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MERCURY IN EDIBLE WILD-GROWN MUSHROOMS FROM HISTORICAL MINING AREA – SLOVAKIA: BIOACCUMULATION AND RISK ASSESSMENT

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ABSTRACT

In the present paper, we focused on assessment of the contamination levels of five species (n = 33) of edible wild mushrooms (*Macrolepiota procera, Boletus reticulatus, Suillus grevillei, Russula xerampelina* and *Xerocomellus chrysenteron*). We collected samples of above-ground parts of the macroscopic fungi species in historical mining and processing area surrounding Banská Bystrica (Central Slovakia) in 2014. Within 2 m radius of the samples, we also took samples of underlying substrate. On the basis of the substrate, along with the monitored contaminant – mercury, we calculated bioaccumulation factors for individual species and their anatomical parts (cap and stipe). From the obtained results of the mercury content in the edible mushrooms, we then determined provisionally tolerable weekly intake (PTWI). The limit value for mercury (0.350 mg Hg kg^{-1} for an individual with average weight of 70 kg) is defined by the World Health Organization (WHO). Our results suggest that despite the relatively low level of Hg in the underlying substrate, the species *Macrolepiota procera* (1.98 mg kg^{-1} ± 68.2 (0.41 - 3.20 mg kg^{-1} DW)) is characterized by extremely high bioaccumulation ability, as confirmed by the bioaccumulation factors (BAFc = 15.3; BAFs = 8.02). PTWI value was exceeded by almost 20%. In case of the other studied edible wild mushroom species, we did not record any increased risk of mercury intake by consumers. Generally it can be stated that consumption of wild mushrooms represents a relatively small but significant risk of negative impact on the consumer´s health.

Keywords: Mercury, mushroom, contamination, bioaccumulation, human health risk

INTRODUCTION

The level of environmental contamination by heavy metals presents a significant risk in relation to the quality of the food chain **(ATSDR, 2007)**. In the last decades, a significant increase in the content of contaminating elements such as cadmium, mercury and arsenic in all components of the environment was reported **(Granero-Domingo, 2002; Li *et al.*, 2008)**. It is mainly due to continuous increase of industrialization of human society **(Huang *et al.*, 2007)**. Increasing demands for raw materials result in adverse interventions in nature. The level of environmental contamination on the local scale is also amplified by metallurgical industry, which increases the level of contamination of topsoil in forest ecosystems mainly through atmospheric deposition **(Biester *et al.*, 2002)**.
Mercury (Hg) is regarded as a toxic element due to its potential impacts on the environment and public health **(Fang *et al.*, 2004; Leitch *et al.*, 2007)**. Some natural emissions of mercury may results from volcanoes, forest fires, evaporation of soil and water **(Feng *et al.*, 2003)**, however, anthropogenic emissions, such as mining, chemical industry, coal combustion, municipal solid waste incineration **(Jiang *et al.*, 2006)**, electronic, paper and pharmaceutical industries **(Rodrigues *et al.*, 2006)**, are major sources of Hg in the environment. Mercury is listed as a precedence-controlled pollutant for its persistence, bioaccumulation and toxicity by many international agencies such as UNEP, WHO and FAO. Mercury levels in global environment, compared to that of the natural background, have been continually increasing recently **(Streets *et al.*, 2005)**.
Edible mushrooms (*Macromycetes*) are valuable health foods, both for their texture and flavor as well as for their low energy content, high proportion of indigestible fiber, specific β-glucans and antioxidant constituents **(Kalač, 2009, Kalač, 2013)**. In addition, they contain significant amounts of vitamins, minerals and trace elements like Fe, Zn, Se, K **(Elmastas *et al.*, 2007; Wang *et al.*, 2014)**. Due to the characteristic position of mushrooms in the human food chain, they present a high risk of heavy metals transfer, especially of mercury, cadmium, lead, zinc and copper into the human body **(Gursoy *et al.*, 2009)**, which is caused by higher levels of contaminant uptake compared to plant species. Depending on the natural habitat (areas of geochemical anomalies, anthropogenically polluted soils), there is an increased intake of heavy metals into edible parts of mushrooms, which increases the load level to animal and human food chain **(Aloupi *et al.*, 2012; Falandysz *et al.*, 2012)**.
The present paper aims to determine the levels of mercury transfer from substrate to above-ground parts of macroscopic edible mushrooms collected in the historical mining area of central Slovakia (Banská Bystrica district). The area is characterized by former mining and processing activities of precious metals (gold and silver), as well as copper and some accompanying metals. From the data obtained, we calculated bioaccumulation factors for the various anatomical parts of mushrooms (cap and stipe). Given the popularity of collecting edible wild mushrooms in Central Europe (**Kalač, 2009; Árvay *et al.*, 2014**) we investigated a level of health risk arising from their consumption.

