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Intake of heavy metals in selected varieties of onion (*Allium cepa* l.) Grown in the different locations[1]

Akumulacja metali ciężkich w wybranych odmianach cebuli (*Allium cepa* L.) uprawianych w różnych warunkach

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Słowa kluczowe: cebula (*Allium cepa* L.), metale ciężkie, dopuszczalne limity

Abstract

The environmental study, carried out in Slovak Republic, was aimed at the assessment of quality of onion based on the contents of selected heavy metals (Zn, Cu, Ni, Pb and Cd) as well as the possible correlations among heavy metals in soil and onions (*Allium cepa* L.).
Gained results showed that in some monitored localities the measured values were exceeded in comparison with limit values given by the Law No. 220/2004 (valid in the Slovak Republic) as well as threshold values proposed by European Commission (2006). In our paper, the values of total cadmium content were in the range from 1.15 to 1.34 mg·kg^{-1} and the content of mobile form of lead was in the range from 0.19 to 1.09 mg·kg^{-1}. The lead content in all samples (except cv. Red matte grown in locality Klasov) of the onions was also exceeded and the values ranged from 0.05 to 0.21 mg·kg^{-1}. Among the varieties statistically significant differences (P < 0.05) in the intake of heavy metals were found (Multifactorial analysis of variance, LSD-test contrast P < 0.05) was used to process gained data.

Streszczenie

Badania środowiska, przeprowadzone na Słowacji miały na celu ocenę jakości cebuli poprzez oznaczenie zawartości wybranych metali ciężkich (Zn, Cu, Ni, Pb i Cd), jak również możliwych korelacji pomiędzy obecnością metali ciężkich w glebie i cebuli (*Allium cepa* L.).
Uzyskane wyniki wskazują, że w niektórych monitorowanych lokalizacjach zmierzone wartości zostały przekroczone w stosunku do wartości granicznych określonych w Ustawie nr 220/2004 (obowiązującej w Republice Słowackiej), jak również wartości granicznych zaproponowanych przez Komisję Europejską (KE) (2006). Wyniki naszej pracy wskazują, że wartości całkowitej zawartości kadmu wahają się w zakresie od 1,15 do 1,34 mg·kg^{-1}, a zawartość ołowiu w postaci mobilnej w zakresie od 0,19 do 1,09 mg·kg^{-1}. Zawartość ołowiu we wszystkich próbkach cebuli (z wyjątkiem odmiany Red mat hodowanej w miejscowości Klasov) jest również przekroczona, a wartości wahają się w zakresie od 0,05 do 0,21 mg·kg^{-1}. Wśród odmian stwierdzono statystycznie istotne różnice (p<0,05) w pobieraniu metali ciężkich (porównania wielokrotne dla metali ciężkich w zależności od odmiany, przy 95% przedziale ufności).

1. INTRODUCTION

The onion (*Allium cepa* L.) is cultivated and used around the world and it is a very important vegetable in the Slovak Republic. Onions are one of the most consumed vegetables with very diverse uses. It can be consumed raw in salad or cooked.
Onion composition is variable and is derived from environmental and genetic factors. High quality of vegetables is very important for human health. Nutrients play a significant role in improving productivity and quality of crops [Al-Fraihat 2014]. Different types of soils have different characteristics that influence growth and yield crops. The increasing presence of heavy metals in water, soil, and foodstuff is an alarming phenomenon around the world [Stasions et al. 2014]. Some of the heavy metals are also essential micronutrients for normal plant growth. They are constituents of enzymes and hormones and regulate a variety of physiological processes [Kitata, Chandravanshi 2012]. In high concentrations, heavy metals represent a high stress factor for plants [Kalafová et al. 2012].
Cd and Pb exposure cause a broad range of adverse health effects in humans and animals [Zhai et al. 2015]. One of the major heavy metal effects is oxidative stress [Markiewicz-Górka et al. 2015]. Metals increase lipid peroxidation and cripple antioxidant defences in tissues by altering the activity of antioxidant enzymes [Jomova, Valko 2011]. Cadmium is toxic to all animal species, and is accumulated in the kidney and to a lesser extent in liver [Bampidis et al. 2013]. Metal uptake by plants can be affected by several factors. It depends on plant species, types of soil and metals, soil pH, cation exchange capacity and weather conditions [Tangahu et al. 2011; Pinto et al. 2014].

