

HEAVY METALS DETERMINATION IN EDIBLE WILD MUSHROOMS GROWING IN FORMER MINING AREA – SLOVAKIA: HEALTH RISK ASSESSMENT

Zuzana Záhorcová, Július Árvay, Martin Hauptvogel, Ján Tomáš, Ľuboš Harangozo

ABSTRACT

The aim of the paper is to assess a contamination level of forest substrates and aboveground parts of edible wild mushroom (*M. procera* (Scop.) Singer, *B. recitulatus* Schaeff., *C. cibarius* Fr., *S. grevillei* (Klotzsch) Singer, *A. campestris* L., *R. xerampelina* (Schaeff.) Fr., *L. salmonicolor* R. Heim & Leclair, *C. gibba* (Pers. Ex Fr.) Kumm., *X. chrysenteron* (Bull.) Quéf., *M. oreades* (Bolton) Fr.; n = 70) by heavy metals (Cd, Cu, Pb and Zn). The studied location was a broader surroundings of the historical mining and metal processing area of Banská Bystrica. The collected mushroom samples and underlying substrate samples were analysed using Flame Atomic Absorption Spectrophotometry and Flame Absorption Spectrophotometry with graphite furnace. Bioaccumulation factors (BAF) for individual species and their anatomical parts were calculated from the results obtained. In order to assess a health risk resulting from regular consumption of the mushrooms, provisional tolerable weekly intake (PTWI) was calculated from the results of the monitored heavy metal concentration. Limit values for the studied contaminants (Cd: 0.49 mg.kg⁻¹ and Pb: 1.75 mg.kg⁻¹ for an individual with an average weight of 70 kg) are defined by FAO and WHO. Our results indicate that *S. grevillei* has a high bioaccumulation ability of Cd. It was confirmed by bioaccumulation factors (BAF_H = 3.47 and BAF_{RFB} = 2.30). The PTWI_{Cd} value was exceeded by 4.11 times. A similar situation occurred in the case of Pb where the highest bioaccumulation factor (BAF_H = 0.24 and BAF_{RFB} = 0.19) was also recorded in the samples of *S. grevillei* and the PTWI_{Pb} value was exceeded by 1.35 times. In general, it can be stated that a consumption of edible wild mushrooms represent a relatively small risk of negative impact on the health of consumers.

Keywords: edible wild mushroom; heavy metal; contamination; bioaccumulation; health risk assessment; Slovakia

INTRODUCTION

Heavy metals are ubiquitous environmental components, the origin of which is natural or anthropogenic (Jiang et al., 2006; Feng et al., 2003). Environmental contamination with heavy metals is increasingly coming to the fore and it is one of the most serious problems of modern society nowadays. Their riskiness arise from the substantial persistence, toxicity and ability to bioaccumulate into environmental components and consequently into the food chain (Burgess et al., 2015; Douay et al., 2013; Roman and Popiela, 2011). Long-time industrialization of society and subsequent rapid urbanization lead to an increased amount of xenobiotics and thus also heavy metals in the urban environment (Szolnoki et al., 2013; Luo et al., 2012) but also in non-urban areas (Luo et al., 2014), which represents a significant risk to the global ecosystem and the health of human populations (Siciliano et al., 2009).

Some heavy metals (Hg, Cd, Cr, Ni, Pb), arsenic and essential trace elements (Cu, Zn) pose a significant risk to the quality of the environment, which influences on the health of the human population (Alloway, 2013; Jomová and Valko, 2011). They enter the environment via natural activities (volcanic activity, weathering, etc.) and anthropogenic activities (e. g. extraction and processing of

minerals, combustion of fossil fuels and waste, etc.). (Hooda, 2010). Cadmium and lead belong to non-essential trace elements and are classified as toxic metals that are harmful to plants, animals and human body even at very low concentrations. They are introduced to the body mostly by inhalation and/or resorption and consequently damage individual systems of the human body (Timoracká et al., 2011; Silva et al., 2003). However, high amounts of the heavy metals can get into the body also by food. Zinc and copper are classified as essential trace elements (Wuan and Okieimen, 2011; John et al., 2010), however they can be toxic to humans in higher concentrations (Licata et al., 2012). They participate in the regulation of various physiological functions, including inflammatory and oxidative processes (Mocchegiani et al., 2012; Malavolta et al., 2010). For example, increased concentration of copper has adverse effects on the activity of the central nervous system and certain physiological processes (Grandner et al., 2013; Cappuccio et al., 2011).

Edible wild mushrooms represent a natural part of forest ecosystems and play an important role in the cyclic pathways of elements and organic matter (Petkovšek and Pokorný, 2013). They are able, together with micro-organisms, to biodegrade substrate and thus utilize waste from agricultural production and/or human activities

(Ouzouni et al., 2009). Some mushroom species are considered as a delicacy in many countries, including countries of Central and Eastern Europe. Fruiting bodies of the mushrooms are popular not only for their texture and flavor, but also for their nutritional properties (Cheung, 2013; Kalač, 2013). They are characterized by low energy value and high concentration of essential biologically valuable elements, specific β -glucans and antioxidant substances (Kalač, 2013; Kalač, 2009). Moreover, they provide a valuable source of fiber, vitamins and minerals such as thiamin, riboflavin, vitamin D, potassium, phosphorus, iron and calcium (Wang et al., 2014; Falandysz and Borovicka, 2013). It has been known for long time that mushrooms are able to accumulate large amounts of heavy metals (Zhang et al., 2008), what makes them ideal for biomonitoring of environmental pollution – particularly contamination of forest ecosystems (Radulescu et al., 2010). There are many factors that influence the presence of metals in mushrooms, for example climate, environmental conditions and concentration of macromolecules in the cell wall of each specific species (Ostos et al., 2015). Studies of the interaction of heavy metals in the system soil/substrate – mycelium showed that mushrooms have several fold higher bioaccumulation capacity to uptake xenobiotics – heavy metals from the substrate compared to higher plants (intake from the atmosphere is negligible) (Falandysz, 2015; Saba et al., 2015; Zhu et al., 2011; Gursoy et al., 2009).

Under natural conditions, the concentration of heavy metals in certain species of edible mushrooms can be higher, even if the soil contamination level is low (Falandysz et al., 2003). The highest concentrations of trace elements are mostly found in the hymenophore, lower values are in the spores and the lowest values are in

the stem (Árvay et al., 2015a; Krasínska and Falandysz, 2015; Falandysz et al., 2007; Alonso et al., 2003).

The aim of the paper is to determine the level of transition of the studied heavy metals (Cd, Cu, Pb and Zn) from the substrate into the aboveground parts of edible macroscopic mushrooms collected in the broader area of Banská Bystrica, which is characterized by historic mining and metalworking activity (mining and processing of ore rich in precious metals, copper, lead and associated components: mercury, cadmium, etc.). Bioaccumulation factors (BAF) for individual anatomical parts of mushrooms (hymenophore - H and rest of fruit bodies - RFB) were calculated. Due to the popularity of collecting wild edible mushrooms in Central Europe (Árvay et al., 2014; Kalač, 2009), a health risk arising from their regular consumption was investigated.

