REGULAR ARTICLE

THE CONTENT OF MERCURY IN EDIBLE MUSHROOMS FROM MIDDLE SPIŠ AREA

Marek Slávik[1], Tomáš Tóth[1], Ľuboš Harangozo[1], Július Árvay[1], Radovan Stanovič[1], Juraj Miššík[2]*

Address: Ing. Marek Slávik,

[1]Slovak University of Agriculture, Faculty of Biotechnology and Food, Department of Chemistry, Tr. Andreja Hlinku 2, 949 76 Nitra, Slovakia, phone number: +421 37 641 4497.

[2]Slovak University of Agriculture, Faculty of Biotechnology and Food, Department of Chemistry, Tr. Andreja Hlinku 2, 949 76 Nitra, Slovakia.

*Corresponding author: marekslavik87@gmail.com

ABSTRACT

Accumulation of total mercury by mushrooms, was studied in midle spiš area. This area is laden high contents of mercury in the soil. To determine of the contamination of edible mushrooms in the middle Spiš, we used samples of different types of edible mushrooms (*Macrolepiota procera, Lecinum piceinum, Lycoperdon pyriforme, Russula sp. Suillus And Grevillea*). These fungi were collected in Spišsko Gemerské-rudohorie. Here at the sampling point GPS coordinates are. We also carried out the determination of the exchange soil reaction: pH (CaCl2), soil humus content and the content of total mercury in the soil horizon A (0-15 cm). The concentration of mercury in edible mushrooms was more extreme. The highest amount of mercury 176.409821 $mg.kg^{-1}$. dry matter was determined in *Macrolepiota procera*. Contrast, the lowest measured concentration was 0.091684 $mg.kg^{-1}$. dry matter for species *Lecinum piceinum*. To determine the concentration of mercury in the samples, we used the device AMA 254 (Advanced Mercury Analyser).

Keywords: (mercury, mushrooms, soil, contamination,)

INTRODUCTION

Mercury (Hg) is released in the atmosphere by natural (e.g.volcanic eruptions, forestfires, evaporation from soils and water) and anthropogenic processes (e.g. fossil fuel combustion, gold mining, ore roasting and processing) (**Swain *et al.,* 2007; Zhang *et al.*, 2002).** In this area especially the activities of the former iron mine Rudňany. **(Vilček *et al.,* 2012)**. In soils Hg is highly immobile and mainly accumulates in the top layers due to its strong affinity to organic matter and soil minerals thereby reducing the concentrations in the soil solution (**Rieder *et al.,* 2011; Farhana *et al.*, 2005**). Therefore the bioavailability of Hg in soils is usually low. Accumulation of Hg in soil organisms is important in particular with respect to the estimation of the risk of secondary poisoning. Mushrooms are well known to accumulate Hg. **(Rieder *et al.,* 2011)**. The results of the soil studies showed a large-surface dimension of soil contamination by mercury. This is evident especially in middle Spiš and northern areas of Gemer – in the emission areas of Rudňany, where are present also natural endogenic geochemical anomalies of siderite and piryt lode systems (the surourdings of Rudňany, Gelnica, Krompachy, Slovinky and Markušovce). One of the sources of Hg is also evaporation from mining in the Rudňany-Poráč area, from stacks, setling pits, etc. (**Vilček *et al.,* 2012)**. The soils of these areas are within Slovakia, but also in europe, among the most contaminated with Hg, As, Cu, Zn and Pb (**Vilček *et al.,* 2012; Brehuv, 2003)**.

Mushrooms are consumed as a delicacy, particularly for their unique aroma and texture. Mushrooms do not constitute a significant portion of the human diet, but the consumption of wild and cultivated mushrooms has become increasingly popular in recent years. (**Melgar *et al.*, 2009**). The term mushroom will be used for the fruiting body (carpophore, mycocarp), mostly above ground, of higher fungi (macrofungi). A fruiting body is formed from spacious underground mycelia (hyphae) by the process of fructification. The lifetime of the bulk of fruiting bodies is only 10–14 days. (**Kalač, 2009; García *et al.*, 2009**). The mycelia of higherfungi spread over large areas (several square meters) and their relationships with soil and dead organic matter and their symbiotic relationship with plant roots allow for intensive exchange with substrates. Heavy metal content in many terrestrial fungi correlates with the high metal concentration in the soil where they grow, although some authors report higher metal concentrations in younger fruiting bodies than in adult ones. This is explained by the transport of metal ions from the mycelium to the fruiting body occurring predominantly during the start of fructification. During the stages of growth of the fruiting body mass, the metal concentration decreases (**Kalač and Svoboda, 2000; Melgar *et al.,* 2009**).