MATERIAL AND METHODS

Study area, sampling and pre-analytical procedure

Samples of the above-ground parts of macroscopic edible mushrooms were collected during 2014 in Banská Bystrica district, in the administrative area of seven municipalities where former mining and processing of precious and non-ferrous metals (gold, silver, copper) took place. Accompanying elements of the mining process were cadmium, lead, zinc and mercury. The latter is characterized by high volatility and its subsequent transfer through the atmosphere, resulting in a high risk of secondary contamination of adjacent areas **(Árvay *et al.*, 2014)**. The sampling points of the above ground parts of edible mushroom together with underlying substrate were defined by GPS coordinates and are shown in Figure 1.

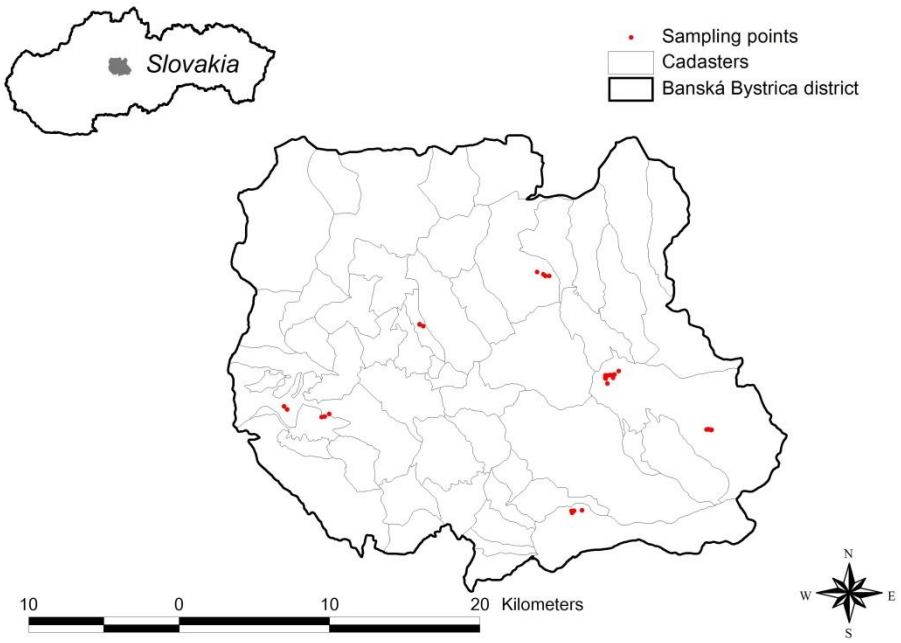

Figure 1 Map showing the study area and the sampling sites

Basic characteristics of the mushroom samples are shown in Table 1. Mushroom samples (n=33) representing 5 species (*Macrolepiota procera (Scop.) Singer, Boletus recitulatus Schaeff., Suillus grevillei (Klotzsch) Singer, Russula xerampelina (Schaeff.) Fr.* and *Xerocomellus chrysenteron (Bull.) Šutara*) were cleaned from inorganic and organic impurities by ceramic knife and we separated hymenophor (H) from the rest of fruit bodies (RFB) immediately after the sampling. After the collection, initial cleaning and slicing, the mushroom samples were dried at 105 °C to constant weight. The dried samples were pulverized in ceramic mortar and afterwards stored in pre-cleaned polyethylene bottles until performing subsequent pre-analytical operations. High-purity chemicals for all operations were used. Homogenized mushroom samples (1.000 g) were mineralized 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 deionized water (0.054 µS cm^{-1}) from Simplicity185 (Millipore, France). Digestion conditions for the applied microwave system comprised of the heat which ran up to 160°C for 15 minutes and keeping at constant for 10 minutes. A blank sample was carried out in the same way. The digest were subsequently filtered through a quantitative filter paper Filtrak 390 (Munktell, Germany) and filled up with deionized water to a volume of 50 cm^3 **(Svoboda *et al.*, 2006;Árvay *et al.*, 2013; Árvay *et al.*, 2014)**.