MATERIAL AND METHODOLOGY

Study area, sampling and pre-analytical procedure

For the needs of our work, 10 species of the most commonly collected wild mushrooms, which generally represent the most frequently collected mushrooms in Slovakia were chosen. The samples of edible wild mushrooms and substrate (N = 70) were collected in 2014 in the broader area of Banská Bystrica, in the cadastral areas of villages Ľubietová, Radvaň, Malachov, Selce, Nemce, Hrochoť and Podkonice that are characteristic by historical mining and metalworking activity. Identification of the sampling points was made using GPS coordinates (Figure 1). The concentration of heavy metals (Cd, Cu, Pb and Zn) was studied in individual parts of edible wild growing mushrooms. Studied species and their respective sampling frequencies are included in Table 1.

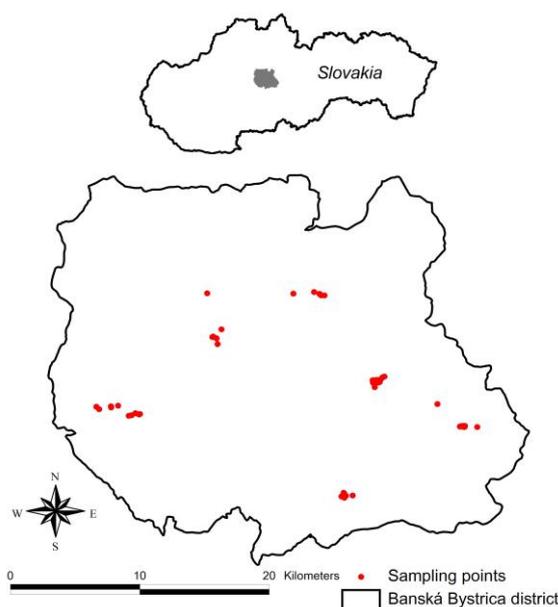


Figure 1 Map of the studied area with sampling points.

Table 1 The heavy metals concentration (mg.kg⁻¹ DM) in substrate.

Species*	N	Cd	Pb	Cu	Zn
		Median ±SD (range)			
<i>Macrolepiota procera</i> (Scop.) Singer	11	2.43 ±0.80 (0.58 – 3.66)	45.3 ±15.7 (28.5 – 88.8)	23.3 ±16.0 (10.0 – 66.9)	97.8 ±31.0 (58.6 – 155)
<i>Boletus reticulatus</i> Schaeff.	9	2.89 ±1.60 (1.76 – 6.94)	49.4 ±12.1 (36.6 – 76.6)	19.4 ±9.0 (11.6 – 38.5)	122 ±66.9 (59.4 – 278)
<i>Cantharellus cibarius</i> Fr.	3	2.68 ±0.60 (2.24 – 3.37)	47.2 ±3.15 (43.7 – 49.8)	20.3 ±8.02 (13.0 – 28.9)	112 ±24.1 (95.2 – 139)
<i>Suillus grevillei</i> (Klotzsch) Singer	11	2.49 ±0.68 (1.66 – 3.51)	41.9 ±16.2 (25.3 – 75.1)	18.1 ±9.91 (3.10 – 38.8)	41.9 ±16.2 (25.3 – 75.1)
<i>Agaricus campestris</i> L.	3	2.74 ±0.19 (2.53 – 2.90)	49.8 ±25.6 (34.4 – 79.3)	31.1 ±17.0 (14.8 – 48.7)	155 ±65.5 (97.0 – 226)
<i>Russula xerampelina</i> (Schaeff.) Fr.	8	2.44 ±0.54 (1.72 – 3.40)	58.2 ±14.5 (41.4 – 76.6)	27.0 ±11.9 (11.3 – 48.1)	58.2 ±14.5 (41.4 – 76.6)
<i>Lactarius salmonicolor</i> R. Heim & Leclair	10	2.82 ±0.41 (2.25 – 3.50)	61.1 ±23.9 (42.7 – 113)	23.2 ±8.84 (13.0 – 43.1)	101 ±24.4 (70.7 – 141)
<i>Clitocybe gibba</i> (Pers. Ex Fr.) Kumm.	3	2.52 ±0.13 (2.34 – 2.66)	43.5 ±4.65 (37.8 – 49.2)	19.8 ±11.7 (11.2 – 36.4)	108 ±28.7 (67.9 – 131)
<i>Xerocomus chrysenteron</i> (Bull.) Quél.	7	2.03 ±0.38 (1.37 – 2.38)	39.3 ±5.23 (31.2 – 47.1)	18.7 ±6.49 (8.40 – 25.8)	39.3 ±5.23 (31.2 – 47.1)
<i>Marasmius oreades</i> (Bolton) Fr.	5	2.22 ±0.43 (1.81 – 2.94)	59.1 ±11.5 (44.1 – 73.6)	25.5 ±10.1 (16.2 – 38.6)	144 ±58.9 (84.9 – 241)

N, number of samples; SD, standard deviation; *Index fungorum (2015)

Organic and inorganic debris was removed mechanically by ceramic knife and the cap (hymenophore) was separated from the rest of fruit body immediately after collecting of the mushroom samples. Later, the samples were sliced and dried at 45 °C to constant weight. The dried samples were homogenized in a porcelain mortar and then stored in polyethylene bags. After the collection of the mushroom samples, substrate samples were taken from the same spot to a depth of 10 cm. In the laboratory, the substrate samples were dried to a constant weight, and afterwards they were sieved through a sieve with mesh width of 2 mm.

One gram (1 g.) of dried mushroom samples (accuracy to 4 decimal places) were mineralized by 5 cm³ of concentrated HNO₃ (Merck, Germany) and the same volume of deionized water using microwave mineralization system in MARS X-press 5 (CEM, USA). Afterwards, the sample was filtered through filter paper 390 Filtrak (Munktell, Germany) and filled with deionized water to 50 cm³. The substrate samples were mineralized the same way as the mushroom samples in the mixtures of HNO₃ and HCl (Merck, Germany) in the ratio 1:1. After the mineralization, the digest was filtered through filter paper 390 Filtrak (Munktell, Germany) and diluted with deionized water to a total volume of 100 cm³ (Árvay et al., 2015b; Árvay et al., 2014).

Analytical procedure

Quantitative determination of the concentration of the studied trace elements (Cd, Cu, Pb, Zn) was carried out in

the mineralized samples by flame atomic absorption spectrometry (F-AAS) in Varian AA 240 FS apparatus (Varian, Australia), by method published in Árvay et al. (2014).

Statistical analysis and risk assessment

All data on the concentration of the studied contaminants in the samples were processed by descriptive statistical analysis at the level of the minimum and maximum values, median values and standard deviation in Statistica 12 software (StatSoft, USA).

