The Investigation of Sensitivity of Different Types of Onion To Heavy Metal Intake From Contaminated Soil

Bystrická, J.*, Árvay, J., Musilová, J., Vollmannová, A., Tóth, T. and Lenková, M.

Department of Chemistry, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture in Nitra, Tr. A Hlinku 2, 949 76 Nitra, Slovak Republic

ABSTRACT: Onion (Allium cepa L.) is widely used around the world and it is very important vegetable in the Slovak Republic (SR). Six varieties of onion (Karmen, Kamal, Amika, Hector, Diamant, White Dry) were studied and the contents of selected heavy metals, their polyphenol contents as well as the possible correlations among selected heavy metals in soil and onions were analysed. Six soil sampling sites were selected and the analyses of pH/KCl, P, K, Mg and certain heavy metals (as total and mobile fraction) were provided. The concentrations of minerals and heavy metalswere determined by atomic absorption spectrophotometry and the content of total polyphenols was estimated by Folin-Ciocalteau reagent.Results revealed the excess in maximum amounts for total Cd content, where values ranged from 0.90 to 1.24 mg/kg as well as for mobile form of cadmium and lead where values were in the range 0.06 - 0.14 mg/kg and 0.6 - 1.07 mg/kg, respectively. The content of three metals (Cr, Cd, Pb) in the dry matter (DM) of the onions exceeded the limits set by the European Union and Food Codex of Slovak Republic. Polyphenols concentration varied in the range from 162.84 mg/kg (white variety Diamant) to 1387.89 mg/kg FW (red variety Kamal).Among the varieties statistically significant differences (P < 0.05) in intake of heavy metals and in the content of polyphenols were found.

Key words: Onion, Heavy metals, Pollution, soil, Food safety

INTRODUCTION

Onion (Allium cepa L.) is one of the most important groups of vegetables in the Slovak Republic. Onions possess strong, characteristic aromas and flavours, which have made them to be important ingredients of food (Ye et al., 2013). Onions are consumed in different ways; it can be eaten raw or cooked in to different tastes. Onion is also considered as part of a group named "functional foods", which offer a particular health benefit over the traditional nutrients they contain (Kitata and Chandravanshi, 2012). Two classes of phytochemicals found in onion and other Alliums show health-promoting activity. These are phenolic compounds and sulphur containing alk(en)ylsulfoxides (Reilly et al., 2014). Numerous studies have suggested that Allium species has a beneficial effects on the human health (Vishnu et al., 2009; Bernaert et al., 2012; Salami et al., 2012). Phytochemical studies show that onions are rich source of quercetin (3,3',4',5,7-pentahydroxyflavón). Quercetin was reported to have protective effects in reducing the risk of cardiovascular disease and act as anti-cancer and antioxidant agent due to its antiprostanoid and anti-

inflammatory responses and to decrease the rate of DNA degradation (Crystal et al., 2003). Onion contains vitamin A and C and ahigh amount of mineral elements to the human body (Paul 2006; Yahaya et al., 2010).

At present time the contamination of environment and foods by heavy metals draw great attention. Growth media including soil, nutrient solution, water and air are main sources of heavy metals for vegetables and other crops, which enter through roots or foliage by two main bio-sorption mechanisms (adsorption and/ or absorption) and are accumulated in their tissues (Adeyeye et al., 2005; Abdullahi et al., 2008). The absorption and translocation of heavy metals into plants is highly dependent of their physiologic condition. Certain elements are considered as especially suitable for successful crop growth. If they are lacking or improperly balanced, normal development does not occur (Adeyeye et al., 2005).

Contaminants in soil can directly pose significant human health risks through oral ingestion, dermal contact and particle inhalation (Saleem et al., 2014). The

^{*}Corresponding author E-mail: judita.bystricka@uniag.sk

heavy metals like cadmium and other pollutants in agricultural soils have led to bioaccumulation of various toxicants in food crops (Nagajyoti et al., 2010), they are easily absorbed by soil and accumulated in different plant parts such as root, stem and leaf (Arya and Mukherjee, 2014). Lead is the best-known heavy metal that occurs naturally and to a greater extent from anthropogenic activities. Acute lead poisoning in humans may cause severe dysfunction of kidney, reproductive system, liver, brain and central nervous system, which leads to sickness or death (Taghipour and Mosaferi, 2013). The aim of this work was to evaluate the quality of six onion cultivars based on the contents of heavy metals (Zn, Cr, Cu, Pb, and Cd) as well as the possible correlations among selected heavy metals in soil and in onion (Allium cepa L.).

MATERIALS & METHODS

Climate conditions of location: This study was carried out in Klasov, the village in Slovak Republic in Nitra district. It is located in the middle part of Zitavska highlands in valley of Babindol stream about 4 km west of town Vrable towards to town Nitra. Altitude of the area is in the range from 160 to 238 meters above the sea level. In terrier of village Klasov predominate typical black soils, carbonate soils, and deep soils without skeleton. In terrier territory of village is found about 1085 ha of agricultural soil, predominantly arable soil (80%). Climatic conditions: this area belongs to the warm climatic area (climatic and paedological situation in the West Slovak Region), regional middle dry. The annual mean temperature is about 10 C, during growing season (April-September) about 15.5 C. Annual mean rainfalls range in values from 600 to 700 mm.

Plant samples: Six cultivars of onions: 2 red (Karmen and Kamal), 2 yellow (Amika and Hector), and 2 white (Diamant and White Dry) were obtained directly from a producer in Klasov, Slovak Republic. The investigated onion cultivars were conventionally cultivated in the same locality and under the same conditions. Only NPK fertilization was used for the achievement of favourable soil macroelements content. The soils on which the onions were grown, can be characterized as acidic to neutral (pH/KCl = 6.373 - 6.99), with medium to high content of humus (% Hum. = 2.84 to 3.21), with good to very high phosphorus content (P = 82.80 - 185.80 mg/kg), with high to very high content of magnesium (Mg = 388.6 - 512.9 mg/kg).