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The aim of the work was an assessment of quality of onion cultivars from different locations with the emphasis on the contents of selected heavy metals in onion bulbs.

2. MATERIAL AND METHODS

2.1. Climate conditions of locations

This study was carried out in Klasov, Pruzina and Stiavnik. Altitude of Klasov is in the range from 160 to 238 meters above the sea level. In cadaster village Klasov predominate typical black soils, carbonate soils and deep soils without skeleton. In the cadaster territory village 1085 ha of agricultural soil predominantly arable soil (80%) is found. Climatic conditions: this area belongs to the warm climatic area (climatic and pedological situation in The West Slovak Region), regional middle dry.
The annual mean temperature is 10°C, during growing season (April to September) it is 15.5°C. Annual mean rainfalls range in values from 600 to 700 mm.
Pruzina is located under the Strázovské hills – Strázov. The altitude of the village is in the middle of 381 m above the sea level. Pruzina belongs to the mild cold climate zone, average annual air temperature is 7°C, annual rainfall is 800–1000 mm. Average relative humidity is 87%. The soil type of locality Pruzina is brown soils**.**
The altitude of Stiavnik is in the range from 345 to 1059 meters above the sea level. Stiavnik belongs to the mild cold climate zone, average annual air temperature is 6°C, annual rainfall is 800–900 mm.

2.2. Plant samples

Two cultivars of onions Red Mate (red), Boston (yellow) were obtained directly from a producer in Klasov, Pruzina and Stiavnik, Slovak Republic. The investigated onion cultivars were conventionally cultivated in the same locality under the same conditions. Only NPK fertilisation was used for the achievement of favourable soil macroelements content.
Samples of onion cultivars were collected at full maturity stages from areas of Klasov, Pruzina and Stiavnik. From the same places, from the arable layer (0–20 cm), soil samples were also taken with pedological probe GeoSampler fy. Fisher.

2.3. Chemicals

High-purity analytical reagents were used for all operations. Conventional chemicals: ammonium nitrate, ACS-reagent ≥ 98% (Merck, Germany), hydrochloric acid, TitriPUR® (Merck, Germany), nitric acid and SupraPUR® (Merck, Germany).

2.4. Chemical analysis of the soil

In each soil sample, the exchangeable reaction (pH/KCl), the contents of available nutrients (K, Mg, P, Ca) were determined by the method of Mehlich [1978] and content of humus by Tjurin [1951] method was determined. The pseudototal content of risk metals was assessed in soil extract by *aqua regia* and the content of mobile forms of selected heavy metals in soil extract by NH_4NO_3 (c = 1 mol·dm^{-3}). Analytical ending was flame AAS (AAS Varian AA Spectr DUO 240 FS/240Z/UltrAA). For the calibration of instruments (AAS Varian AA Spectr DUO 240 FS/240Z/UltrAA), CertiPUR® (Merck, Germany) calibration solution was used.

2.5. Heavy metals in the plant material

Homogenised samples were mineralised in a closed system of microwave digestion using Mars X-Press 5 (CEM Corp., USA) in a mixture of 5 cm^3 HNO_3 (SupraPUR®, Merck, Germany) and 5 cm^3 of deionised water (0.054 mS·cm^{-1}) from Simplicity 185 (Millipore, UK). Digestive conditions for the applied microwave system comprised heating to 160 °C for 15 minutes and keeping it constant for 10 minutes. A blank sample was treated in the same way. The digested substances were subsequently filtered through a quantitative filter paper Filtrak 390 (Munktell, Germany) and filled up with deionised water to a volume of 50 cm^3.
The solutions were analysed by flame AAS (AAS Varian AA Spectr DUO 240 FS/240Z/UltrAA) (Varian, Australia).

