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MERCURY ACCUMULATION IN WILD MUSHROOMS AT ABANDONED Hg-DEPOSIT MALACHOV (SLOVAKIA)

Peter ANDRÁŠ[1], Pavol MIDULA[1], Ján GROFČÍK[2], Marek DRÍMAL[1], Vojtech DIRNER[1], Miroslav RUSKO[3], Jana DADOVÁ[4] & Ingrid TURISOVÁ[1]

[1]*Faculty of Natural Sciences, Matej Bel University in Banska Bystrica, Tajovského 40, 974 01 Banská Bystrica, Slovakia, peter.andras@umb.sk; pavol.midula@umb.sk; marek.drimal@umb.sk; ingrid.turisova@umb.sk*
[2]*Technical University in Zvolen, T. G. Masaryka 24, 960 01 Zvolen, Slovakia; jan.grofcik@gmail.com*
[3]*Slovak Society for the Environment, Bratislava | Universty of Ss. Cyril and Methodius in Trnava, Institute of Management, Trnava, Slovakia, mirorusko@centrum.sk*
[4]*State Nature Conservancy of the Slovak Republic, Tajovského 28B, 974 01 Banská Bystrica, Slovakia, jana.dadova@sopsr.sk*

Abstract: The aim of the presented article was to determine the Hg content in the fruiting bodies of 13 generally consumed mushroom species (*Boletus reticulatus, Clitocybe nebularis, Lactarius deliciosus, Macrolepiota procera, Russula* spp., *Suillus grevillei, Tricholoma* spp.) growing at the area of abandoned mercury deposit Malachov. The Hg concentrations were analyzed by thermal decomposition-gold amalgamation atomic absorption spectroscopy, using AMA-254 Advanced Mercury Analyzer. The Hg concentrations in soil varied widely (ranging from 0.01 to 2.44mg·kg^{-1}), furthermore, they were particularly depended on the mushroom species. The fruiting bodies of *Russula ochroleuca* contained the highest concentrations of Hg (up to 16.69mg·kg^{-1}). The lowest concentrations were detected in *Russula aeruginea* (from 0.04 to 0.06 in stipe stems and from 0.05 to 0.06mg·kg^{-1} in pileus) and in *Russula vesca* (0.05 in stipe stems; 0.09mg·kg^{-1} in pileus). Mercury is preferentially accumulated in the mushroom pileus (ranging from 0.05 in *Russula vesca* to 16.69mg·kg^{-1} in *Russula ochroleuca*). The bioconcentration factor was calculated for the rate of the Hg content in soil substrate vs. its concentration in the mushroom pileus (ranging from 0.03 to 29.22). The results indicate that some investigated mushroom species can be referred as Hg excluders (e.g. *Russula vesca*) whereas some other species as accumulators (e.g. *Russula ochroleuca* or *Tricholoma portentosum*). The obtained results were compared with the Government Decrees of Slovak Republic, showing that the substantial part of the studied mushroom species exceed the legal tolerance limit (0.25 mg kg^{-1}) suggested for Hg in plant food and therefore they can be considered as inappropriate for human consumption.

Key words: mushrooms, mercury, accumulation, thermal decomposition-gold amalgamation atomic absorption spectroscopy

1. INTRODUCTION

Mercury belongs to the most toxic elements (e. g. Rauf et al., 2020). Accumulation of Hg in wild growing mushrooms at the area of abandoned Hg-mine Malachov has been a matter of high concern. The mine was exploited since 1390 and after several interruptions, the mining activity continued up to 1990 (Andráš et al., 2015; Bárdiová, 2019).