Collection of samples: Samples of six cultivars of onions were collected at full maturity stages from area of Klasov. Within one variety we took the sample for 4 times from 4 times from 4 random places. From the same places, from the arable layer (0-20 cm), soil samples weretaken with paedological probe GeoSampler (Fisher scientific, Slovakia). The dried onion samples were pulverized in Grindomix 200 GD (Retsch, Germany) and next stored in pre-cleaned polyethylene bottles until subsequent pre-analytical operations.

Chemicals: High-purity analytical reagents were used for all operations.Conventional chemicals: ammonium nitrate (Merck, Germany), hydrochloric acid (Merck, Germany), nitric acid (Merck, Germany). Folin-Ciocalteu reagent and gallic acid were purchased from (Merck Germany). Sodium carbonate and methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Chemical analysis of the soil: In each soil sample the exchangeable reaction (pH/KCl), the contents of available nutrients (K, Mg) and content of humus by Tjurin method in modification of Nikitin and Fishman (1969) were determined. The content of phosphorus was determined by Fiala et al. (1999). The contents of risk metals including all of the forms besides residual metal fraction were assessed in soil extract by aqua regia and contents of bioavailable forms of selected heavy metals in soil extract by NH4NO3 (c = 1 mol/dm3). Gained results were evaluated according to Law No. 220/2004 (valid in the Slovak Republic) as well as threshold values proposed by European Commission (EC, 2006). Analytical ending presented flame AAS determination (AAS Varian AA Spectr DUO 240 FS/240Z/ UltrAA, Australia).

Chemical analysis of the plant material: Homogenized onion samples were mineralized in a closed system of microwave digestion using Mars X-Press 5 (CEM Corp., USA) in a mixture of 5 mLHNO3 (Suprapur, Merck, Germany) and 5 mL deionized water (0.054 mS/ cm) obtained with Simplicity 185 (Millipore, UK). For each variety 4 samples were processed. Digestive conditions for the applied microwave system comprised heating to 160 C for 15 minutes and keeping it in constant temperature 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 deionized water to a volume of 50 mL. The solutions were analysed by flame AAS (atomic absorption spectrometry) method:Cd and Pb: GF-AAS; Zn and Cu: F-AAS (VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with a D2 lamp background correction system, using air-acetylene flame, Varian, Ltd., Mulgrave, Australia). The measured results were compared with the multielemental standard for GF AAS (CertiPUR, Merck, Germany). Content of Zn, Cu, Cd and Pb was assessed at wavelength 213.9, 324.8, 228.8, and 217.0 nm. The limits of detection (LOD) for Zn (Cd, Cu and Pb) were 0.3 (0.05, 0.1 and 1.0) mg/kg, and limits of quantification (LOQ) for Zn (Cd, Cu and Pb) were 0.9 (0.15, 0.3 and 3.0) mg/kg. Gained results were evaluated according to the Food Codex of the Slovak Republic valid in the Slovak Republic (FC SR) as well as according to Commission Regulation 1881/2006 (CR). Maximum levels for the content of risky metals in foodstuffs in these legislative norms are given in mg.kg-1 wet weight or in mg/kg of consumption of foodstuff.

Determination of total polyphenol content (TPC) in the plant material: The total polyphenol content (TPC) was estimated using Folin-Ciocalteau reagent (Merck, Germany) according Lachman et al. (2003). Sample extract (0.05 to 1 mL to the expected polyphenol content), 2.5 mL Folin-Ciocalteau reagent and 3 - 5 mL H2O were added to a 50 mL flask. After 3 min. 7.5 mL of 20% Na2CO3 (Sigma-Aldrich, USA) were added to the flask and diluted to 50 mL with H2O. The mixture was incubated for 120 min. at laboratory temperature and the absorbance was measured at 765 nm on the spectrophotometer Shimadzu 710 (Shimadzu, Japan) against the blank sample. The total polyphenol content was expressed as gallic acid equivalents (GAE) in mg/kg DM (dry matter). The linearity range for this assay was determined at 200 - 1000 mg GAE/mL.

Statistical analysis: Results were statistically evaluated by the Analysis of Variance (ANOVA - Multiple Range Tests, Method: 95.0 percent LSD) using statistical software STATGRAPHICS (Centurion XVI.I, USA). The comparison of the monitored parameters (heavy metals, pH, TPC, content of humus) was examined using Pearson's correlation coefficients. The limit of statistical significance was set up at P 0.05 for all statistical analysis and P 0.01 for correlation coefficients.

RESULTS & DISCUSSION

The uptake and accumulation of heavy metals in food chain may cause possible health risks. The soil chemical characteristic (the content of macroelements, % of humus, exchange soil reaction) are presented in Table 1. The monitored soils, on which the onions were grown, can be characterized as acidic to neutral. The soil pH reaction in soil samples from the Klasov area had the average value 6.70 with standard deviation \pm 0.24.

The mobility of heavy metals depends not only on the element concentration in the soil, but also the most important factors which affect their mobility are pH, sorbent nature, concentration of organic matter and mineralogy of soil (Violante et al., 2010, Fijalkowski et al., 2012). The most mobile elements include the Cd, Zn and Mo, while the least mobile are Cr, Ni and Pb (Fijalkowski et al., 2012). Higher solubility of heavy metals in soil solution at alkaline pH was attributed to enhanced formation of organic matter metal complexes after ionization of weak acid groups (Sherene, 2010).

Trace elements are metals present in very small quantities in plants and in the body. After overload the certain concentration (excess will) the health of consumer through the food chain can be seriously threatened. Pseudototal content of risk metals in soil, including all of the forms besides residual metal fraction was assessed in solution of aqua regia. The results are shown in Table 2.

