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Essential (Cu and Zn) and trace (Pb and Cd) heavy metal loads in onion and potato

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Summary

Heavy metals are one of many pollutants that can be found on the surface and in tissue of fresh vegetables. Therefore, the aim of this paper was to assess and analyse concentrations of essential (Cu and Zn) and trace (Pb and Cd) heavy metals in onion (*Allium cepa* L.) and potato (*Solanum tuberosum* L.) produced in Vojvodina. The concentration of Cu, Zn, Pb and Cd was determined in edible plant parts, onion bulbs and potato tubers by atomic absorption spectrophotometry. In only two samples of onion and four samples of potato, the concentration of Cd was above the limit set by regulations of the Republic of Serbia.

Key words: onion, potato, copper, zinc, lead, cadmium

Introduction

As a source of vitamins, minerals, proteins and carbohydrates, vegetables play an important role in human nutrition. Therefore, high quality of vegetables is very important for human health. Diversity and quantities of chemicals that are added to agricultural soils have substantially increased with development of industrial technology, augmenting the risk of contamination of crops and vegetables (Nicholson et al., 2003). Heavy metals are one of many pollutants that can be found on the surface and in tissue of fresh vegetables. Vegetables mainly take up metals from soil solution and sometimes through the above-ground parts (Khairiah et al., 2004; Chojnacka et al., 2005). Sometimes, vegetable species may accumulate significant amounts of heavy metals, decreasing the quality and biological value of products without visible symptoms of their damage.

High concentrations of Pb and Cd in the diet are associated with development of many diseases, particularly cardiovascular, kidney, nerve and bone tissue (WHO, 1992, Steenland and Boffetta, 2000; Jarup, 2003). It has been proved that these heavy metals are carcinogenic, mutagenic and teratogenic (Radwan and Salama, 2006).

Given the importance that the concentrations of Cu, Zn, Pb and Cd have for the quality of vegetables and their health safety, we found it important to determine their concentrations in conventionally produced onion and potato, which are very common in our region. Onion bulbs and potato tubers develop in the soil, and therefore, the aim of this work was also to compare concentrations of Cu, Zn, Pb and Cd in those two vegetable species.

According to the regulations of the Republic of Serbia ("Official Gazette", no. 5/92, 11/92 - amended and 32/2002 and "Official Gazette RS", no. 25/2010 - another regulation and 28/2011 - another regulation), the maximum permitted concentration of Pb is 1 mg kg^{-1} and of Cd is 0.05 mg kg^{-1} in fresh vegetables, whereas according to international regulations (CODEX STAN 193-195) the maximum permitted Pb concentration is 0.1 mg kg^{-1} Pb, 0.1 mg kg^{-1} Cd for potato and 0.05 mg kg^{-1} for bulb vegetables.

Materials and methods

Plant material

Thirty two onion (*Allium cepa* L) samples, belonging to 15 different cultivars (Angela, Bonus, Burgos, Croquete, Daytona, Densitor, Holandski žuti, Kalcedon, Lazar, Manas, Redwing, Sedona, Stanfield, Talon and Vitez) were collected from 12 different sites, directly from farmers. Twenty nine potato (*Solanum tuberosum* L) samples, belonging to 10 different cultivars (Aladin, Bella Rosa, Desiree, Cleopatra, Kondor, Kuroda, Laura, Madeleine, Manitou and Trezor) were collected from 11 sites. Onion and potato samples were collected from: Bački Petrovac, Begeč, Čurug, Deronje, Despotovo, Erdevik, Gložan, Gospođinci, Iđoš, Kikinda, Kruščić, Lalić, Rusko Selo, Sakule and Zrenjanin.