Due to the popularity of the collection and subsequent consumption of edible wild mushrooms in Slovakia (Árvay et al., 2015a; Árvay et al., 2015b; Árvay et al., 2014; Kalač, 2009), tolerable weekly intake (PTWI) was calculated, based on the data obtained on the concentration of the studied heavy metals, for a standardized person weighing 70 kg with a consumption of 300 g of fresh edible wild mushrooms per day. The parameter is defined by FAO/WHO (1993) for cadmium and lead separately. The value for cadmium is 0.007 mg.kg⁻¹ of body weight of a consumer. The value for lead is 0.025 mg.kg⁻¹ (JECFA, 2010; WHO, 1993). The legislation does not state PTWI values for the zinc and copper. Due to the high water concentration (which is dependent on weather conditions), generally accepted value of 90% was used for conversion of the water concentration in the mushroom samples (Kalač, 2009).

RESULTS AND DISCUSSION

Table 2 The heavy metals concentration in hymenophore (mg.kg⁻¹ DM) and hymenophore and rest of fruit bodies bioaccumulation factors.

Species		Cd	Pb	Cu	Zn
		Median ±SD (range)			
<i>Macrolepiota procera</i> (Scop.) Singer	H	3.98 ±6.48 (0.48-22.9)	6.46 ±3.38 (2.45-13.2)	81.1 ±56.4 (23.7-207)	106 ±63.6 (42.3-247)
	BAF _H	1.64	0.14	3.48	1.08
	BAF _{RFB}	1.34	0.11	2.44	0.83
<i>Boletus reticulatus</i> Schaeff.	H	5.08 ±7.14 (0.66-21.9)	6.58 ±3.63 (2.32-15.0)	57.5 ±34.3 (23.6-122)	226 ±157 (86.9-585)
	BAF _H	1.76	0.13	2.97	1.86
	BAF _{RFB}	1.44	0.11	2.21	1.51
<i>Cantharellus cibarius</i> Fr.	H	0.56 ±0.20 (0.39-0.78)	4.07 ±1.32 (2.55-4.90)	52.1 ±6.57 (47.5-59.6)	75.3 ±3.79 (71.6-79.2)
	BAF _H	0.21	0.09	2.56	0.67
	BAF _{RFB}	0.07	0.06	1.80	0.52
<i>Suillus grevillei</i> (Klotzsch) Singer	H	8.64 ±9.87 (1.72-29.7)	10.1 ±10.0 (1.33-30.0)	42.2 ±36.1 (12.8-138)	118 ±35.2 (71.7-174)
	BAF _H	3.47	0.24	2.33	1.35
	BAF _{RFB}	2.30	0.19	1.69	1.09
<i>Agaricus campestris</i> L.	H	1.44 ±1.12 (0.69-2.72)	6.20 ±5.08 (2.73-12.0)	43.1 ±20.6 (21.3-62.1)	113 ±51.8 (69.7-170)
	BAF _H	0.52	0.12	1.39	0.73
	BAF _{RFB}	0.41	0.09	1.25	0.51
<i>Russula xerampelina</i> (Schaeff.) Fr.	H	2.97 ±3.09 (0.86-10.2)	6.02 ±5.11 (0.97-13.1)	43.8 ±25.3 (15.1-96.5)	93.9 ±40.0 (51.9-182)
	BAF _H	1.22	0.10	1.62	0.84
	BAF _{RFB}	0.83	0.07	0.97	0.57
<i>Lactarius salmonicolor</i> R. Heim & Leclair	H	1.11 ±1.01 (0.50-3.47)	3.17 ±1.08 (1.50-5.67)	15.7 ±7.22 (8.30-31.8)	184 ±132 (45.6-419)
	BAF _H	0.39	0.05	0.67	1.83
	BAF _{RFB}	0.34	0.04	0.46	1.16
<i>Clitocybe gibba</i> (Pers. Ex Fr.) Kumm.	H	5.29 ±5.64 (1.91-11.8)	2.93 ±0.88 (1.93-3.62)	49.6 ±12.6 (37.9-62.9)	131 ±44.7 (83.1-171)
	BAF _H	2.10	0.07	2.50	1.21
	BAF _{RFB}	1.73	0.05	1.99	1.04
<i>Xerocomus chrysenteron</i> (Bull.) Quél.	H	1.84 ±0.78 (0.67-3.22)	6.77 ±3.76 (2.85-12.0)	35.8 ±15.7 (17.5-63.6)	177 ±132 (98.5-448)
	BAF _H	0.90	0.17	1.91	2.10
	BAF _{RFB}	0.71	0.14	1.09	1.61
<i>Marasmius oreades</i> (Bolton) Fr.	H	2.45 ±1.14 (1.08-3.86)	6.93 ±5.86 (1.81-16.9)	34.3 ±36.8 (4.59-96.0)	99.2 ±29.9 (72.6-145)
	BAF _H	1.10	0.12	1.35	0.69
	BAF _{RFB}	0.95	0.08	0.92	0.61

SD, standard deviation; H, hymenophore; BAF_H, bioaccumulation factor in hymenophore; BAF_{RFB}, bioaccumulation factor in rest of fruit bodies.

Heavy metals in the substrate samples

All concentrations of the studied contaminants in the samples of substrates and edible wild mushrooms are given per dry matter (DM). The concentrations of the studied contaminants in the substrate represent an important factor that influences the bioaccumulation ability of individual species of edible wild mushrooms. Therefore, a variable level of translocation of heavy metals into macroscopic mushrooms can be assumed (Chudzyński *et al.*, 2011). The total concentration of the contaminants in the substrate varied within wide ranges (Table 1). The total cadmium concentration in the substrate samples (N = 70) ranged from 0.58 to 6.94

mg.kg⁻¹ DM, with the highest concentrations (6.94 mg.kg⁻¹ DM) recorded in the substrate samples of *B. reticulatus* (N = 9). The total concentration of lead in the substrate samples (N= 70) ranged between 25.3 – 113 mg.kg⁻¹ DM and the highest concentration (113 mg.kg⁻¹ DM) was recorded in the substrate samples of *L. salmonicolor* (N = 10). The copper concentration in the samples (N = 70) ranged between 3.10 – 66.9 mg.kg⁻¹ DM. The highest concentration (66.9 mg.kg⁻¹ DM) was recorded in the substrate samples of *M. procera* (N = 11). The last studied element was zinc, the concentration of which ranged from 25.3 – 278 mg.kg⁻¹ DM in all samples, with the highest concentrations (278 mg.kg⁻¹) recorded in the substrate