Determined total contents of heavy metals were in ranged 77.60 - 88.20 (Zn), 29.60 - 32.97 (Cu), 22.05 - 24.05 (Cr), 27.37 - 29.13 (Pb), and 1.08 - 1.21 (Cd). Values for Cd limit (0.7 mg/kg) was exceeded in all sampling sites, while the determined total lead content in soil was below the limit value (< 70 mg/kg). The highest value of cadmium (1.21 ± 0.02) mg/kg was measured in sampling site where variety Karmen was grown.

The total contents of heavy metals included all metal forms with exception of their residual fractions. The high heavy metals content in the soil by aqua regiadid not inevitably result in the high content in agricultural plants. The mobile form of heavy metals were more accessible to plant. The results of mobile

Locality	Cultivar	К	Ca	Mg	Р	pH/KCl	Humus (%)	Cox (%)
1	Karmen	302.3	4943	511.9	82.8	6.37	3.02	1.86
2	Kamal	315.2	4254	436.0	125.7	6.99	2.84	2.22
3	Amica	387.4	4032	512.9	100.9	6.46	3.21	2.10
4	Hector	329.9	4728	469.2	106.3	6.74	3.07	1.46
5	Diamant	325.4	4630	472.6	185.8	6.86	2.99	1.79
6	White Dry	343.4	4812	388.6	97.5	6.80	3.15	1.96

Table 1. Agrochemical characteristics and content of nutrients (mg/kg) in soils from locality Klasov

Locality	Cultivar	Zn	Cu	Cr	Pb	Cd
1	Karmen	82.68 ± 0.98	32.97±0.17	$22.30{\pm}1.04$	28.57±0.70	1.21 ± 0.02
2	Kamal	79.20 ± 1.53	31.43±0.29	$23.50{\pm}1.45$	29.13±0.65	1.17 ± 0.01
3	Amica	77.60 ± 1.35	28.67±1.09	22.05 ± 1.21	27.37±0.87	1.12±0.06
4	Hector	88.20 ± 0.97	$29.92{\pm}1.07$	$24.05{\pm}0.61$	28.02 ± 0.61	1.20 ± 0.02
5	Diamant	81.50 ± 0.49	29.60±0.55	22.16 ± 0.97	27.45±0.55	1.08±0.13
6	White Dry	80.77 ± 1.02	31.0 ± 1.83	23.65 ± 0.40	28.17±1.02	1.19±0.02
Lim it *		150	60	50	70	0.7
Treshold val	ue**	100	40	30	50	0.5

Table 2. Content of heavy metals (mg/kg) in soil extract by aqua regia

*Limit value for aqua regia - Law No. 220/2004, **European Commission (2006)

Table 3.Content of heav	v metals (mg/kg) in soi	l extract by NH4NO3	(c = 1 mol/dm3)

Locality	Cultivar	Zn	Cu	Cr	Pb	Cd
1	Karmen	$0.12 {\pm} 0.009$	$0.157{\pm}0.01$	$0.150{\pm}0.01$	1.06 ± 0.01	0.10 ± 0.01
2	Kamal	$0.09 {\pm} 0.005$	0.185 ± 0.005	0.140 ± 0.008	0.975 ± 0.1	0.14 ± 0.006
3	Amica	$0.12 {\pm} 0.006$	0.162 ± 0.012	$0.127 {\pm} 0.01$	0.75±0.06	0.09 ± 0.006
4	Hector	0.12 ± 0.01	0.162 ± 0.008	0.133 ± 0.01	1.01 ± 0.08	0.11 ± 0.01
5	Diamant	0.13±0.01	$0.167 {\pm} 0.02$	0.122 ± 0.012	0.70 ± 0.08	0.08 ± 0.008
6	White Dry	0.13±0.01	0.165±0.006	0.130±0.008	0.825 ± 0.1	0.07 ± 0.017
Lim it *		2.00	1.00	·	0.10	0.10

*Limit value for 1 M NH4NO3 - Law No. 220/2004

fraction of heavy metals in tested soils are shown in Table 3.

From observed heavy metals in 1 M NH4NO3 only the contents of Pb in all observing sites were exceeded. In our work the determined contents of lead were in ranged from 0.75 to 1.06 mg/kg. In collecting site number 1, where the variety Karmen was grown, Pb content was 10.6 times higher than limit value valid in the Slovak Republic (0.1 mg/kg). In collecting site number 2 and 4 the Cd content was higher than limit value (0.1 mg/kg) The contents of all other heavy metals (Zn, Cu and Cr) in 1 M NH4NO3 were lower than hygienic limits (Zn < 2.0 mg/kg, Cu < 1.0 mg/kg).

Table 4.Content of risk metals (mg/kg FW) in cultivars of onionLead is one of the ubiquitously distributed and most abundant toxic elements in the soil. It exerts adverse effect on morphology, growth and photosynthetic processes of plants (Nagajyoti et al., 2010). Stress caused by an excess of heavy metals in the beginning of disturbances in the metabolism of plants and can lead to disturbances in the collection, transport and assimilation of macro-and micronutrients (Fijalkowski et al., 2012). Moriarity et al. (2014) reported that gastrointestinal symptoms may be the first manifestation of lead toxicity. The gastrointestinal symptoms generally do not seem to occur until lead levels are very high.

It is important to carry out monitoring of heavy metals in edible parts of plants. The determination of metal content of onion and other vegetables across different parts of the globe were conducted from viewpoints: health risk assessment, nutrient content analysis for consumers, to trace geographic origin of food products, nutritional status assessment of growing plants and assay of suitability of soil and water for farming and as bio-indication for monitoring of environmental pollution (Kitata and Chandravanshi, 2012). The evaluation of heavy metals in particular varieties of onions was realised in this paper. The results are shown in Table 4.