3. RESULTS AND DISCUSSION

The present study reports on the heavy metal content of Zn, Cu, Ni, Pb and Cd determined in two different varieties of onions as well as the possible correlations between selected heavy metals in soil and onion bulbs (*Allium cepa* L.). The observed concentrations of Zn, Cu, Ni, Pb and Cd in soils were compared with the recommended limit resulting from Law No. 220/2004 (valid in the Slovak Republic) and threshold values proposed by European Commission (2006) and heavy metals concentrations observed in bulb of onions were compared with the Foodstuffs Codex of the Slovak Republic valid in the Slovak republic (FC SR) as well as according to Commission Regulation 1881/2006 (CR).
Soil reaction is important for the mobility and acceptability of risky elements by the plant. The monitored soils on which the onions were grown can be characterised as neutral (Klasov, Pruzina) to alkaline (Stiavnik). A low pH increases the mobility of heavy metals thereby making them more bioavailable [Walker et al. 2006]. The soil reaction in soil samples in the area of Klasov had the average value 6.70±0.76, in the area of Stiavnik 7.32±0.60 and in the area of Pruzina 7.18±0.66.
The pseudototal content of risk metals including all of the forms besides residual metal fraction was assessed in solution *aqua regia*. The results are shown in Table 1.
The total content of heavy metals includes all metal forms with the exception of their residual fractions. Determined total contents of heavy metals were ranging from 81.69 to 304.90 (Zn), 30.45 to 36.11 (Cu), `21.97 to 49.02 (Ni), 21.46 to 25.27 (Cr), 28.11 to 29.70 (Pb), and 1.15 to 1.34 (Cd). Values observed for Cd (Cd limit 0.7 mg·kg^{-1}) were more than the Cd limit in all monitored localities. The highest value of cadmium (1.34±0.11) mg·kg^{-1} was measured in the sampling site Pruzina. In the two monitored sites (Stiavnik, Pruzina) Ni content was in the threshold limit given by

Table 1. Content of heavy metals (mg·kg^{-1}) in soil extract by *aqua regia*

Locality	Zn	Cu	Ni	Cr	Pb	Cd
Klasov						
Mean	81.69	30.45	21.97	22.56	28.11	1.16
SD	5.96	2.42	1.73	0.82	2.29	0.09
Range	74.5-89.1	27.6-33.5	19.8-23.8	21.87-23.54	25.3-30.9	1.05-1.27
Stiavnik						
Mean	143.03	34.17	49.02	25.27	29.7	1.15
SD	11.68	3.09	3.92	2.05	2.65	0.09
Range	128.8-157.4	30.1-37.5	44.1-53.7	22.5-27.1	26.2-32.0	1.04-1.28
Pruzina						
Mean	304.9	36.11	40.10	21.46	29.3	1.34
SD	24.55	1.53	3.24	1.34	2.40	0.11
Range	275.8-335.8	36.9-37.89	36.45-44.25	19.78-22.58	26.46-32.34	1.21-1.47
*Limit**	*150*	*60*	*40*	*150*	*70*	*0.7*
*Threshold value***	*100*	*40*	*30*	*50*	*50*	*0.5*

SD –standard deviation;
**Limit value for aqua regia – Law No. 220/2004*
***European Commission (2006)*

Table 2. Content of heavy metals (mg·kg^{-1}) in soil extract by NH_4NO_3 (c = 1 mol·dm^{-3})

Locality	Zn	Cu	Ni	Cr	Pb	Cd
Klasov						
Mean	0.12	0.16	0.29	0.13	0.19	0.08
SD	0.014	0.009	0.012	0.008	0.014	0.009
Range	0.10-0.13	0.15-0.17	0.28-0.31	0.12-0.14	0.18-0.21	0.07-0.09
Stiavnik						
Mean	0.32	0.22	0.21	0.042	0.84	0.08
SD	0.02	0.014	0.02	0.005	0.07	0.006
Range	0.29-0.34	0.20-0.23	0.19-0.23	0.036-0.048	0.78-0.92	0.075-0.088
Pruzina						
Mean	1.26	0.16	0.20	0.13	1.09	0.09
SD	0.09	0.008	0.02	0.008	0.08	0.015
Range	1.14-1.35	0.15-0.17	0.18-0.22	0.12-0.14	0.97-1.15	0.08-0.11
*Limit**	*2.00*	*1.00*	*1.50*		*0.10*	*0.10*

SD, standard deviation.
**Limit value for 1 M* NH_4NO_3 *– Law No. 220/2004*

Law No. 220/2004 for *aqua regia*. Ni content was more than the threshold limit given by European Commission (2006).