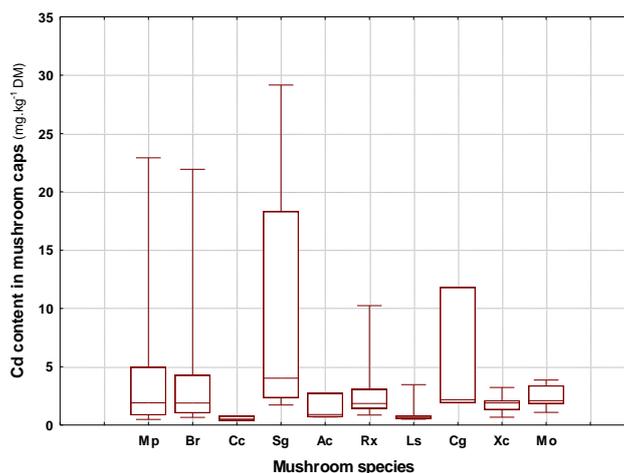


Figure 2 Range (min. – max.) and median, upper and lower quantile values of the cadmium concentration in the caps (mg.kg^{-1} DM) of individual species of edible wild mushrooms. **MP**, *M. procera*; **BR**, *B. recitulatus*; **CC**, *C. cibarius*; **SG**, *S. grevillei*; **AC**, *A. campestris*; **RX**, *R. xerampelina*; **LS**, *almonicolor*; **CG**, *C. gibba*; **XC**, *X. chrysenteron*; **MO**, *M. oreades*.

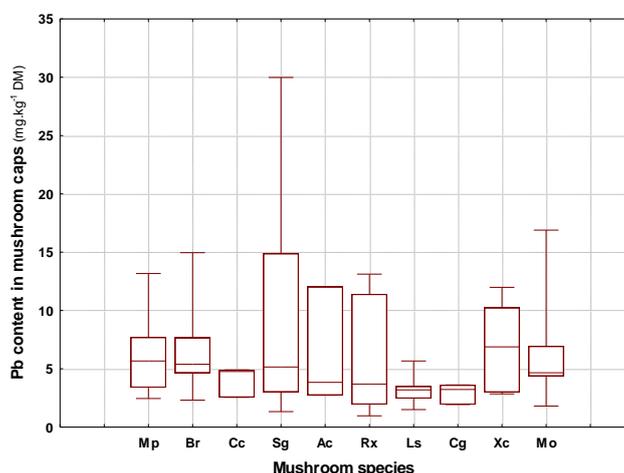


Figure 3 Range (min. – max.) and median, upper and lower quantile values of the lead concentration in the caps (mg.kg^{-1} DM) of individual species of edible wild mushrooms. **MP**, *M. procera*; **BR**, *B. recitulatus*; **CC**, *C. cibarius*; **SG**, *S. grevillei*; **AC**, *A. campestris*; **RX**, *R. xerampelina*; **LS**, *L. salmonicolor*; **CG**, *C. gibba*; **XC**, *X. chrysenteron*; **MO**, *M. oreades*.

samples of *B. recitulatus* ($N = 9$). High variability of the zinc concentration in the substrate indicates significant heterogeneity of the zinc concentration in the studied sites.

Heavy metals in mushroom samples

Macroscopic mushrooms are considered to be an important bioaccumulator of xenobiotics (especially heavy metals) (Árvay *et al.*, 2015a; Islam *et al.*, 2014), which was reflected in the concentration of the contaminants in individual anatomical parts of the studied mushroom species. The highest concentration of cadmium was recorded in the samples of *S. grevillei*, where the values in the hymenophore ranged from $8.64 \pm 9.87 \text{ mg.kg}^{-1}$ DM (Figure 2). The ability of the species to bioaccumulate cadmium is the highest among all species ($\text{BAF}_H = 3.47$ and $\text{BAF}_{RFB} = 2.30$). It was confirmed by the findings of Árvay *et al.*, (2014). The cadmium concentration in the

hymenophore of individual species was in the following order: *S. grevillei* > *C. gibba* > *B. recitulatus* > *M. procera* > *R. xerampelina* > *M. oreades* > *X. chrysenteron* > *A. campestris* > *L. salmonicolor* > *C. cibarius*.

Similarly, in the case of the lead concentration the maximum values were recorded in the samples of *S. grevillei* ($10.1 \pm 10.0 \text{ mg.kg}^{-1}$ DM, 1.33 – 30.0 mg.kg^{-1} DM) (Figure 3). This species had also the highest bioaccumulation factor $\text{BAF}_H = 0.24$ and $\text{BAF}_{RFB} = 0.19$. The lead concentration in the hymenophore of individual species was in the following order: *S. grevillei* > *M. oreades* > *X. chrysenteron* > *B. recitulatus* > *M. procera* > *A. campestris* > *R. xerampelina* > *C. cibarius* > *L. salmonicolor* > *C. gibba*.

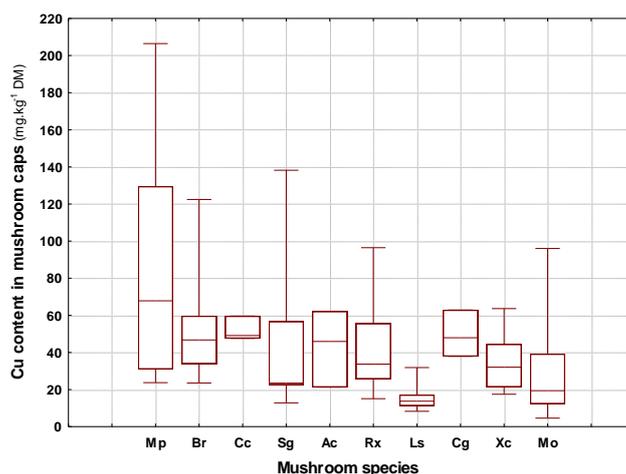


Figure 4 Range (min. – max.) and median, upper and lower quantile values of the copper concentration in the caps (mg.kg^{-1} DM) of individual species of edible wild mushrooms. **MP**, *M. procera*; **BR**, *B. recitulatus*; **CC**, *C. cibarius*; **SG**, *S. grevillei*; **AC**, *A. campestris*; **RX**, *R. xerampelina*; **LS**, *L. salmonicolor*; **CG**, *C. gibba*; **XC**, *X. chrysenteron*; **MO**, *M. oreades*.

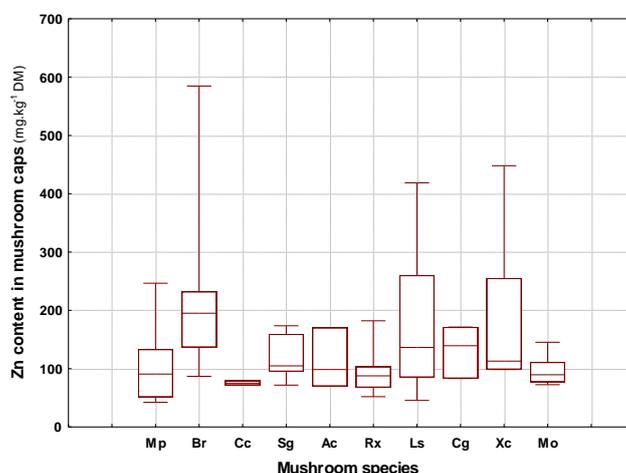


Figure 5 Range (min. – max.) and median, upper and lower quantile values of the zinc concentration in the caps (mg.kg^{-1} DM) of individual species of edible wild mushrooms. **MP**, *M. procera*; **BR**, *B. recitulatus*; **CC**, *C. cibarius*; **SG**, *S. grevillei*; **AC**, *A. campestris*; **RX**, *R. xerampelina*; **LS**, *L. salmonicolor*; **CG**, *C. gibba*; **XC**, *X. chrysenteron*; **MO**, *M. oreades*.