BAF bioaccumulation factor: Contents of the monitored heavy metals in varieties (Karmen, Kamal- red, Amica, Hector-yellow, Diamant, White Dry-white) of onions (Allium cepa L.) varied at different intervals (11.0 - 19.4 mg/kg Zn, 5.6 - 8.8 mg/kg Cu, 1.0 - 1.4 mg/kg Cr, 0.11 - 0.60 mg/kg Pb, 0.02 - 0.04 mg/kg Cd). Similar results were published also by other authors (Gebrekidan et al., 2013; Amin et al., 2013; Behbahni et al., 2015).

The lead content in all samples of the onions ranged from 0.11 to 0.60 mg/kg FW. The level of Pb limit value (0.10 mg/kg) was exceeded according to Commission Regulation 1881/2006. The highest value of lead (0.60 ± 0.04) was recorded in the variety Karmen. Pb content in the variety Karmen was 6 times higher

Locality	Cultivar	Zn	Cu	Cr	Pb	Cd
1	Karmen	16.4±0.18d	6.60±0.08 cd	$1.2 \pm 0.08 a$	0.60±0.04a	$0.04\pm0.002bc$
	BAF				0.020	0.033
2	Kamal	$16.0 \pm 1.15d$	$8.80 \pm 0.08e$	$1.4 \pm 0.08 a$	0.25±0.09e	0.04±0.003c
	BAF				0.008	0.034
3	A m ic a	$11.0 \pm 0.82a$	$7.0 \pm 0.82 d$	$1.0 \pm 0.57 a$	0.11±0.03 b	0.03±0.001 ab
	BAF				0.004	0.026
4	Hector	$19.4 \pm 0.08e$	$5.60 \pm 0.12a$	$1.0 \pm 0.58a$	$0.22\pm0.06d$	$0.036 \pm 0.002 bc$
	BAF				0.008	0.030
5	Diam ant	$12.6 \pm 0.08 b$	$6.0 \pm 0.15 ab$	$1.0 \pm 0.04 a$	0.22±0.05 d	$0.028 \pm 0.002ab$
	BAF				0.008	0.026
6	White Dry	$14.4 \pm 0.08c$	5.80±0.08 ab	1.20±0.11a	0.19±0.03c	0.022±0.001a
	BAF				0.007	0.018
L im it *			10	2.5	0.1	0.1
Maximal l	evel**				0.1	0.05

Table 4.Content of risk metals (mg/kg FW) in cultivars of onion

*Limit value according to the Food Codex of the Slovak Republic

**Maximal level according Commission Regulation 1881/2006(CR)

than limit value (0.1 mg/kg) according to Commission Regulation 1881/2006.

The contents of other heavy metals (Zn, Cu, Cr, Pb and Cd) in varieties of onion were lower than limit value according the Food Codex of the SR as well as values according toCommission Regulation 1881/2006 (CR). Limit value for Zn content in food is not determined in the Food Codex of the SR as well as in Commision Regulation 1881/2006 (CR).

In this work we found statistically significant differences in content of Pb among studied onion cultivars, except two cv. Hector and cv. Diamant (P-value 0.05). Vegetables take up metals mainly from soil solution and sometimes through the above-ground parts (Chojnacka et al., 2005). Pb uptake can also be promoted by pH of the soil and the level of organic matter in the soil (Zeng et al., 2011; Amin et al., 2013).

The phenolic compounds are important for plant due to their various biological functions including UV protection, pollen tube growth, antimicrobial activity, and insect resistance (Winkel-Shirley, 2002). Several studies showed (Michalak, 2006; Eicholz et al., 2011; Rivas-San Vicente and Plasencia, 2011; Sytar et al., 2014) that induction of phenolic compounds in plants could be a response to multiple stresses. Heavy metals act as stress factor for plants and may affect secondary metabolites in plants. Diáz et al. (2001) showed an increase in the activity of the enzymes involved in the metabolism of phenolic compounds after heavy metal exposure. In our work the total polyphenol contents in six cultivars of onions were measured. The results are shown in Table 5. Many studies have suggested (Pérez-Gregorio et al., 2010; Abdel-Gawad et al., 2014) that red onion has a high quantities of flavonoids and also anthocyanins.

Statistically significant differences in polyphenol content of tested cultivars were evaluated, while the highest content of polyphenols was detected in cultivar Karmen (1387.89±12.72), which also accumulated the highest content of lead.In red variety Kamal we measured also the second highest value of polyphenols (1248 mg/kg), however, in this case the accumula-

Locality	Cultivar	Pb	TPC
1	Karmen	0.60±0.04a	1387.89±12.72e
2	Kamal	0.25±0.09e	1248.67±15.49f
3	Amica	0.11±0.03b	386.75±14.82c
4	Hector	0.22±0.06d	424.22±11.15d
5	Diamant	0.22±0.05d	162.84±6.87a
6	White Dry	0.19±0.03c	205.51±12.88b