Nickel is often mobile in plants. The uptake of nickel by plants is related to its toxicity, which may have possible implications with respect to humans and animals through the food chain [Lyaka 2011].

The mobile form of heavy metals is very important because it is more accessible to the plant. The results are shown in Table 2.

From observed heavy metals in 1 M NH_4NO_3 lead in all monitored localities was more than the limit. In our work, the values of lead ranged from 0.19 to 1.09 mg·kg^{-1}. The highest value (1.09 mg·kg^{-1}) was measured in sampling site Pruzina. Pb content determined in the soil extract by NH_4NO_3 was 10-fold higher than limit value. Soil and plants can be contaminated by lead from car exhaust, gases from various industrial sources, from pesticides and fertilisers [Bhatti et al. 2013]. Several studies have shown that lead causes oxidative stress by inducing the generation of reactive oxygen species [Capcarova et al. 2009].

The growth and yield of plants are affected directly or indirectly in response to environmental stresses [Hussain et al. 2013].

Table 3. Content of risk metals (mg·kg^{-1}) in cultivars of onion

Locality	Cultivar	Zn	Cu	Ni	Pb	Cd
Klasov	Red matte	1.32±0.08a	0.70±0.08ab	0.05±0.02a	0.05±0.02a	0.02±0.008a
Stiavnik	Red matte	1.51±0.02b	0.72±0.02ab	0.07±0.008ab	0.10±0.04a	0.03±0.004ab
Pruzina	Red matte	1.72±0.08c	0.84± 0.03c	0.17±0.01cd	0.17±0.01b	0.04±0.008b
Klasov	Boston	1.92±0.12d	0.67±0.08a	0.12±0.008bc	0.19±0.01b	0.02±0.008a
Stiavnik	Boston	1.97±0.08d	0.79± 0.02bc	0.19±0.01d	0.20±0.08b	0.04±0.01b
Pruzina	Boston	2.32±0.12e	1.06± 0.08d	0.31±0.08e	0.21±0.01b	0.03±0.01ab
*Limit**			*10.00*		*0.10*	*0.10*
*Maximal level***					*0.10*	*0.05*

**Limit value according to the Food Codex of the Slovak Republic*
***Maximal level according to Commission Regulation 1881/2006*

The accumulation of heavy metals with descriptive statistics in different varieties of onion is shown in Table 3.
Contents of the monitored heavy metals in varieties of onion varied at different intervals (see Table 3). From observed heavy metals (Zn, Cu, Ni, Pb and Cd) only the content of Pb in onions was exceeded. The lead content in all samples of the onions ranged from 0.05 to 0.21 mg·kg^{-1}. The highest value of lead (0.21±0.01) was recorded in the yellow variety Boston, where it was grown in the collecting site Pruzina. Pb content in the yellow variety Boston was 2.1 times higher than limit value (0.1 mg·kg^{-1}) to Commission Regulation 1881/2006. On the basis of obtained results, we can conclude that yellow cultivars of onion accumulated higher levels of lead than red cultivars of onion. The limit values for Cd in the fresh matter of onion samples were not exceeded at any monitored localities. In the environment lead is known to be toxic to plants, animals and microorganisms [Tangahu et al., 2011]. Similarly to Rafique et al. [2011] in the work we have found positive correlation among the content of Pb in the soil and the content of Pb in the studied cultivars (P-value < 0. 05).

4. CONCLUSION

Soil is the starting point for the entry of heavy metals into plants and then into the food chain. The results of monitored heavy metals (Zn, Cu, Ni, Pb and Cd) revealed that the content of Pb is the main polluting factor of soil in this region (Klasov, Stiavnik and Pruzina).
Increased levels of heavy metal (Pb) in soil are reflected in increased Pb concentration in onions. The highest value of Pb was recorded in yellow variety Boston. From the aspect of other heavy metals (Zn, Cu, Ni and Cd) content, the onion cultivation in the monitored localities is safe.

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