Analytical procedure

The total mercury content in underlying substrate and pulverized dried mushroom samples (0.005 - 0.01 mg DW) was determined by cold-vapour AAS analyzer AMA 254 (Altec, Czech Republic) with a detection limit of 1.5 ng kg^{-1} DW.

Statistical analysis and risk assessment

All statistical analyses were carried out using the statistical software Statistica 12.0 *(Statsoft,* USA). Descriptive data analysis included minimum value, maximum value, average, standard deviation and relative standard deviation. The comparison of the mercury in fruiting bodies of the mushrooms and mercury in underlying substrate was examined using Pearson´s correlation coefficients. The limit of statistical significance was set up at $p < 0.05$ for all statistical analysis.
Given the popularity of collecting wild mushrooms in Central Europe (**Kalač, 2009**), we calculated from the obtained data provisional tolerable weekly intake (PTWI) of the observed contaminants for standardized person weighing 70 kg and weekly intake of 300 g of fresh mushrooms, defined by the European Food Safety Authority and afterwards we draw conclusions whether regular consumption of wild mushrooms from the studied locality poses a health risk (**JECFA, 2010; WHO, 1993**). Due to the high water content, which is dependent on climatic conditions of the site, we used commonly accepted value of 90% for the conversion of water content in the mushroom samples (**Kalač, 2009**).

RESULTS AND DISCUSSION

Mercury in substrate

Mercury is regarded as a toxic element due to its potential impacts on the environment and public health (**Fang *et al.*, 2004; Chudzyński *et al.*, 2012**). The content of total mercury in the underlying substrate varied within a relatively wide range (Table 1). The obtained data on the content of Hg in the substrate ranged from 0.05 to 0.27 mg kg^{-1} (n=33), while the average value of Hg content in the substrate in the case of mushroom samples with the highest content of mercury (*Macrolepiota procera (Scop.) Singer*, n=5) was around 0.13 mg kg^{-1} ± 61.7 (mean ± RSD) ranging from 0.06 to 0.22 mg kg^{-1}. The data of mercury content in the substrate show that we did not record an increased concentration of Hg in the substrate, in either case (n=33).

Mercury in mushrooms

Macroscopic mushrooms are characterized by high bioaccumulation ability (**García *et al.*, 2009, Árvay *et al.*, 2014**), which was reflected in the content of the monitored contaminant in individual anatomical parts of the studied mushroom species. The highest concentration of mercury was recorded in samples of *Macrolepiota procera*, where we recorded on average 1.98 mg kg^{-1} ± 68.2 (0.41 to 3.20 mg kg^{-1} DW) in the cap and 1.4 mg kg^{-1} ± 67.1 (0.12 - 1.75 mg kg^{-1} DW) in the stipe. Despite the relatively low level of mercury content in the substrate, we recorded the highest concentration of Hg in this species, confirmed by the extremely high bioaccumulation factor (BAFc=15.3, BAFs=8.02). Such high bioaccumulation factors are characteristic for *Macrolepiota procera*, which is confirmed also by findings of other authors (**Árvay *et al.*, 2014; Falandysz *et al.*, 2012; Jarzyńska *et al.*, 2011**). The obtained contents of Hg in *Macrolepiota procera* are statistically significant (Rc=0.95, Rs=0.92, $p<0.05$). All collected data on the mercury content in the substrate and individual anatomical parts of ual comparison in Figure 2. The order of the studied mushroom species according to the average content of Hg in the cap is as follows: *Macrolepiota procera* > *Russula xerampelina* > *Boletus recitulatus* > *Suillus grevillei* > *Xerocomellus chrysenteron*.