Table 5.Content of Pb (mg/kg FW) and TPC (mg/kg FW) in cultivars of onion

	Zn_{AR}	CUAR	Cr_{AR}	Pb_{AR}	CdAR	Zn_{AN}	Cu _{AN}	Cr_{AN}	Pb_{AN}	CdAN	$2n_0$	Cuo	Cr_0	Pb_0	Cd_0	TPC	Ηd	Hum.
$Zn_{\rm AR}$	1																	
CUAR	-0.46	-1																
Cr _{AK}	0.6)	-000	1															
Pb_{AR}	-0.89	0.63	0.28	1														
$\mathbf{Cd}_{\mathbf{AR}}$	-02	0.96	-030	0.42														
ZnAN	0.97	-037	-058	-0.93	-0.11	Г												
CUAN	0.45	-0.66	034	-0.81	-0.57	056	1											
Cran	10.0-	-087	0.57	-0.31	-0.95	-0.05	0.64	_										
Pb_{AN}	-083	0.56	0.77*	0.58	0.38	-066	-0.09	60'(r	1									
Cdan	0.84*	-0.05	-097	-0.51	0.19	0.76*	0.0)	-0.45	-0.82	1								
Z_{n_O}	0.63	-043	-0.79	-0.31	-0.30	043	-0.19	Ū	-0.95	0.76	H							
Cu _o	-05	-048	. 60	0.12	-0.67	-048	043	0.85**	043	-0.85	-0.45	1						
$\dot{\mathrm{Cr}}_{\mathrm{o}}$	0.5	0.48	60-	-0.12	0.67	0.48	-0.43	-0.85	-0.43	0.85"	045	-	1					
Pb_0	0.74*	-051	-0.05	-0.95	-0.32	0.85**	"Ĵ60	63	-0.3	0:30	0	0	0	1				
Cu _o	-0.54	-024	0.27	0.58	-0.45	-0.72	-0.43	0.43	0	-0.43	022	-0.50	-0.5	-0.71	-			
DHI.	0.62	-097	002	-0.81	-0.87	0.58	<u>979</u>	0.78*	<u>85.0-</u>	0.17	038	-0.35	-0.35	0.71*	0.02	1		
Ηd	0.81^{+}	0.14	-088	-0.54	0.40	0.81°	0	09'(r	-0.60	0.94	049	0.9^{+}	#60	0.42	20-	0.04	1	
Hum.	0.24	0.45	-0.04	-0.33	0.59	0.45	032	-1.48	032	0.16	-0.51	0.38	C 38	053	-094	-021	0.49	1
Notes	: AR - co	ntent of h	Paur met	uuu in an	temen er	AND INV	uue utant of he		ale in MI	NINO2 (nonta	uru nt of hom	uno en contra la					TDC 170- WC

Table 6. Pearson correlation coefficients of monitored parameters in samples (in cv. Karmen)

	Zn_{AR}	CuAR	$\mathrm{Cr}_{\mathrm{AR}}$	Pb_{AR}	Cd_{AR}	Zn_{AN}	CuAN	Cran	Pb_{AN}	CdAN	Zn_0	Cu _D	Cr_0	Pb_{O}	Cd_0	TPC	Ηd	Hum.
Zn _{AR}	1																	
CUAR	-0.84	Ţ																
AK	1/10-	039	1															
AR	19'0-	0,63	C80*	1														
Cd _{AR}	0.76^{*}	060-	-0.09	-0.24	-													
IAN	0.39	60.0	-0.86	-0.45	-030	1												
NVI	0.11	030	003	650	0	050	Г											
AN	0.62	-043	-0.05	0.25	0.71°	0	0.71	1										
NA	-0.14	-000	-0.30	-0.70	-030	600	-0.9	-0.85	1									
AN	0.11	030	003	0.59	0	030	l**	0.71*	060-	-								
lo	92.0-	•0 0 0	600	0.24	Ļ	030	0	1//0-	0.30	0	-							
-0	-0.45	0.85	COR	6-0	170-	043	0.71*	0	-0.43	0.71*	0.71*	1						
0	0.62	-043	-0.05	0.25	0.71°	0	0.71*	<u>،</u>	-0.85	0.71*	-071	0	1					
0	0.62	-0.43	-0.05	0.25	0.71	0	0.71*	1**	-0.85	0.71*	-0.71	0	1**	1				
lo	0.11	020	CO3	0.59	0	000	1**	C.71*	-0.90	1.*	0	0.7]*	071*	0.71*	1			
ç	0.06	027	-0.75	-0.52	-059	0.88**	-0:0-	-0.47	0.48	-0:07	059	0.37	-0.47	0.79*	0.07	1		
Ŧ	-0.24	01.0	0.81*	0.83*	032	-0.72	0.45	0.54	-0.75	0.45	-032	0.09	054	0.54	-0.45	-080	1	
III.	0.00	060	-0.73	-0.87	19.0	030	-033	0.24	0.3	-033	-0,67	0.7]*	024	0.24	-033	0.16	-0.49	1

Table 7. Pearson correlation coefficients of monitoredparameters in samples (in cv. Kamal)

	Znar	CUAR	$\mathrm{Cr}_{\mathrm{AR}}$	Pb_{AR}	CdAR	Zn_{AN}	CUAN	Cran	PbAN	CdAN	Zn_0	Cu_0	Cr_0	Pb_0	Cd ₀	TPC	Ηd	Hum.
AR	1																	
AR	090-	Ţ																
AK	0.57	-088	1															
AR	-050	-0.01	-0.34	1														
AR	-0.12	0.86	-0.77	-0.34	-													
AN	0.94	-034	625	-0.54	0.17	1												
NA	650-	-020	53	000	-1).73	-0.79	I											
AN	0.28	-0.73	033	020	69'(r	0.21	035	_										
NA	0.43	0.12	-0.44	9000	046	0.69	-090	030	1									
NN	0.43	0.12	-0.44	9000	0.46	0.69	-0.69	030	1*	-								
0	0.39	0.49	-0.46	-0.51	0.86	0.65	-097	043	0.71*	0.71*	1							
_0	0.54	.098	°77*	018	-0.86	0.32	032	085"	0	0	-050	1						
0	0.90	0.81	087**	-0.57	-0.46	0.69	-023	030	0	0	0	0.71*	1					
0	-021	033	015	-0.62	022	-032	0	0.85**	0.71*	0.71*	0	0.50	0	1				
10	0.93**	0:49	031	036	0	.97	0.65	043	0.71*	0.71*	0.50	0.50	071*	-0.50	1			
Q	0.73*	0.95"	::960	-0.32	-0.73	0.46	01.0	0,49	-0.18	-0.18	-032	0.87*	094**	0.07	0.54	1		
Hd	-0:44	760	.8/10	-0.25	192	-020	-045	-0.85	0.11	0.11	190	-66.0	065	0.46	-038	0.54*	I	
Ш.	0.01	034	013	0.81	038	-006	-028	0.89	049	-0.49	026	-0.52	012	<u>.96</u>	-026	0.04	0.52	-