Chemical analyses

Onion bulbs and potato tubers were oven dried at 60 °C to constant mass and weighed to determine the dry weight biomass production. Concentrations of Cu, Zn, Pb and Cd were determined in edible plant parts, onion bulbs and potato tubers. Common household practice was applied before the samples were prepared for the analysis of elemental composition. Onion bulbs were peeled and potato tubers were peeled and washed with running tap water. Excess water was absorbed with filter paper. The total concentration of Cu, Zn, Cd and Pb was determined by atomic absorption spectrophotometry (AAS SHIMADZU AA-6300) using flame technique (for Cu and Zn) and graphite furnace (for Pb and Cd) after ashing the plant material at t = 500° C and dissolving it in deionised hot water in the presence of 0.25 M HCl. The analyses were done in two consecutive years, in three replications. According to the regulations ("Official Gazette", no. 5/92, 11/92 - amended and 32/2002 and "Official Gazette RS", no. 25/2010 - another regulation and 28/2011 - another regulation), limiting concentration of trace elements in

vegetables, concentrations of Cu, Zn, Pb and Cd are expressed in mg g^{-1} fresh weight, and the same was done in this paper.

Statistics

The data were statistically processed by Statistica for Windows, version 10.0 (Statosft Inc., Tulsa, OK, USA). The comparison of genotypes was done using Duncan's test, at $\alpha < 0.05$.

The heavy metal pollution index (HPI) was calculated with the aim to compare total heavy metal load in onion and potato, as described by Usero et al. (1997):

$HPI = (Cf_1 \times Cf_2 \times Cf_3 \times \cdots \times Cf_n)^{1/n}$, where Cf is the concentration of *n* heavy metals in vegetable samples.

Results and discussion

The mean concentrations of heavy metals in onion (Tab. 1) and potato (Tab. 3) were in the following decreasing order: Zn, Cu, Pb, Cd, which is in accordance with results of Sharma et al. (2008). When onion and potato are compared, the latter contained 18% more Zn, 70% more Cu, 25% more Pb and 37% more Cd. For all four elements, the average concentration in potato was 37.5% higher than in onion. However, as the dry matter percentage of potato was in average 34.67% higher than that of onion, potato dry matter contained about half of Zn compared to onion, about double amount of Cu, about 10% less Pb and nearly equal concentration of Cd. The ratio of Zn/Cd concentration, however, was 26% higher in onion than in potato.

Since Cu and Zn in vegetables have only food and feed but not public health significance, there are no limits set for those elements. Average Zn concentration in onion bulbs is between 30 and 100 mg kg^{-1} dry weight (Bauer, 1971) and in potato tubers between 20 and 40 mg kg^{-1} (Geraldson et al., 1973). When concentrations analysed in this paper are expressed per dry weight, they are 12.67 mg kg^{-1} for onion and 10.1 mg kg^{-1} for potato. This means that both onion and potato in average have about a half of the average minimum concentration of Zn. It should be noted that the percentage of dry matter differed significantly between both onion (one had very high and one very low % of DM) and potato (one had much lower % of DW) cultivars (Tab. 1 and Tab. 3, respectively).

The average Cu concentration in onion bulbs is 7.1 mg kg^{-1} dry weight (Babilla-Ohlbaum et al., 2001) and if the concentration that was measured in this paper was expressed on the basis of dry weight, it would be much lower (average is 4.55 mg kg^{-1}). There were significant differences between onion cultivars with respect to Cu concentration in fresh weight. However, it should be noted that percentage of dry matter significantly differed between onion cultivars – one had much higher and another one much lower % of DW than the other cultivars (Tab. 1). Onion belongs to a group of vegetables that have high response to Cu whereas potato is classified as having a low response to it (Swiader and Ware, 2002).

Although potato is low copper-containing food, it is consumed frequently enough to be considered a substantial dietary source of copper (Lurie et al., 1989). Therefore, Cu concentration in potato may deserve more attention.