Although copper is considered an essential trace element for almost all organisms, its high levels may have a negative impact on physiological processes in the body (Árvay *et al.*, 2014; Wuana and Okieimen, 2011). The highest copper concentration in the samples was recorded in the hymenophore samples of *A. procera* (Scop.) Singer, where the copper concentration was $81.1 \pm 56.4 \text{ mg.kg}^{-1}$ DM ($23.7 - 207 \text{ mg.kg}^{-1}$ DM) (Figure 4). This species had the highest ability to bioaccumulate copper among all species tested ($\text{BAF}_H = 3.48$ and $\text{BAF}_{RFB} = 2.44$). The concentration of copper in individual species was in the following order: *M. procera* > *B. recitulatus* > *C. cibarius* > *C. gibba* > *R. xerampelina* > *A. campestris* > *S. grevillei* > *X. chrysenteron* > *M. oreades* > *L. salmonicolor*.

Although copper is considered an essential trace element for almost all organisms, its high levels may have a negative impact on physiological processes in the body (Árvay *et al.*, 2014; Wuana and Okieimen, 2011). The highest copper concentration in the samples was recorded in the hymenophore samples of *M. procera*, where the copper concentration was $81.1 \pm 56.4 \text{ mg.kg}^{-1}$ DM

($23.7 - 207 \text{ mg.kg}^{-1}$ DM) (Figure 4). This species had the highest ability to bioaccumulate copper among all species tested ($\text{BAF}_H = 3.48$ and $\text{BAF}_{RFB} = 2.44$). The concentration of copper in individual species was in the following order: *M. procera* > *B. recitulatus* > *C. cibarius* > *C. gibba* > *R. xerampelina* > *A. campestris* > *S. grevillei* > *X. chrysenteron* > *M. oreades* > *L. salmonicolor*.

Zinc, like copper, is considered an essential trace element. Individual mushroom species showed significant ability to bioaccumulate zinc, with higher accumulation values on locations with lowest zinc concentration in substrate. The highest zinc concentration was recorded in the samples of *B. recitulatus* Schaeff., with the concentration around $226 \pm 157 \text{ mg.kg}^{-1}$ DM ($86.9 - 585 \text{ mg.kg}^{-1}$ DM) (Figure 5). The highest ability to bioaccumulate zinc was recorded in the samples of *X. chrysenteron* ($\text{BAF}_H = 2.10$ and $\text{BAF}_{RFB} = 1.61$). The zinc concentration in the hymenophore of individual mushroom species was in the following order: *B. recitulatus* > *L. salmonicolor* > *X. chrysenteron* > *C. gibba* > *S. grevillei* >

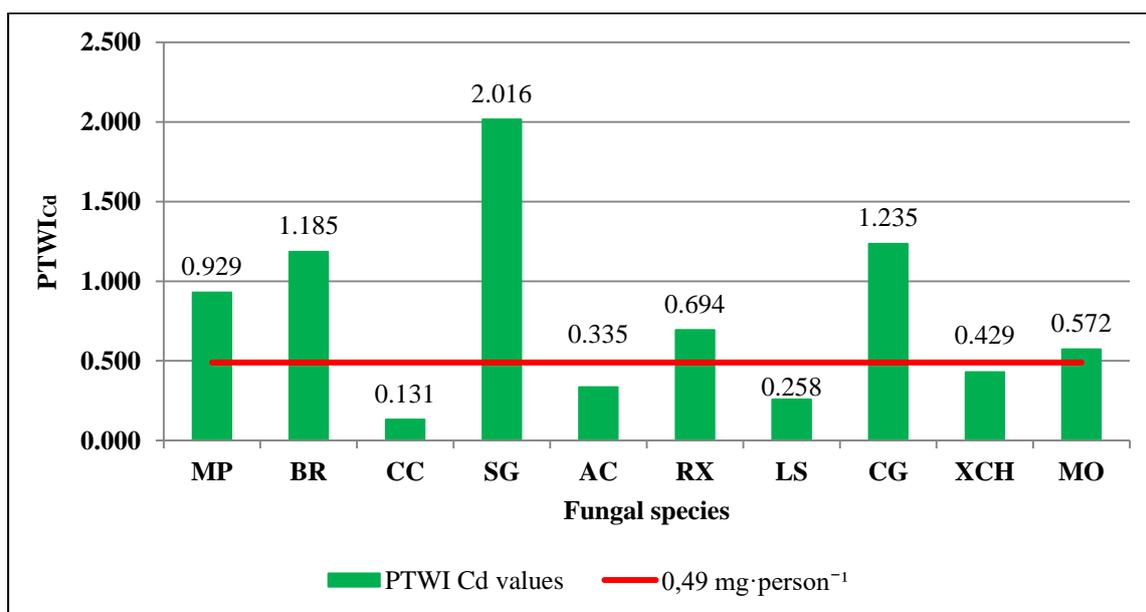


Figure 6 The comparison of weekly intake of cadmium with 300 g of various mushroom species per day to PTWI_{Cd} limit for adult person (0.490 mg.kg⁻¹). *MP*, *M. procera*; *BR*, *B. recitulatus*; *CC*, *C. cibarius*; *SG*, *S. grevillei*; *AC*, *A. campestris*; *RX*, *R. xerampelina*; *LS*, *L. salmonicolor*; *CG*, *C. gibba*; *XC*, *X. chrysenteron*; *MO*, *M. oreades*.