434

Table 8. Pearson correlation coefficients of monitoredparameters in samples (in cv. Amica)

	7.0	2		Dh	r c	"		3	20	C	7.0	2	č	Dh	r's	TBC	n c	Пини
	ZUAR	CUAR	LIAR	I UAR	CUAR	Z-IIAN	CUAN	CIAN	I UAN	NYN	7110	Cu0	010	L U0	0m	112	цц	IIII
ZnAR																		
Cuar	0.99**	Ţ																
	0.15	0	1															
4	02.0	014	061	-														
٨R	N7.N	110	100	-														
AR	-020	-020	026	0.86	1													
NA	0.49	0.57	-0.26	053	0.56	1												
NA	-030	-020	-0.85	-0.53	10.64	-027	1											
Z	-0.73	-0.61	-0.75	-0.36	0.16	0.04	0.64	1										
Z	-0.04	-0.19	086**	0.14	-0.18	-070	-0.46	-0.65	-									
NA	-032	-023	-0.36	0.44	0.81*	19.0	-0.09	064	-0.69	1								
0	-0:48	-045	-0.45	-0.54	-0.76	-074	0.85**	043	0.05	-0.43	1							
-	0.82^{*}	0.87	-0.40	-0.33	-0.53	039	030	-0.30	-0.38	-030	0	1						
	0.82*	0.87^{*}	-0.40	0 .33	-0.53	650	030	030	-0.38	-030	0	1	1					
	-033	-0.19	-0.80	-0.07	038	0.55	0,43	0.85**	-0.92	0.85**	0	0	0	-				
0	0.82^{*}	0.87"	6.40	-0.33	-0.53	650	030	-0.30	-0.38	-030	0	1**	1*	0	1			
C	0.70*	0.63	026	1E.0-	-0.75	-027	00	-0.76	0.45	-060	0.16	0.65	0.65	0.75*	065	1		
Hd	0.78	0.75	900	95.0-	-0.76	11:0-	0.12	-0.67	022	-0.79	0.14	0.81	0.81	-0.57	-0.81	160	I	
н.	0.41	-0.54	0.70	-0.02	-0.17	-0.86	-0.25	-0.31	0.93	-0.56	0.29	-0.62	-0.62	-0.73	-0.62	0.19	-0.04	1

	Zn_{AR}	CuAR	Cr_{AR}	Pb_{AR}	Cd_{AR}	Znan	CuAN	Cr_{AN}	Pb_{AN}	Cd_{AN}	Zn_0	Cllo	Cr_0	Pb_0	Cd_0	TPC	ЪН	Hum.
\mathbf{l}_{AR}																		
JAR	67.0-	-																
CrAR	11.0-	800	1															
AR	0.59	-0.45	-0.18	1														
1 _{AR}	0.64	-0.09	-0.66	0.80^{*}	1													
IAN	-0:43	0.75*	-0.28	61.0-	-027	1												
IAN	650-	0.75*	-0.06	060-	-048	0.97	I											
AN	0.32	0	-0.21	$0.89^{}$	0.87^{-1}	-048	-0,61	1										
NAN	-050	095**	-023	4.0	0.06	0.85**	.79*	0	1									
AN	Ŧ	0.73*	071*	-0.59	-0.64	0.43	059	-0.32	050	I								
o	1**	-0.73	-0.71	0.59	0.64	-043	-050	-0.32	-0.50	7	, -							
01	0.7]*	-0.72	-0.13	0.94	0.63	060-	860-	690	-0.71	-0.71	0.71*	1						
0	0	-0.62	046	-031	-0.72	-030	-0.14	-0.69	17.0-	0	0	0	-					
0	0.50	-0.66	020	-030	-032	0	0	-0.65	-0.50	-0.50	0.50	0	0.71*	1				
0	020-	000	029	0:30	0.32	0	0	0.65	020	020	-0.50	0	-0.71	Ţ	1			
Q	0.07	0.04	014	0.84*	0.65	-058	-063	0.94**	-0.07	-0.07	0.07	0.65	-0.54	-0.76	0.76*	1		
Ŧ	0.52	800	6.4	-0.15	070	0.55	036	-0.08	039	-0.52	0.52	-0.18	-0.37	670	-039	-041	-	
III.	0	0.62	-0.46	0.31	0.72	0:00	0.14	690	071	0	0	0	÷	-0.71	-0.71	0.54	0.37	-