Tab. 1. Average concentrations of Cu, Zn, Pb and Cd, dry weight, Zn/Cd ratio and HPI in onion bulbs (n.d., not detected)

Prosječne koncentracije Cu, Zn, Pb i Cd, težine u suvom stanju, omjera Zn/Cd i HPI u lukovicama crnog luka (n.d, not detected)

ONION	Cultivar	Concentration (mg kg^{-1})				% dry weight	Zn/Cd	HPI CuZnPbCd
		Cu	Zn	Pb	Cd			
1.	Angela	0.712	1.458	0.182	n.d.	10.760	-	-
2.	Bonus	0.204	0.570	0.164	0.042	8.080	13.538	0.174
3.	Burgos	0.371	1.249	0.046	0.022	9.120	55.777	0.021
4.	Croquete	0.803	1.385	0.136	0.019	10.440	72.073	0.214
5.	Daytona	0.237	0.910	0.129	0.028	7.580	32.946	0.171
6.	Densitor	0.171	0.501	0.133	0.026	6.645	19.159	0.231
7.	Holandski žuti	0.592	1.820	0.211	0.016	15.940	138.396	0.125
8.	Kalcedon	0.558	1.253	0.156	n.d.	9.200	-	-
9.	Lazar	0.350	0.986	0.140	0.019	7.507	51.801	0.249
10.	Manas	0.081	0.452	0.058	0.008	3.130	59.204	0.166
11.	Redwing	0.818	2.025	0.135	0.013	10.760	159.720	0.232
12.	Sedona	0.472	1.142	0.166	0.024	9.545	48.424	0.148
13.	Stanfield	0.185	1.634	0.129	0.034	8.950	47.975	0.191
14.	Talon	0.308	1.120	0.135	0.018	8.323	61.325	0.131
15.	Vitez	0.778	1.568	0.144	0.022	12.625	71.756	0.168

None of the onion samples had Pb concentration above the limit set by regulations of the Republic of Serbia, but according to international standards, in 25 samples, it was above the limit. In one onion cultivar, Pb concentration was significantly higher, and in another one, it was significantly lower than in the others (Tab. 1). The concentration of Pb in potato was within the limits set by Serbian regulations but above it in 22 samples according to international regulations (Tab. 3). There were significant differences between potato cultivars with respect to Pb concentration.

Out of 32 samples of onion (belonging to 15 cultivars), the concentration of Cd was above the limit set both by regulations of the Republic of Serbia and international regulations in only two of them (Tab. 1). In 28 potato samples (belonging to 10 cultivars), concentration of Cd was above the limits in 4 as set by Serbian regulations and it was above the limit in only one of these according to international regulations (Tab. 3). The concentration of Cd was significantly higher in one potato cultivar than in the other nine, whereas in onion, differences between

cultivars, with respect to Cd concentration, were smaller. The coefficient of variation was the highest with respect to Cd in both onion (Tab. 2) and potato (Tab. 4), in comparison with the other elements being analysed.

Tab. 2. Descriptive statistics of concentrations of Cu, Zn, Pb and Cd, Zn/Cd ratio and dry weight of onion bulbs

Deskriptivna statistika koncentracija Cu, Zn, Pb i Cd, omjera Zn/Cd i težine lukovica crnog luka u suvom stanju

ONION	Concentration (mg kg^{-1})				Zn/Cd	% dry weight
	Cu	Zn	Pb	Cd		
Mean	0.437	1.229	0.147	0.020	93.166	9.689
Range	0.033-0.898	0.297-3.121	0.033-0.383	0-0.119	0-1594.4	2.921-28.550
Std.Dev.	0.279	0.587	0.066	0.021	226.032	4.536
Coef.Var.	63.741	47.78	44.765	109.275	242.611	46.811

There is a correlation between Zn supply and the uptake of Cd by plants. Low plant available Zn in soil promotes Cd uptake. It was found that in laboratory animals marginal deficiency of Zn may enhance Cd absorption as much as ten-fold from food containing low Cd concentrations (Reeves and Chaney, 2008). This indicates that the food that is nutritionally marginal with respect to Zn has much higher risk of containing more Cd, which is highly undesirable. Therefore, we compared Zn/Cd ratio in onion and potato samples. Overall, Zn/Cd ratio was higher in onion (93.16) than in potato (68.29) but ranges in both vegetables were very similar (Tab. 2 and Tab. 4, respectively). There were no significant differences between onion and potato cultivars with respect to Zn/Cd concentration.