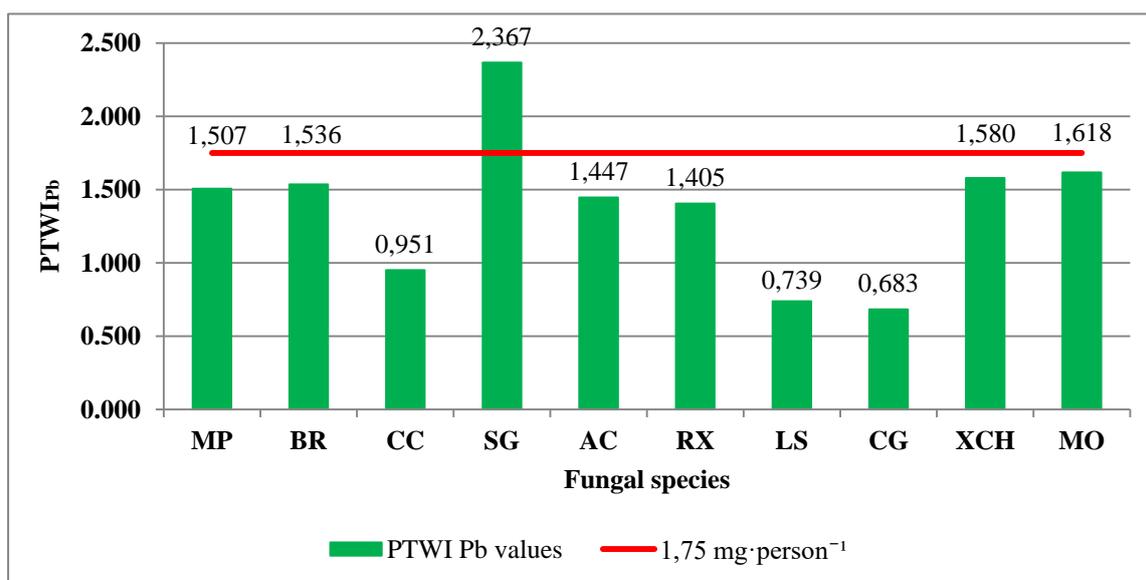


Figure 7 The comparison of weekly intake of lead with 300 g of various mushroom species per day to PTWI_{Pb} limit for adult person (1.750 mg.kg⁻¹). *MP*, *M. procera*; *BR*, *B. recitulatus*; *CC*, *C. cibarius*; *SG*, *S. grevillei*; *AC*, *A. campestris*; *RX*, *R. xerampelina*; *LS*, *L. salmonicolor*; *CG*, *C. gibba*; *XC*, *X. chrysenteron*; *MO*, *M. oreades*.

A. campestris L. > *M. procera* > *M. oreades* > *R. xerampelina* > *C. cibarius*.

All data on the concentration of the studied contaminants in the substrate and individual anatomical parts of mushrooms are shown in Tables 1 and 2.

Health risk assessment

Provisional tolerable weekly intake (PTWI) is a value set by the FAO and WHO (JECFA, 2010) and defined as the maximum quantity of contaminants that may a consumer weighing 70 kg intake per one week. We assumed that the person consumes 300 g fresh mushrooms or 30 g of dried mushrooms per day. The legislation states the following

PTWI indices for individual heavy metals: Cd: 0.007 mg.kg⁻¹ of bodyweight (0.490 mg Cd.person⁻¹) and Pb: 0.025 mg.kg⁻¹ of bodyweight (1.750 mg Pb.person⁻¹). For the evaluation of the PTWI values of the studied contaminants, their median concentration in the hymenophore were used. The median values were multiplied by the weight of 70 kg. The result was the maximum amount of the contaminants that a consumer can intake per week (Cd: 0.49 mg and Pb: 1.75 mg). The PTWI_{Cd} values were exceeded in several samples. The highest exceedance was recorded in the samples of *S. grevillei* (4.11 fold). In the case of lead, the PTWI_{Pb} values

were exceeded only in the samples of *S. grevillei* (1.35 fold). It indicates a potential risk of intoxication, since it is often collected and consumed species, characterized by significant bioaccumulation ability. The comparison of the calculated $PTWI_{Cd}$ and $PTWI_{Pb}$ values with the defined limit values are shown in Figures 6 and 7.

CONCLUSION

The aim of this study was to assess the contamination level of the substrate and the aboveground part of the edible wild mushroom species collected in the surrounding area of Banská Bystrica characterized by significant mining activity in the past. Macroscopic mushrooms represent a part of the environment that is sensitive to the increased amount of contaminants, which is reflected by their increased concentration in the aboveground parts of wild mushrooms. The results showed that the health risk resulting from the consumption of the studied mushroom species decreases as follows: *M. procera* (Cd) > *R. xerampelina* (Cd) > *S. grevillei* (Cd, Pb) > *B. recitulatus* (Cd, Pb) > *C. gibba* (Cd) > *M. oreades* (Cd, Pb) > *X. chrysenteron* (Cd, Pb) > *A. campestris* (Pb) > *L. salmonicolor* > *C. cibarius*.