Environmental pollution by mercury is an ongoing problem, mercury is found with high abundance in the fruiting bodies of some edible mushroom species of both saprophytic and mycorrhizal natures (**Falandysz *et al.*, 2007**). Due to its toxicity, the World Health Organization (WHO) established intake guidelines for humans, and set the maximum weekly intake by humans of total mercury to 300 µg,. Some species of higher mushrooms, however, accumulate in their fruiting bodies levels of mercury that are higher than these limits. (**Falandysz *et al.*, 2007; Dogan *et al.*, 2006**).

Our objective was to determine the level of mercury contamination in edible mushrooms of the middle spiš area, of the safety the food chain.

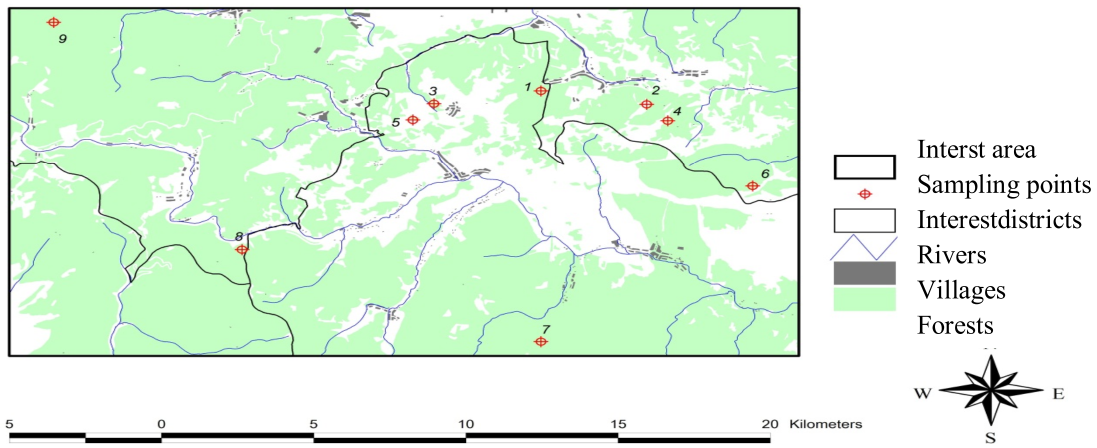

Figure 1 Points of supply samples of edible fungi and soil found in the districts of Spišská nová Ves and Gelnica located in the mountains Volovské vrchy - Spišsko-gemerské rudohorie

MATERIAL AND METHODS

Processing of samples

Mushrooms

Edible mushrooms we collected overall per nine different locations. The sampling site coordinates were subtracted using GPS device Garmin GPSmap 60 Cx. The collected samples aerial parts of edible mushrooms were cleaned from soil and vegetation. Samples were collected during two periods I: 30 July - 1st August 2012

II: 1 October - 3rd October 2012.

Cleaned mushrooms we had to air-dry on filter paper for two weeks. After drying, we homogenized mushrooms and set mercury content.

Soil

Fot the removal of soil, we used soil probe Eijkelkamp 2402.0120 Fisher Scientific. Before removing the soil we removed vegetation cover. Soil we collected from the outer horizon A (0 -15 cm). Sampling was performed in 3 repeatings. Then we let the soil dry bulk. After two weeks, we homogenized and sieved soil into fine earth II (particle diameter of 0.125 mm).

Analytical methods

Determination of exchange reactions in soil $CaCl_2$ ($pH/CaCl_2$)

Twenty grams of soil samples were taken. Subsequently 40 ml of $CaCl_2$ (c = 0.01 M) was added. The suspension was allowed 10 minutes to shake by shaker Heidolphpromax 1020 at a frequency of 180 oscilation per minute. After shaking and settled solution we filtered suspension through filter paper *FILTRAK* 390. After filtering the suspension, we measured the pH of the filtrate to a pH meter Metrohm 691, we calibration aparat to two buffers at pH 4 and 7. The resulting values were subtracted from pH meter display with two decimal places.

Determination of organic carbon and humus in the soil according to Turin and the modifications by Nikitin

Soil organic carbon is oxidized with oxygen in chromo-sulfuric mixture. The amount of oxygen consumed in the oxidation is determined by the difference consumed and unconsumed chromo-sulfuric mixture. Humus content was found by calculation according to the following of relations:

$$C_{ox} = \frac{(a-b)\times 0{,}03\times 1{,}17\times f_{mohr}}{n}\ [\%]$$

(a - b) = difference between sample and blank test

f_{mohr} = accurate substance concentration of Mohr salt

n = sample weight in g

$$\text{humus content} = c_{ox} \times 1.724 \quad [\%]$$

c_{ox} = percentage of oxidizable carbon

1. 724 = conversion factor to humus content in the soil sample.