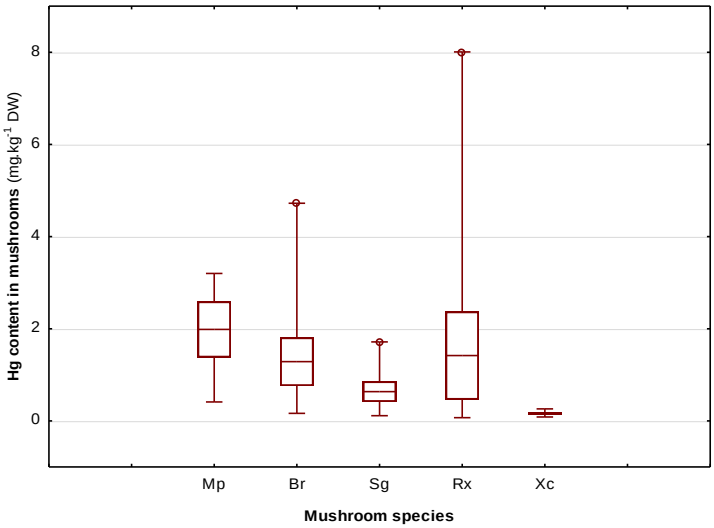

Figure 2 Comparison of total mercury content in monitoring mushroom species with descriptive statistics (min., max., mean, relative standard deviation and extreme values). (*Mp – Macrolepiota procera, Br – Boletus recitulatus, Sg – Suillus grevillei. Rx – Russula xerampelina and Xc – Xerocomellus chrysenteron*).

Risk assessment

The Joint FAO/WHO Expert Committee on Food Additives **(JECFA, 2010)** recommends that provisional tolerable weekly intakes (PTWI) of Hg is 0.005 mg $kgbw^{-1}$ $week^{-1}$. Therefore, the PTWI of Hg for a person weighing 70 kg would be 0.350 mg. In order to evaluate an exceeding of tolerable weekly intake of the monitored contaminant, we used its average levels in hymenophore. Assuming a daily consumption of 300 g of fresh mushrooms (30 g DW), we calculated that the amount of mercury intake from the consumption of *Macrolepiota procera* was 0.418 mg. The calculated weekly intake indicates that consuming a standard amount of *Macrolepiota procera*, the consumer receives almost 20% more mercury than allowed by the relevant legislation **(JECFA, 2010)**. We did not record an exceeding of the allowed hygienic standard in other species.

Table 1 The mercury content in underlying substrate and mushrooms ($mg.kg^{-1}$ DW), bioaccumulation factor in cap and stipe and $Q_{c/s}$ factor.

Species* (Family)	**N**	**Hg - substrate** mean ± RSD (range)		**Hg - mushrooms** mean ± RSD (range)
Macrolepiota procera (Scop.) Singer (Lepiotaceae)	5	0.13 ± 61.7 (0.06-0.22)	Cap	1.98 ± 68.2 (0.41-3.20)
			Stipe	1.04 ± 67.1 (0.12-1.75)
			BAF_C	15.3
			BAF_S	8.02
			Qc/s	1.91
Boletus recitulatus Schaeff. (Boletaceae)	8	0.12 ± 54.3 (0.06-0.27)	Cap	1.29 ± 115 (0.16-4.72)
			Stipe	1.03 ± 114 (0.11-3.84)
			BAF_C	10.7
			BAF_S	8.54
			Qc/s	1.25
Suillus grevillei (Klotzsch) Singer (Suillaceae)	7	0.08 ± 35.0 (0.05-0.13)	Cap	0.64 ± 91.2 (0.11-1.71)
			Stipe	0.39 ± 93.6 (0.08-1.06)
			BAF_C	8.39
			BAF_S	5.16
			Qc/s	1.63
Russula xerampelina (Schaeff.) Fr. (Russulaceae)	8	0.12 ± 42.6 (0.06-0.20)	Cap	1.42 ± 190 (0.07-8.01)
			Stipe	1.00 ± 202 (0.03-5.95)
			BAF_C	11.7
			BAF_S	8.30
			Qc/s	1.41
Xerocomellus chrysenteron (Bull.) Šutura (Boletaceae)	5	0.08 ± 49.8 (0.05-0.16)	Cap	0.15 ± 41.0 (0.09-0.26)
			Stipe	0.13 ± 38.9 (0.06-0.20)
			BAF_C	1.85
			BAF_S	1.52
			Qc/s	1.22

Legend: BAFc – bioaccumulation factor in cap, **BAFs** – bioaccumulation factor in stipe, **N** – number of samples, **Qc/s** – cap to stipe quotient.
* Index fungorum, 2014

CONCLUSION

In the present paper, we aimed to assess the contamination level of fruiting bodies of edible wild mushrooms in the area of historical mining and ore´s processing operation. Mushrooms represent a component of the environment that is susceptible to the increased amount of environmental contaminants, which is immediately reflected by the higher amount of these contaminants in fruiting bodies of the wild-growing edible mushrooms. The mercury content was studied in five mushroom species (n=33) that are subject to picking activities and are used for consumption. The results show that the consumption of species with high bioaccumulation ability (e.g. *Macrolepiota procera*) may negatively affect the health of consumers.

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