REFERENCES

- Alloway, B. J. 2013. Introduction. *Alloway, B. J. (Ed.), Environmental Pollution. Heavy Metals in Soils*. Springer, Netherlands, p. 3-9. http://dx.doi.org/10.1007/978-94-007-4470-7_1
- Alonso, J., Garcia, M. A., Perez-Lopez, M., Melgar, M. J. 2003. The concentrations and bioconcentration factors of copper and zinc in edible mushrooms. *Archives of Environmental Contamination and Toxicology*, vol. 44, no. 2, p. 180-188. <http://dx.doi.org/10.1007/s00244-002-2051-0>
- Árvay, J., Tomáš, J., Hauptvogel, M., Kopernická, M., Kováčik, A., Bajčan, D., Massanyi, P. 2014. Contamination of wild-grown edible mushrooms by heavy metals in a former mercury-mining area. *Journal of environmental science and health part B: pesticides, food contaminants and agricultural wastes*, vol. 49, no. 11, p. 815-827. <http://dx.doi.org/10.1080/03601234.2014.938550>
- Árvay, J., Tomáš, J., Hauptvogel, M., Massányi, P., Harangozo, L., Tóth, T., Stanovič, R., Bryndzová, Š., Bumbalová, M. 2015a. Human exposure to heavy metals and possible public health risks via consumption of wild edible mushrooms from Slovak Paradise National Park, Slovakia. *J. Environ. Sci. Health pt. B.*, vol. 50, p. 838-848. <http://dx.doi.org/10.1080/03601234.2015.1058107>
- Árvay, J., Záhorcová, Z., Tomáš, J., Hauptvogel, M., Stanovič, R., Harangozo, L. 2015b. Mercury in edible wild-grown mushrooms from historical mining area-Slovakia: bioaccumulation and risk assessment. *J. Microbiol. Biotech. Food Sci.*, vol. 4, special issue 3, p. 1-4. <http://dx.doi.org/10.15414/jmbfs.2015.4.special3.1-4>
- Burges, A., Epelde, L., Garbisu, C. 2015. Impact of repeated single-metal and multimetal pollution events on soil quality. *Chemosphere*, vol. 120, p. 8-15. <http://dx.doi.org/10.1016/j.chemosphere.2014.05.037>
- Cappuccio, F. P., Cooper, D., D'Elia, L., Strazzullo, P., Miller, M. A. 2011. Sleep duration predicts cardiovascular outcomes: a systematic review and meta-analysis of prospective studies. *Eur. Heart J.*, vol. 32, p. 1484-1492. <http://dx.doi.org/10.1093/eurheartj/ehr007>
- Douay, F., Pelfrène, A., Planque, J., Fourrier, H., Richard, A., Roussel, H., Girondelot, B. 2013. Assessment of potential health risk for inhabitants living near a former lead smelter. Part 1: metal concentrations in soils, agricultural crops, and home grown vegetables. *Environ. Monit. Assess.*, vol. 185, no. 5, p. 3665-3680. <http://dx.doi.org/10.1007/s10661-012-2818-3>
- Falandysz, J., Borovička, J. 2013. Macro and trace mineral constituents and radionuclides in mushrooms: Health benefits and risks. *Applied Microbiology and Biotechnology*, vol. 97, no. 2, p. 477-501. <http://dx.doi.org/10.1007/s00253-012-4552-8>
- Falandysz, J., Kawano, M., Swieczkowski, A., Brzostowski, A., Dadej, M. 2003. Total mercury in wild - grown higher mushrooms and underlying soil from Wdzydze Landscape Park, Northern Poland. *Food Chemistry*, vol. 81, no. 1, p. 21-26. [http://dx.doi.org/10.1016/s0308-8146\(02\)00344-8](http://dx.doi.org/10.1016/s0308-8146(02)00344-8)
- Falandysz, J., Kunito, T., Kubota, R., Bielawski, L., Mazur, A., Falandysz, J. J. K., Tanabe, S. 2007. Selected elements in Brown Birch Scaber Stalk *Leccinum scabrum*. *Journal of Environmental Science and Health, Part A*, vol. 42, no. 14, p. 2081-2088. <http://dx.doi.org/10.1080/10934520701626993>
- Falandysz, J., Zhang, J., Wang, Y. Z., Saba, M., Krasinska, G., Wiejak, A., Li, T. 2015. Evaluation of Mercury Contamination in Fungi *Boletus* species from Latosols, Lateritic red earths, and red and yellow earths in the Circum-Pacific mercuriferous belt of Southwestern China. *PLoS One*, vol. 10, no. 11, p. 1-19. <http://dx.doi.org/10.1371/journal.pone.0143608>
- Feng, X., Tang, S., Shang, L., Yan, H., Sommar, J., Lindqvist, O. 2003. Total gaseous mercury in the atmosphere of Guiyang, PR China. *The Science of the Total Environment*, vol. 304, no. 1-3, p. 61-72. [http://dx.doi.org/10.1016/S0048-9697\(02\)00557-0](http://dx.doi.org/10.1016/S0048-9697(02)00557-0)
- Grandner, M. A., Sands-Lincoln, M. R., Pak, V. M., Garland, S. N. 2013. Sleep duration, cardiovascular disease, and proinflammatory biomarkers. *Nat. Sci. Sleep*, vol. 5, p. 93-107. <http://dx.doi.org/10.2147/NSS.S31063>
- Gursoy, N., Sarikurku, C., Cengiz, M., Solak, M. H. 2009. Antioxidant activities, metal contents, total phenolic and flavonoid of seven *Morchella* species. *Food chemistry and toxicology*, vol. 47, no. 9, p. 2381-2388. <http://dx.doi.org/10.1016/j.fct.2009.06.032>
- Hooda, P. S. 2010. *Trace elements in soils*. 1st ed. Chichester, Hooda PS, editor. United Kingdom: John Wiley & Sons Ltd. ISBN 978-1-405-16037-7. <http://dx.doi.org/10.1002/9781444319477.ch1>
- Cheung, P. C. K. 2013. Mini-review on edible mushrooms as source of dietary fiber: preparation and health benefits. *Food Science and Human Wellness*, vol. 2, no. 2-3, p. 162-166. <http://dx.doi.org/10.1016/j.fshw.2013.08.001>
- Chudzyński, K., Jarzyńska, G., Stefańska, A., Falandysz, J. 2011. Mercury content and bio-concentration potential of Slippery Jack, *Suillus luteus*, mushroom. *Food Chemistry*, vol. 125, no. 3, p. 986-990. <http://dx.doi.org/10.1016/j.foodchem.2010.09.102>
- Index Fungorum, 2015. Available at: <http://www.indexfungorum.org/Names/Names.asp> (accessed Jan. 2016).
- Islam, M. S., Han, S., Masunaga, S. 2014. Assessment of trace metal contamination in water and sediment of some rivers in Bangladesh. *Journal of Water and Environment Technology*, vol. 12, no. 2, p. 109-121.