Determination of total mercury content

To determine the content of total mercury in samples of edible mushrooms and soil, we used the same device. AMA 254 (Advanced Mercury Analyser) is special purpose atomic absorption spectrophotometer for the determination of mercury. It is designed for direct determination of mercury in solid and liquid samples without the need for chemical pretreatment of the sample (mineralization etc.). Using the technique of generating a vapor of metallic mercury with subsequent interception and enrichment on a gold amalgamator achieves a high sensitivity setting and independence the result of determining the sample matrix. All mercury concentrations were expressed in mg kg^{-1} dry matter.

RESULTS AND DISCUSSION

Table 1 Content of monitored parameters in samples

Sampling point	Positions VGS 84 LAT	LON	pH $CaCl_2$	Humus content	Hg in soil (mg.kg^{-1})	Hg in mushrooms (mg.kg^{-1})	Name of mushroom	Ecophysiological group
1	48°52.46592	20°39.425298	4.44	2.48	19.974483	35.499367	*Russula sp.*	Mycorrhizal
2	48°52.248264	20°42.286986	3.87	5.33	12.547046	176.409821	*Macrolepiota procera*	Saprophyt
3	48°52.058166	20°36.581688	4.63	6.6	10.66492	69.602943	*Lycoperdon pyriforme*	Saprophyt
4	48°51.881412	20°42.887088	3.73	7.32	8.930301	101.347298	*Macrolepiota procera*	Saprophyt
5	48°51.655476	20°36.045054	5.35	4.05	0.59534	5.44258	*Lycoperdon pyriforme*	Saprophyt
6	48°50.413548	20°45.288636	5.1	1.75	0.504638	12.424401	*Macrolepiota procera*	Saprophyt
7	48°46.541076	20°39.913086	7.29	6.29	6.071416	21.303539	*Russula sp.*	Mycorrhizal
8	48°48.41592	20°31.725048	4.37	7.87	1.677527	0.091684	*Lecinum piceinum*	Mycorrhizal
9	48°53.600718	20°26.217648	4.61	5.87	0.242641	0.669339	*Suillus grevillei*	Mycorrhizal

The table1 indicates the set values of monitored parameters. In terms of risk to human health is the most important naturally contained toxic mercury in edible mushrooms. Our Dietary Code does not limit value for mercury content in mushrooms The FAO/WHO set a provisional maximum weekly intake of Hg of 4.3µg per kg of body weight, or 0.26 mg Hg week^{-1} for a person with a body weight of 60 kg. According to the EU (EEC Directive 2001/22/EC) is the value 5.0 mg. kg^{-1} dry mater in wild growing mushrooms. In our samplesmthe highest observed value was determined for a sample of 2 *Macrolepiota procera*. (176.409821 mg. kg^{-1}). It is a favorite and popular type of mushroom, because this kind of consumption can pose significant health risks. Extremely hygienic crossing the limit (0.5 mg.kg^{-1}) was recorded in a sample of soil on the site of sampling, 12.540 746 mg.kg^{-1}, is a 25 times the limit value. Elevated mercury concentrations in fungi indicate (**Kalač, 2009**), (**Svoboda** ***et al.*****, 2006**), (**Falandysz** ***et al.*****, 2002**). Low and tolerable concentrations of mercury were found only in two samples of number 8 (0.091684 $mg.kg^{-1}$) species *Lecinum piceinum* and number 9 (0.669339 $mg.kg^{-1}$) at species *Suillus grevillea.* In saprofyt types were determined higher concentrations of mercury than in the mycorrhyzals species. Same results were also recorded by (**Melgar** ***et al.*****, 2009; Borovička, 2007**). Mushrooms were collected in extremely contamined area which is documented by the fact that only one sample of soil meets the hygienic limit. It is a sample number 9.

