5 mg/kg dry soil. The obtained values indicated to some extent an increasing trend of heavy metal contamination of agricultural soils comparing with the contamination level detected for several previous years.

Landfills, along with tailings from the mines, and waste materials near canals and roads, etc., are all other sources of air, soil and water pollution. Emission of windblown dust is one of the main sources of air and soil contamination with metals, such as Pb, Cd, and Cr (Ettler et al., 2012). Results from our research confirm this pattern: vegetables grown at sites exposed to windblown dust contained the largest concentrations of heavy metals. Environmental pollution caused by these hazardous elements has a significant impact on human health, not only at a local and regional level but also at the global level. Numerous studies indicate the significance of understanding the effect of toxic compounds, heavy metals, metalloids, and other harmful substances on plants, animals, and human health (Zheng et al. 2007; Osaili et al. 2016). Therefore, it is necessary to control food production, which includes monitoring growth conditions together with the chemical composition of plants, in order to obtain valuable data for screening population health risks. The prediction of heavy metal content in the edible parts of vegetables was reported in a recent study by Gan et al. (2017). The authors developed a mathematical model for evaluation of heavy metal contents in vegetables grown under the influence of multiple environmental factors, including soil pH, organic matter content, total soil metal content, irrigation water metal content, and the distribution of heavy metals along plant tissue.

Taking into account all abovementioned, the influence of different abiotic factors combine with anthropogenic activity strongly contribute to overall vegetable pollution and can cause yearly variation in concentrations of some of the heavy metals.

Food safety control is very important, because hazardous contaminants and metals may persist in the soil for a long time, resulting in prolonged consumption of polluted vegetables. A number of studies have focused on the health risks caused by consumption of vegetables potentially contaminated with heavy metals (Li et al. 2006; Martorell et al. 2011). Therefore, hazard quotients for Cd and Pb in food were calculated and compared with their safe limits. Further, the metal pollution indices of different vegetables, which represent a marker of overall health risk, might be increased due to the synergistic effects of different metal combinations (Galal 2016).

Conclusion

The content of the tested contaminants, cadmium, lead, nickel, and chromium in the selected vegetables varied considerably as a function of plant species and plant edible organs, as well as growth location. The obtained results from this survey indicate that continuous consumption of locally grown vegetables potentially might be a health threat, due to the cumulative toxic effects of specific metals in plants grown in specific areas. Results of the present study should provide a basis for future planning of agricultural areas and methods which could be used for improved cultivation of vegetables important in human nutrition. In particular, soil quality should be analyzed prior to plant cultivation. Vegetables should be beneficial for the human population and are highly recommended by nutritionists. Thus, evaluation of the potential health risks from vegetable consumption is highly recommended.

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