Considerably Hg contamination of country com-ponents in this area was studied by Dadová et al., (2014) and Andráš et al., (2015). High contents of Hg and of other potentially toxic elements (mainly metal-lic elements and metalloids and radionuclides) accu-mulations especially in the higher fungi were described by numerous authors (Allen & Steinnes, 1978; Bargagli & Baldi, 1984; Kalač et al., 1996; Falandysz, 2002; Falandysz et al., 2002, 2004; Melgar et al., 2009; Stihi et al., 2009; Ndimele et al., 2017). High Hg accumulations in edible mushrooms may pose signi-ficant risk to human health as a consequence of its migration potentiality in trophic chain (Udochukwu et al., 2014; Rzymski et al., 2016; Záhorcová et al., 2016; Ndimete et al., 2017; Świsłowski & Rajfur, 2018).

2 MATERIAL AND METHODS

Fruiting bodies of mushrooms (13 species; including 2 inedible species *Rusula ochroleuca* and *Tricholoma terreum*) were collected from the wide area of the ore-field in summer 2019. The number of samples depended on number of availability of indi-vidual mushroom species during the season: *Macro-lepiota procera* (3 samples), *Suillus grevillei* (3 samples), *Lactarius deliciosus*. (5 samples), *Russula* spp. (8 samples), *Clitocybe nebularis* (5 samples), *Tricholoma* spp. (5 samples), *Boletus* sp. (2 samples), *Picipes* (3 samples). All the studied mushrooms were growing in forest kambisoil at former ore-field.

The underlying soil substrate samples were collected according to Garcia et al., (2013) at the sampling sites from A horizon (0 – 15 cm), dried at the laboratory temperature for 20 days, homogeni-zed and then sieved in plastic bags. The rinse pH was measured in water suspension in a ratio 1: 5 using pH-meter Multi 340 instrument (WTW, Germany) equipped with SenTix 41 electrodes. The device was adjusted to pH 7.0 using the pH 7.00 buffer.

The fresh mushrooms were cleaned, washed in deionized water, and dried at laboratory temperature and finally weighed. Total mercury contents were studied separately in caps (pileus) and stipe stems of the mushrooms. Both, the soil and in the mushrooms, samples were analysed using thermal decomposition-gold amalgamation atomic absorption spectroscopy (AMA-254 Advanced Mercury Analyzer, Altec Ltd.) in laboratories of Technical University Zvolen.

The bioconcentration factor (BCF) was calculated individually for each sample: i) the BCF represents a ratio of mercury contents in the caps of mushrooms vs. contents in soil samples from the root ball of the relevant samples; ii) as the ratio of average element content in roots vs. element content in soil; and iii) as the ratio of average element content only in the aerial parts of plants to average element content in soil (Brooks, 1998; Boussen et al., 2013; Boim et al., 2016). The BCF value<1 identifies the mushroom as excluder, the BCF = 1 indicates that the mushroom can be referred as an indicator and for BCF > 1, the mushroom can be outlined as accumulator or hyper-accumulator (Baker, 1981).

The nomenclature of mushroom species is used according to Index Fungorum Database (Copper & Kirk, 2019).

Dependence of Hg contents in mushrooms and soil were determined by Spearman rank correla-tion. In order to detect a statistical difference between the contents in pileus and stripes the paired t-test was performed with significance level at $p \leq 0.005$. All statistic evaluations were performed by software application R 3.6.3.