- JECFA, 2010. Joint FAO/WHO Expert Committee of Food Additives. Summary and conclusions. *Proceedings of the Seventy-second meeting, Rome, 16-25 February 2010*. JECFA/72/SC, Food and Agriculture in Nitra Organization of the United Nations World Health Organization. Issued 16th March 2010.
- Jiang, G. B., Shi, J. B., Feng, X. B. 2006. Mercury pollution in China. *Environmental Science and Technology*, vol. 40, p. 3672-3678. <http://dx.doi.org/10.1021/es062707c>
- John, E., Laskow, T. C., Buchser, W. J., Bruce, R. P., Basse, P. H., Butterfield, L. H., Kalinski, P., Lotze, M. T. 2010. Zinc in innate and adaptive tumor immunity. *J. Transl. Med.*, vol. 8, p. 118. <http://dx.doi.org/10.1186/1479-5876-8-118>
- Jomova, K., Valko, M., 2011. Advances in metal-induced oxidative stress and human disease. *Toxicology*, vol. 283, no. 2-3, p. 65-87. <http://dx.doi.org/10.1016/j.tox.2011.03.001>
- Kalač, P. 2009. Chemical composition and nutritional value of European species of wild growing mushrooms: a review. *Food Chemistry*, vol. 113, p. 9-16. <http://dx.doi.org/10.1016/j.foodchem.2008.07.077>
- Kalač, P. 2013. A review of chemical composition and nutritional value of wild growing and cultivated mushrooms. *Journal of science food and Agriculture in Nitra*, vol. 93, no. 2, p. 209-218. <http://dx.doi.org/10.1002/jsfa.5960>
- Kalač, P., Svoboda, L., Havličková, B. 2004. Contents of detrimental metals mercury, cadmium and lead in wild growing edible mushrooms: A review. *Energy Education Science and Technology*, vol. 13, p. 31-38.
- Krasińska, G., Falandysz, J. 2015. Mercury in Orange Birch Bolete *Leccinum versipelle* and soil substratum: bioconcentration by mushroom and probable dietary intake by cosumers. *Environmental Science and Pollution Research (in press)*. <http://dx.doi.org/10.1007/s11356-015-5331-8>
- Licata, P., Di Bella, G., Potorti, A. G., Lo Turco, V., Salvo, A., Dugo, G., et al. 2012. Determination of trace elements in goat and ovine milk from Calabria (Italy) by ICP-AES. *Food Additives and Contaminants: Part B: Surveillance*, vol. 5, no. 4, p. 268-271. <http://dx.doi.org/10.1080/19393210.2012.705335>
- Luo, X. S., Yu, S., Zhu, Y. G., Li, X. D. 2012. Trace metal contamination in urban soils of China. *Science of the Total Environment*, vol. 421-422, p. 17-30. <http://dx.doi.org/10.1016/j.scitotenv.2011.04.020>
- Luo, X. S., Ip, C. C. M., Li, W., Tao, S., Li, X. D., 2014. Spatial-temporal variations, sources, and transport of airborne inhalable metals (PM10) in urban and rural areas of northern China. *Atmos. Chem. Phys. Discuss.*, vol. 14, p. 13133-13165. <http://dx.doi.org/10.5194/acpd-14-13133-2014>
- Malavolta, M., Giacconi, R., Piacenza, F., Santarelli, L., Cipriano, C., Costarelli, L. et al. 2010. Plasma copper/zinc ratio: an inflammatory/nutritional biomarker as predictor of all-cause mortality in elderly population. *Biogerontology*, vol. 11, p. 309-319. <http://dx.doi.org/10.1007/s10522-009-9251-1>
- Mocchegiani, E., Costarelli, L., Giacconi, R., Piacenza, F., Basso, A., Malavolta, M. 2012. Micronutrient (Zn, Cu, Fe)-gene interactions in ageing and inflammatory-age-related diseases: implications for treatments. *Ageing Res. Rev.*, vol. 11, no. 2, p. 297-319. <http://dx.doi.org/10.1016/j.arr.2012.01.004>
- Ostos, C., Pérez-Rodríguez, F., Arroyo, B. M., Moreno-Rojas, R. 2015. Study of mercury content in wild edible mushrooms and its contribution to the Provisional Tolerable Weekly Intake in Spain. *Journal of Food Composition and Analysis*, vol. 37, p. 136-142. <http://dx.doi.org/10.1016/j.jfca.2014.04.014>
- Ouzouni, P. K., Petridis, D., Koller, W. D., Kyriakos, A., Riganakos, K. A. 2009. Nutritional value and metal content of wild edible mushrooms collected from West Macedonia and Epirus, Greece. *Food Chemistry*, vol. 115, no. 4, p. 1575-1580. <http://dx.doi.org/10.1016/j.foodchem.2009.02.014>
- Petkovšek, S. A. S., Pokorny, B. 2013. Lead and cadmium in mushrooms from the vicinity of two large emission sources in Slovenia. *Science of the Total Environment*, vol. 443, p. 944-954. <http://dx.doi.org/10.1016/j.scitotenv.2012.11.007>
- Radulescu, C., Stihl, C., Busuioac, G., Gheboianu, A. I., Popescu, I. V. 2010. Studies concerning heavy metals bioaccumulation of wild edible mushrooms from industrial area by using spectrometric techniques. *Bulletin of Environmental Contamination and Toxicology*, vol. 84, p. 641-646. <http://dx.doi.org/10.1007/s00128-010-9976-1>
- Roman, A., Popiela, E. 2011. Studies of chosen toxic elements concentration in multiflower bee honey. *Potravinarstvo*, vol. 5, no. 2, p. 67-69. <http://dx.doi.org/10.5219/134>
- Saba, M., Falandysz, J., Nnorom, I. C. 2015. Accumulation and distribution of mercury in fruiting bodies by fungus *Suillus luteus* foraged in Poland, Belarus and Sweden. *Environmental Science and Pollution Research*. vol. 2015, p. 1-9. <http://dx.doi.org/10.1007/s11356-015-5513-4>
- Siciliano, S. D., James, K., Zhang, G., Schafer, A. N., Peak, J. D. 2009. Adhesion and enrichment of metals on human hands from contaminated soil at an Arctic urban brownfield. *Environ. Sci. Technol.*, vol. 43, no. 16, p. 6385-6390. <http://dx.doi.org/10.1021/es901090w>
- Da Silva, J. B. B., Borges, D. L. G., Da Veiga, M. A. M. S., Curtius, A. J., Welz, B. 2003. Determination of cadmium in biological samples solubilized with tetramethylammonium hydroxide by electrothermal atomic absorption spectrometry, using ruthenium as permanent modifier, *Talanta*, vol. 60, no. 5, p. 977-982. [http://dx.doi.org/10.1016/S0039-9140\(03\)00182-6](http://dx.doi.org/10.1016/S0039-9140(03)00182-6)
- Szolnoki, Z., Farsang, A., Puskás, I. 2013. Cumulative impacts of human activities on urban garden soils: origin and accumulation of metals. *Environmental Pollution*, vol. 177, p. 106-115. <http://dx.doi.org/10.1016/j.envpol.2013.02.007>
- Timoracká, M., Vollmannová, A., Ismael, S. D. 2011. Minerals, trace elements and flavonoids content in white and coloured kidney bean. *Potravinarstvo*, vol. 5, no. 1, p. 56-60. <http://dx.doi.org/10.5219/116>
- Wang, X. M., Zhang, J., Wu, L. H., Zhao, Y. L., Li, T., Li, J. Q., et al. 2014. A mini-review of chemical composition and nutritional value of edible wild-grown mushroom from China. *Food Chemistry*, vol. 151, p. 279-285. <http://dx.doi.org/10.1016/j.foodchem.2013.11.062>
- WHO. 1993. Evaluation of certain food additives and contaminants, 41st Report of the Joint FAO/WHO Expert Committee on Food Additives. Technical Reports Series No 837. World Health Organization, Geneva (Switzerland).
- Wuana, R. A., Okieimen, F. E. 2011. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecology, Article ID 402647*, p. 20. <http://dx.doi.org/10.5402/2011/402647>
- Zhang, D., Gao, T., Ma, P., Luo, Y., Su, P. 2008. Bioaccumulation of heavy metal in wild growing mushrooms from Liangshan Yi nationality autonomous prefecture, China.

Journal of Natural Science, vol. 13, no. 3, p. 267-272.

<http://dx.doi.org/10.1007/s11859-008-0302-2>

Zhu, F., Qu, L., Fan, W., Qiao, M., Hao, H., Wang, X. 2011. Assessment of heavy metals in some wild edible mushrooms collected from Yunnan Province, China. *Environmental Monitoring and Assessment*, vol. 179, no. 1, p. 191-199. <http://dx.doi.org/10.1007/s10661-010-1728-5>

Acknowledgments:

This work was supported by grant VEGA No. 1/0724/12.

Contact address:

Zuzana Záhorcová, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, E-mail: zuzana.zahorcova@uniag.sk.

Július Árvay, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, E-mail: julius.arvay@gmail.com.

Martin Hauptvogel, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Sustainable development, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, E-mail: martin.hauptvogel@uniag.sk.

Ján Tomáš, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, E-mail: jan.tomas@uniag.sk.

Ľuboš Harangozo, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, E-mail: lubos.harangozo@uniag.sk