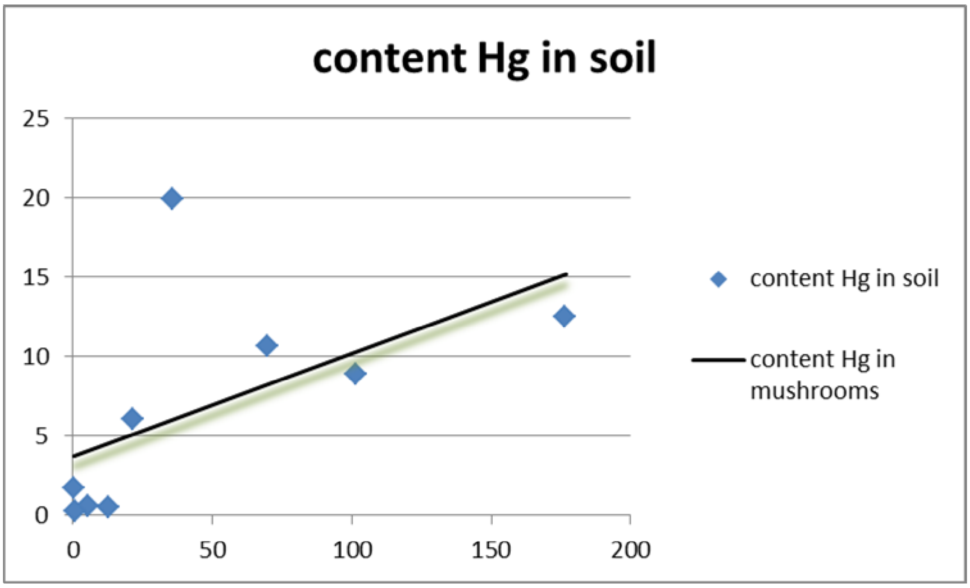

Figure 2 Dependence of mercury in mushrooms from its content in the soil

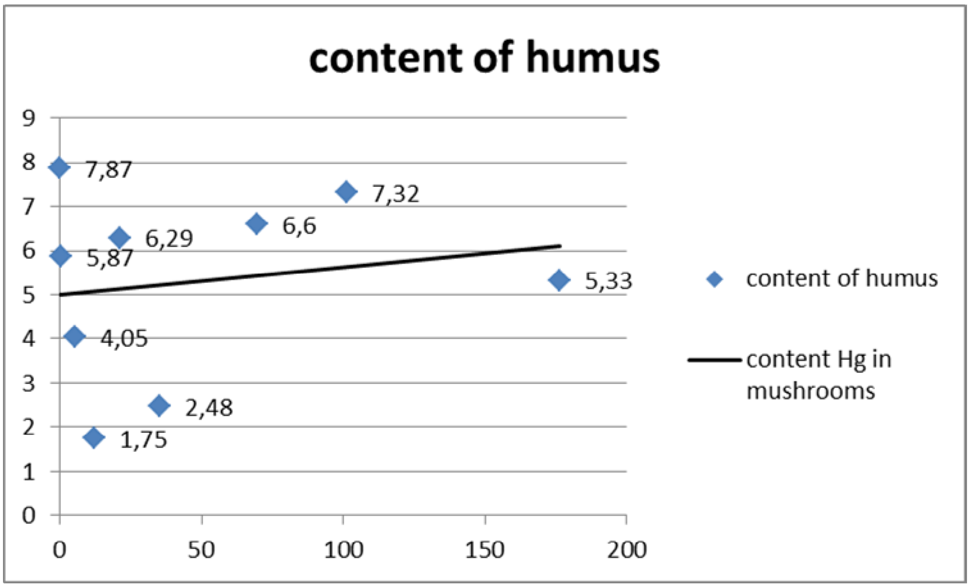

Figure 3 Dependence of mercury in mushrooms from humus content

Figures 2 and 3 document the positive linear dependence of mercury in mushrooms from the mercury content in the soil, which is mainly bound to organic matter of the soil. Mushrooms receive necessary nutrients and energy just breaking down organic matter. Similar conclusions are made by (**Ravichandran**, **2004**) and (**Rieder *et al.*, 2011**).

CONCLUSION

It should be noted that mushrooms, especially saprophytes species are important hyperaccumulator of mercury. Therefore, in areas such as Spiš – gemerské rudohorie, which are heavily contaminated with mercury and other heavy metals. We do not recommend frequent or increased consumption of wild mushrooms, especially high-risk groups of the population. We found that in our study, samples from this area may appear to extreme levels of mercury in edible mushrooms. These values reached mushroom samples 1-7. 176.409821 mg. kg^{-1} in species *Macrolepiota procera* to 5.44258 mg. kg^{-1} in species *Lycoperdon pyriforme.* We found that the Hg content in mushrooms is dependent on the content of Hg in the soil and the humus content in the soil. Other factors that influence the content of Hg in edible mushrooms are also Ecophysiological group, we observed a higher accumulation in saprophyt species. The young fruiting bodies of mushrooms contain more mercury than the old. Weather conditions have influence on it, too.