Table 1 Mercury in mushroom species

Mushroom species	**Hg (mg·kg^{-1})**			**BCF**
	cap	**stipe stem**	**soil**	
Lactarius deliciosus	**0.74**	**0.46**	0.94	0.79
	0.46	**0.42**	1.01	0.45
	11.63	**9.98**	2.44	**4.77**
	0.35	**0.34**	1.54	0.23
	1.38	**0.72**	0.66	**2.09**
Russula ochroleuca	**16.69**	**14.18**	1.54	**10.84**
	12.10	**10.07**	1.01	**11,90**
Russula riomellii	0.09	0.06	2.38	0.04
	0.08	0.06	1.78	0.04
Russula aeruginea	0.05	0.04	1.02	0.05
	0.06	0.06	2.39	0.03
Russula vesca	0.09	0.05	1.54	0.06
	0.09	0.05	1.25	0.07
Clitocybe nebularis	**2.66**	**1.52**	0.56	**4.75**
	1.96	**1.22**	1.25	**1.57**
	1.44	**1.00**	0.98	**1.47**
	2.02	**1.43**	0.74	**2.73**
	1.88	**1.04**	0.85	**2.21**
Tricholoma populinum	**1.30**	**0.92**	0.56	**2.32**
Tricholoma portentosum	**6.43**	**3.64**	0.22	**29.22**
	5.59	**3.29**	1.26	**4.44**
Tricholoma terreum	**5.74**	**4.00**	1.02	**5.63**
	6.04	**5.22**	1.11	**5.44**
Picipes badius	**1.69**	**0.88**	2.13	0.79
	1.70	**1.55**	1.22	**1.39**
	0.89	**0.46**	0.87	**1.02**
Boletus reticulatus	**0.80**	**0.47**	1.78	0.45
	1.31	**0.67**	1.78	0.74
Macrolepiota procera	**2.52**	**1.28**	1.01	**2.50**
	1.35	**1.11**	0.98	**1.38**
	8.72	**5.61**	0.96	**9.08**
Suillus grevillei	**2.78**	**1.40**	1.26	**2.21**
	3.09	**0.99**	1.11	**2.78**
	2.75	**1.72**	0.96	**2.86**

Explanation: The samples exceeding the limits for mercury contents given by Government Decrees MP SR & MZ SR no. 608/3/2004–100 and MZ SR no. 14300/2007-OL for Food Codex regulating contaminants in food and the PCF > 1 are emphasized by bold.

3. RESULTS

The Hg content in underlying soil varies from 0.00 to 2.44mg·kg^{-1} (Table 1). Most of the studied mushroom species are strongly contaminated by Hg. The Hg content is strongly dependent on a mushroom species (Fig. 1). The highest Hg concentration was described in *Russula ochroleuca* (from 10.07 to

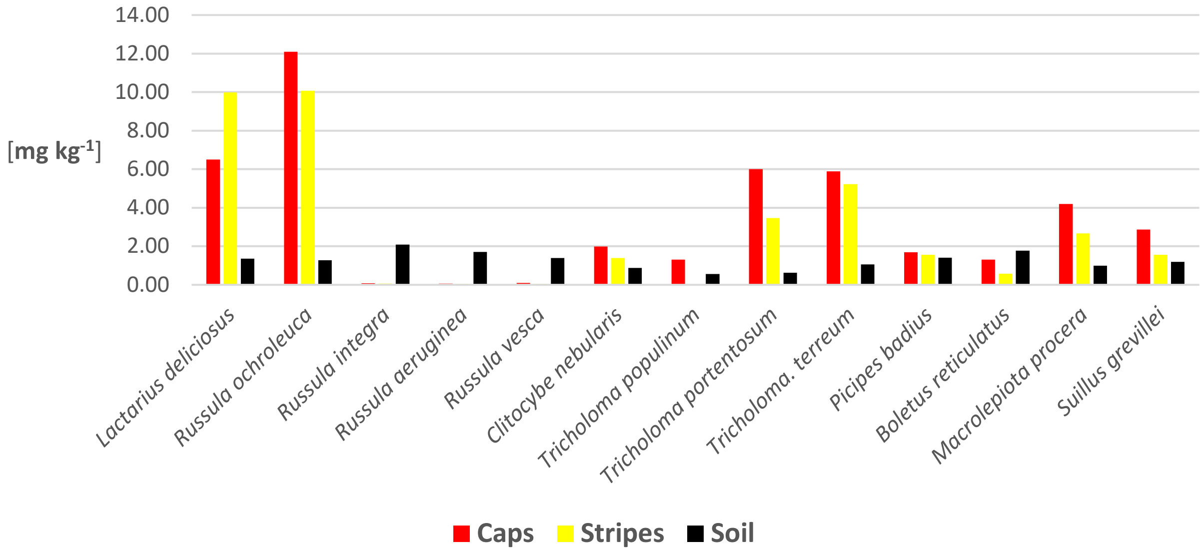

Figure 1. Visualization of mercury concentrations among the investigated mushroom species.