	ZnAR	CuAR	Gr_{AR}	Pb_{AR}	CdAR	Zn_{AN}	CuAN	Cr_{AN}	Pban	CdAN	Zn_0	Cu_0	C_{I_0}	Pb_{O}	Cd_0	TPC	μd	Hum.
ZnAR	-																	
CLAR	7	-																
×	0.34	-036	I															
R	0.98	660-	049	1														
L R	0.77*	-0.78	002	0.78*	-													
N	-0.66	0.66	041	-0.38	-0.87	1												
NA	-0.18	0.16	080	-0.03	-1).46	0.82*	-											
Z	060-	_160	-0.51	-0.96	-1).86	0.58	0	1										
Z	-0.18	0.16	086**	-0.03	-0.46	0.82*	1	0	-									
Cdan	660-	"6 6 0	623	-0.95	-9.78	0.74*	0:30	0.85**	0:30	-								
0	0.40	-038	010	028	1.22	0	0	0	0	-0.43	1							
_	-038	038	040	-0.36	-0.86	0.87	0.71*	050	0.71*	0.43	050	1						
	-036	038	-0.20	-0.48	-0.76	0.41	0	0.71*	0	030	0,71	0.71	1					
-	0.92^{*}	160-	043	0.88	0.46	-0.41	0	-0.71	0	06.0-	0.71 [*]	0	0					
0	-0.40	038	-0.10	-0.28	0.22	0	0	0	0	0.43	Ţ	-0.5	-071	-0.71	1			
0	0.98**	860-	051	1**	0.75*	-0.55	0	-0.95	0	-0.94	031	0.32	-045	0.89**	031	1		
	-66.0	660-	022	-560	0.78	-0.74	-030	-0.85	050-	Ŧ	043	-0.43	-030	_060	-0.43	0.94	-	
Ë.	-029	027	014	-0.14	0.24	0.08	0.20	-0.14	0.20	0.35	76.0-	0.42	-078	-059	10.0-	-0.17	-035	-

Table 11. Pearson correlation coefficients of monitored parameters in samples (in cv. White Dry)

tion of lead was lower (0.25 mg/kg). According to the literature, during the polyphenols production the important role play not only stress factors as heavy metals intake, but also many others as e.g. variety, the date of harvest and storage conditions.

Our work was in coherence with the findings of Perna et al. (2012), Sharma et al. (2014) who indicated correlations between metal content in plants and content of polyphenols and the activity of antioxidative enzymes. In this paper relations among the observed heavy metals in soil, pH, humus and their accumulation in various varieties of onions were evaluated. Table 4 shows calculated bioaccumulation factor (BAF) for Cd and Pb. Obtained values of (BAF) suggest that onion is not an accumulator of heavy metals, what verify also another our findings that even though the soil contained relatively high content of Cd the limit in the onions was not exceed.

Statistical descriptions among parameters from analysed varieties of onion are showed in Tables 6-11. We have found a statistically significant correlation (P-value 0.05) between the total polyphenols and content of Pb in onion cv. Kamal (R=0.79), in cv. Karmen (R=0.71), in cv. Hector (R=0.75) and in cv. White Dry (R=0.89)R=0.89-11).

CONCLUSIONS

Soil is the entrance of the heavy metals into plants and subsequently into the food chain. The results of this research have shown that Pb is the main polluting factor in the soil in studied region. This study was focused on risk elements mentioned in legislative hygienic directions. Region - Klasov is located in the middle of Žitavská upland. Klasov is area without negative influences, emission sources (carbon). Measured higher contents of mobile forms of Pb could have connection with natural content of the particular rock environment. Based on noted increased contents of mobile forms of Pb, that exceeded the limit valid in Slovak Republic many times, we can conclude that the content of Pb is the main polluting factor of the soil in studied region.

In all sampling sites the lead content in onions was exceeded compared to EC 1881/2006. The higher concentrations of Pb in the onions according to the permissible values could be a health risk to consumers. The knowledge about the uptake of heavy metals by different cultivars of onion under the same conditions would by necessary.

ACKNOWLEDGMENTS

The work was supported by scientific grant VEGA 1/0290/14, VEGA 1/0308/14. This work was co-funded

by European Community under project no 26220220180 : Building Research Centre "AgroBioTech".

REFERENCES

Abdullahi, M.S., Uzait, A. and Okunola, O,J. (2008). Determination of some trace metal levels in onion leaves from irrigated farmlands on the bank of river Challawa, Nigeria. Afr J Biotechnol.,**7**,1526-1529.

Adeyeye, E. I. (2005). Distribution of major elements (Na, K, Ca, Mg) in the various anatomical parts of fadama crops in Ekiti state, Nigeria. Bull Chem Soc Ethiop., **19**, 175-183.

Amin, N., Hussain, A., Alamzeb, S. and Begum, S. (2013). Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children, District Mardan, Pakistan. Food Chem., **136**, 1515-1523.

Arya, S. K. and Mukherjee A. (2014). Sensitivity of Allium cepa and Vicia faba towards cadmium toxicity. J Soil Sci Plant Nutr., **14**, 447-458.

Behbahni, M., Abolhasani, J., Amini, M.M., Sadeghi, O., Omidi, F., Bagheri, A. and Salarian M. (2015). Application of mercapto ordered carbohydrate-derived porous carbons for trace detection of cadmium and copper ions in agricultural products. Food Chem., **173**, 1207-1212.

Bernaert, N., De Paepe, D., Bouten, Ch., De Clerq, H., Stewart, D., Van Bockstaele, E., De Loose, M. and Van Droogenbroeck, B. (2012). Antioxidant capacity, total phenolic and ascorbate contentas a function of the genetic diversity of leek (Allium ampeloprasum var. porrum). Food Chem., **134**,669-677.

Crystal, S., Lombard, K. A., Peffley, E. B. and Liu W. X. (2003). Genetic analysis of quercetin in onion (Allium cepa L.). Texas J Agric Nat Res., **16**, 24-28.

Chojnacka, K., Chojnacki, A., Góreck, H. and Górecki, H. (2005). Bioavailability of heavy metals from polluted soils to plants. Sci Total Environ.,**337**,175-182.

Diáz, J., Bernal, A., Pomar, F. and Merino, F. (2001). Induction of shikimate dehydrogenase and peroxidase in pepper (Capsicum annum L.) seedlings in response to copper stress and its relation to lignifications. Plant Sci.,**161**,179-188.

Eicholz, I., Huyskens-Keil, S., Keller, A., Ulrich, D., Kroh, L.W. and Rohn, S. (2011). UV-B-induced changes of volatile metabolites and phenolic compounds in blueberries (Vaccinium corymbosum L.). Food Chem., **126**, 60-64.