The average heavy metal pollution index (HPI) was higher in potato (0.269) (Tab. 3) than in onion (0.166) (Tab. 1) which means that there is species specificity with respect to accumulation of heavy metals in plant parts developing in the soil (bulbs and tubers).

Conclusion

In general, it can be concluded that concentrations of Zn, Cu, Pb and Cd in conventionally produced onion and potato were below the limits set by Serbian regulation, with the exception of 2 (out of 32) onion and 4 (out of 28) potato samples in regards with Cd.

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Tab. 3. Average concentrations of Cu, Zn, Pb and Cd, dry weight, Zn/Cd ratio and HPI in potato tubers

Prosječne koncentracije Cu, Zn, Pb i Cd, težine u suvom stanju, omjera Zn/Cd i HPI u krtolama krompira

POTATO	Cultivar	Concentration (mg kg^{-1})				% dry weight	Zn/Cd	HPI CuZnPbCd
		Cu	Zn	Pb	Cd			
1.	Aladin	0.108	0.435	0.093	0.012	4.611	35.858	0.566
2.	Bella Rosa	0.870	2.090	0.266	0.049	16.498	42.860	0.392
3.	Desiree	0.820	1.703	0.149	0.022	18.273	76.193	0.270
4.	Cleopatra	0.317	0.398	0.246	0.043	11.910	9.330	0.279
5.	Kondor	0.634	1.212	0.129	0.027	13.160	44.669	0.233
6.	Kuroda	0.837	1.388	0.260	0.018	16.660	78.386	0.261
7.	Laura	0.952	2.083	0.479	0.108	17.730	19.288	0.228
8.	Madeleine	1.211	2.196	0.197	0.006	18.665	393.120	0.182
9.	Manitou	0.981	1.655	0.207	0.018	15.405	91.267	0.191
10.	Trezor	0.480	1.075	0.114	0.018	11.917	58.430	0.085

Tab. 4. Descriptive statistics of concentrations of Cu, Zn, Pb and Cd. Zn/Cd ratio and
dry weight of potato tubers

Deskriptivna statistika koncentracija Cu, Zn, Pb i Cd, omjera Zn/Cd i težine krtole krompira u suvom stanju

POTATO	Concentration (mg kg^{-1})				Zn/Cd	% dry weight
	Cu	Zn	Pb	Cd		
Mean	0.744	1.495	0.197	0.318	68.29	14.831
Range	0.052-1.833	0.267-3.730	0.074-0.647	0-0.184	0-1251.6	4.600-22.800
Std.Dev.	0.515	0.849	0.126	0.036	159.901	5.856
Coef.Var.	69.184	56.793	64.003	113.496	234.151	39.484

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Koncentracija neophodnih (Cu i Zn) i štetnih (Pb i Cd) teških metala u crnom luku i krompiru

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Sažetak

Teški metali mogu da se jave kao zagađujuće materije na površini i unutar tkiva povrtarskih kultura. Zato je cilj ovog rada bio da se utvrde koncentracije neophodnih (Cu i Zn) i štetnih (Pb and Cd) teških metala u crnom luku (*Allium cepa* L.) i krompiru (*Solanum tuberosum* L.) proizvedenom u Vojvodini. Koncentracije Cu, Zn, Pb i Cd su određene u jestivim biljnim delovima. lukovicama crnog luka i krtolama krompira. atomskom apsorpcionom spektrofotometrijom. U samo dva uzorka crnog luka i četiri uzorka krompira koncentracija Cd je bila iznad maksimalno dozvoljene u Republici Srbiji.

Ključne reči: luk, krompir, bakar, cink, olovo, kadmijum