14.18mg·kg^{-1}) and the lowest contents in *Russula aeruginea*, *R. riomellii* and *R. vesca* (from 0.04 to 0.09mg·kg^{-1}). The Hg content in pileus is always substantially higher as in the stipe stems (Table 1).

The BCF shows a considerable range of values among the investigated mushroom species (Table 1). The highest BCF was determined in the sample of *Tricholoma portentosum* (29.22) and the lowest in *Russula aeruginea* (0.03).

The significant differences, referring to the results of paired t-test, were detected between pileus and stripes among the mushroom samples ($t = 5.79$; $p \leq 0.005$)

4. DISCUSSION

The country components (soil, groundwater, surface water, some plants) in the surroundings of the Malachov deposit are strongly polluted by Hg (Dadová et al., 2014; Andráš et al., 2015). The Hg content in soil (from to) exceed except one sample (Table 1) the Government Decrees (0.3mg·kg^{-1}) for. Whereas the Hg contents in food commodities (fruits and vegetables) in the residential area outside the ore-field, comply with the provisions of the Government Decrees MP SR a MZ SR č. 608/3/2004–100 and MP SR and of MZ SR 14300/2007-OL (Dadová et al., 2014), the substantial part of the mushrooms from the mining area, except *Russula riomellii*, *Rusula aeruginea* and *Russula vesca*, the Hg content exceed the legal limit (0.25mg kg^{-1}). This finding is important for seasonal mushroom pickers because substantial part of studied mushrooms belongs among the widely consumed species.

The content of Hg differed among studied mushrooms. Similar differences, referring to the results of paired t-test, detected between pileus and stripes are published also by Zimmermannová (2001). The best Hg accumulators among mushrooms are the representants from families *Tricholomataceae* and *Agaricaceae*. The highest concentration of Hg (16.69 and 12.10mg·kg^{-1}) at Malachov ore-field was determined in the pileus of *Russula* sp. (*Russula ochroleuca)*, but there are extraordinary great differences among individual sub-species. While in *Russula ochroleuca* the values are very high, *Russula aeruginea*, and *Russula vesca* they are incomparably lower (from 0.05 up to 0.09mg·kg^{-1}).

Considerably higher Hg contents in comparison with those in stipe stems were found in the pileus of all investigated mushroom species. This finding corresponds with data of Elekes et al., (2010), Falandysz et al., (2015), Širić et al., (2016) and Świsłowski (2020). Such a high Hg content in mushroom pileus is caused by its preferential accumulation in spore-bearing layers (Zimmermannová 2000; Kalač & Svoboda 2000).

The significant correlations between Hg contents and the contents in mushrooms were not confirmed. Considering this findings, it is not proved that Hg contents in mushroom fruiting bodies are exclusively bound to their very local soil substrate as assumed by Kalač & Svoboda (2000), Slávik et al., (2013), Rzymski et al., (2016) or Ndimele et al., (2017). However, similar statement is also supported by results of Nováčková et al., (2007) and Kokkoris et al., (2019).

5. CONCLUSIONS

All the studied mushroom species in the area of abandoned deposit Malachov are Hg-contaminated. The Hg accumulation by mushrooms depends on the individual species, as well as on the part of fruiting body. Both the highest and lowest Hg contents were described in *Russula* spp. (from 0.05 up to 16.96mg·kg^{-1}). With the exceptions of *Russula integra, R. aeruginea* and *R. vesca,* in all the other species exceed the Slovak tolerance limits suggested for Hg in plant foods. As expected, the analyzed mushroom species are not suitable for human consumption.

It was confirmed that the pileus is much more contamined by Hg as the stipe stems of mushrooms. The Hg content in mushroom species is not depended by the Hg content in local soil substrate.

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