Acknowledgments: This work was done with the financial support of the project VEGA 1/0724/12 "Specific points, diffusion and profiled mercury contamination of production areas in central Spiš, northern Gemer inputs and minimize the possibility of Hg in plant products." Big thanks go also to all the staff of the Department of Chemistry who participated in the survey results.

REFERENCES

BREHUV, J. - BOBRO, M. - SLANČO, P. - HANČUĽÁK, J. - FEDOROVÁ, E. 2003. Kontaminácia ovzdušia ortuťou v okolí rudnian, správa z Ústav geotechniky SAV.

BOROVIČKA, J. – ŘANDA, Z. 2007. Distribution of iron, cobalt, zinc and selenium in macrofungi. In *Mycological progress*, vol. 6, 2007, p. 249 – 59.

DOGAN, H. - SANDA, M. – UYANOZ, R. – OZTURK, - CETIN, U. 2006. Contents of metal in some wild mushrooms: its impact in human healt. In *Biological Trace Element Research*, vol. 110, 2006, p. 79 – 94.

FALANDYSZ, J. – FRANKOWSKA, A. - MAZUR A. 2007. Mercury and its bioconcentration factors in King Bolete (Boletus edulis). In *Journal* of *Environmental Science* and *Health* Part A, vol. 42, 2007, p. 2089–2095.

FALANDYSZ, J. - BIELAWSKI, L. - KANNAN, K. - GUCIA, M. - LIPKA, K. - BRZOTOWSKI, A. 2002. Mercury in wild mushrooms and underlying soil substrate from the Great Lakes land in Poland. In *Journal of Environmental Monitoring*, vol. 4, p. 473–476.

FARHANA, Z. - SHAMIM J. R. - SOGHRA K. H. - RIZWAN H. K., 2005, Low dose mercury toxicity and human health, In *Environmental Toxicology and Pharmacology,* vol. 20, 2005, p. 351–360.

GARCÍA, M. A. - ALONSO J. – MELGAR, M. J. 2009. Lead in edible mushrooms. Levels and bioakumulation factors. In *Hazard mater*, vol. 167, 2009, p. 777-783.

KALAČ, PAVEL ,2009, Trace element contents in European species of wild growing edible mushrooms: A review for the period 2000–2009. In *Food Chemistry,* vol. 122, 2010, p. 2–15.

KALAČ, P. - SVOBODA L., 2000, review of trace element content in edible mushrooms. In *Food Chemistry*, vol. 69, 2000 p. 273–281.

MELGAR, M. J. - ALONSO, M. A. - GARCÍA, M. A. 2009. Mercury in edible mushrooms and underlying soil: Bioconcentration factors and toxicological risk. In *Science of the Total Environment*, vol. 407, 2009, p. 5328–5334.

RAVICHANDRAN, M. 2004. Interactions between mercury and dissolvedmatter e a review. In *Chemosphere*, vol. 55, p. 319-331.

RIEDER, S. R. - BRUNNER, I. - HORVAT, M. - JACOBS, A. - FREY, B., 2011, Accumulation of mercury and methylmercury by mushrooms and earthworms from forest soils. In *Environmental Pollution,* vol. 159, 2011, p. 2861-2869.

SVOBODA, L. - KALAC, P. - SPICKA, J. - JANOUSKOVA, D. 2002. Leaching of cadmium, lead and mercury from fresh and differently preserved edible mushroom, Xerocomus badius, during soaking and boiling. In *Food Chemistry,* vol. 79, 2002, p. 41–45.

SWAIN, E. B. - JAKUS, P. - RICE, G. - LUPI, F. - MAXOSON, P. A. - PACYNA, J. M. - PENN, A. - SPIEGEL, S. J. - VEIGA, M. M. 2007. Socioeconomic consequences of mercury use and pollution. In *8th International Conference on Mercury as a Global Pollutant.*

VILČEK, J. - HRONEC, O. - TOMÁŠ, J. 2011. Risk Elements in Soil of Burdened Areas of Eastern Slovakia, In *Pol. J. Environ. Stud.,* vol. 21, 2012, no. 5, p. 1429 – 1436.

ZHANG, M.Q. - ZHU, Y.C. - DENG, R.W., 2002. Evaluation of mercury emissions to the atmosphere from coal combustion, China. In:*Ambio,* vol. 31, no. 6, p. 482–484.