European Commission (EC) No. 1881/2006. Commision

Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. URL: http://eurlex.europa.eu/LexUriServ/ LexUriServ.do?uri=OJ:L:2006:364:0005:0024:EN:PDF (accessed 24/02/2015)

FC SR. Foodstuffs Codex of Slovak Republic, URL: http://www.potravinarstvo.com/pksr/2cast_pksr/10_hlava_kontaminanty_v_potravinach/2004_608%20%203.pdf (accessed 17/03/2015).

Fiala, K., Kobza, J., and Baran?íková, G. (1999). Záväzné metodiky rozborov pôd. 4iastkový monitorovací system-Pôda. Bratislava: VÚPoP, 199s ISBN 80-85361-55-8.

Fijalkowski, K., Kacprzak, M., Grobelak, A. and Placek, A. (2012). The influence of selected soil parameters on the mobility of heavy metals in soils. Inz Ochr Srodowiska **15**, 81-92.

Gebrekidan, A., Weldegebriel, Y., Hadera, A. and Van der Bruggen, B. (2013). Toxicological assessment of heavy metals accumulated in vegetables and fruits grown in Ginfel river near Sheba Tannery, Tigray, Northern Ethiopia. Ecotox Environ Safe., **95**, 171-178.

Kitata, R. B. and Chandravans, B. S. (2012). Concentration levels of major and trace metals in onion (Allium cepa L.) and irrigation water around Meki town and lake Ziway, Ethiopia. Bull Chem Soc Ethiop.,**26**,27-42.

Lachman, J., Pron?k, D., Hejtmánková, A., Pivec, V., and Faitová, K. (2003). Total polyphenol and main flavonoid antioxidants in different onion (Allium cepa L) varieties. Sci Hortic, **30**, 142-147.

Michalak, A. (2006). Phenolic compounds and their antioxidant activity in plants growing under heavy metal stress. Polish J Environ Stud., **15**, 523-530.

Moriarity, R. S., Harris, J. T., and Cox, R. D. (2014). Lead toxicity as an etiology for abdominal pain in the emergency department. J. Emerg Med., **46**, e35e38.

Nagajyoti, P. C., Lee, K. D., and Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a review. Environ Chem Lett.,**8**, 199-216.

Nikitin, V. and Fishman, V. Cn. (1969)

"Химия в сельском хозяйстве" .7,76-77.

Paul, S. (2006). Mineral and Trace Elements, Human Nutrition. Eleventh Edition, Elsevier Churchill Livingstone. Netherlands, 231-249.

Perna, A., Simonett, A., Intaglietta, I., Sof, A. and Gambacorta E. (2012). Metal content of southern Italy

honey of different botanical origins and its correlation with polyphenol content and antioxidant activity. IJFST,47,1909-1917.

Reilly, K., Valverde, J., Finn, L., Gaffney, M., Rai, D. K. and Brunton N. (2014). A note on the effectiveness of selenium supplementation of Irish-grown Allium crops. Irish Journal of Agricultural and Food Research,**53**,91-99.

Rivas-San Vicente, M. and Plasencia, J. (2011). Salicylic acid beyond defence: its role in plant growth and development.J Exp Bot., **62**, 3321-3338.

Salami, H. A., John, A. I. and Ekanem, A. U.(2012). The effect of aqueous preparation of Allium cepa (onion) and Allium sativa (garlic) on erythrocyte osmotic fragility in wistar rats: in vivo and in vitro studies. Niger J Physiol Sci., **27**, 029-034.

Saleem, M., Iqbal, J. and Sha, M. H. (2014). Non-carcinogenic and carcinogenic health risk assessment of selected metals in soil around a natural water reservoir, Pakistan. Ecotoxicology and Environmental Safety,**108**,42-51.

Sharma, N., Hundal G. S., Sharma, I. and Bhardway, R. (2014). 28-Homobrassinolide alters protein content and activities of glutathione-S-transferase and polyphenol oxidase in Raphanus sativus L. plants under heavy metal stress. Toxicol Int., **21**, 44-50.

Sherene, T. (2010). Mobility and transport of heavy metals in polluted soil environment.Biol Forum Int J., **2**,112-121.

Singh, S., Zacharias, M., Kalpana, S. and Mishra, S. (2012). Heavy metals accumulation and distribution pattern in different vegetable crops. JECE,**4**,170-177.

Sytar, O., Borankulova, A., Hemmerich, I., Rauh, C. and Smetanska, I. (2015). Effect of chlorocholine chlorid on phenolic acids accumulation and polyphenols formation of buckwheat plants. Biol Res., **47**,19.

Taghipour, H. and Mosaferi, M. (2013). Heavy metals in the Vegetables Collected from Production Sites. Health Promot Perspect., **3**,185-193.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G.and Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. J Soil Sci Plant Nutr., 10: 268-292.

Vishnu, N., Pankaj, S. K., Vipin, V. D. and Avinash, D. D. (2009). Antifertility activity of ethanolic extracts of Allium cepa Linn in rats. Int J PharmaTech Res., **1**,73-78.

Winkel-Shirley, B.,(2002). Biosynthesis of flavonoids and effects of stress. Curr Opin Plant Biol.,**5**, 218-223.

Yahaya, Y., Birnin Yauri, U. A., and Bagudo, B.U. (2010). Study of nutrient content variation in bulb and stalk of onions (Allium Sepa) cultivated in Aliero, Aliero, Kebbi State, Nigeria. Nig J Appl Sci.,**18**,83-84.

Ye, CH. L., Dai, D. H. and Hu, W. L. (2013). Antimicrobial and antioxidant activities of the essential oil from onion (Allium cepa L.). Food Control,**30**,48-53.

Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu. F. and Zhang, G. (2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. Environ Pollut.,**159**, 84-91.