JMBFS
Journal of Microbiology, Biotechnology and Food Sciences
International peer-reviewed scientific online journal
Published by Faculty of Biotechnology and Food Sciences

HEALTH SAFETY OF EDIBLE WILD MUSHROOMS COLLECTED FROM THE INDUSTRIAL AREA

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doi: 10.15414/jmbfs.2016.5.5.456-459

ARTICLE INFO

Received 4. 11. 2015
Revised 17. 12. 2015
Accepted 18. 12. 2015
Published 1. 4. 2016

Regular article

OPEN ACCESS

ABSTRACT

The health risk associated with consumption of edible mushrooms derived from area surrounding the metallurgical plants was assessed. Three species (*Xerocomus badius* (Fr.), *Suillus luteus* (L.) and *Leccinum scabrum (Bull.) Grey*) of mushrooms have been studied. Samples were collected at increasing distances (0.2, 5, 10, and 15km) from the border of an industrial area. Determination of the content of 13 elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb, Tl, Zn and Se) using ICP-OES method with prior microwave mineralization was made. Among studied metals only Al concentration in mushrooms was distance-dependent. The content of Al in tested samples ranged from 2.8 – 39.6 $mg.kg^{-1}$ dry matter and significantly ($P<0.05$) decreased with increasing distance from the industrial plant. High levels of Fe, Ni and Cu were observed in the mushrooms collected near the aluminum foundry (up to 5 km). For other studied elements (K, Mg, Zn, Mn and Se) no effect of pollutants emitted by foundry for their level in mushrooms was observed.

Keywords: Mushrooms, aluminium, pollution, food safety

INTRODUCTION

Mushrooms as food accompanied mankind from immemorial time **(Patel and Goyal, 2012)**. However, despite the presence of many nutrients in mushrooms **(Rudawska and Leski, 2005; Sas-Golak *et al.*, 2011)**, scientists are divided about their positive impact on the human health. For some of them, mushrooms have been reported to be a therapeutic foods **(Mattila *et al.*, 2000; Mahendra *et al.*, 2005)**, useful in preventing diseases such as hypertension **(Mujić *et al.*, 2011)**, hypercholesterolemia **(Alberts *et al.*, 1989)**, cardiovascular diseases **(Guillamóna *et al.*, 2010)** or cancer (**Rajewska and Bałasińska, 2004; Patel and Goyal, 2012)**. Moreover, their functional characteristics are mainly related to the chemical composition **(Manzi *et al.*, 2001)**.
On the other hand, it was found that different species of mushrooms may accumulate toxic elements (**García *et al.*, 1998; Isildak *et al.*, 2004; Árvay *et al.*, 2014**). So that, consumption of large amounts of fungi can be associated with the risk of high heavy metals intake **(Cocchia *et al.* 2006)**. Due to this ability fungi can be used as bioindicators of environmental contamination with toxic metals **(García *et al.*, 1998; Stihi*et al.*, 2011).** Until now, various studies have shown that accumulation of heavy metals in mushrooms is dependent on: the species of mushrooms, the age of mushrooms as well as mycelium, the source of pollution with heavy metals as well as the distance to this source (**Kalač and Svoboda, 2000).**
The aim of the study was to assess the health risk associated with consumption of edible mushrooms derived from area surrounding the metallurgical plants.

MATERIALS AND METHODS

Material

Three species: *Xerocomus badius* (n=6), *Suillus luteus* (n=5) and *Leccinum scabrum* (n=4) of wild edible mushrooms have been studied (**Table 1**). Samples were collected in forests surrounding two aluminum foundry localized closely to Stalowa Wola Smelter in South-Eastern Poland in 2014. Young mushrooms were collected at various distances from the border of an industrial area in order 0.2, 1, 5, 10, and 15km in the same direction of wind. Selecting points of the harvesting were dependent on the location of forest areas.

Table 1 Points of harvesting analyzed species of fungi

Point	Sample No.	Species	Distance from contaminationsource
A	1	*Xerocomus badius*	up to 200 m
	2	*Leccinum scabrum*	
	3	*Xerocomus badius*	
	4	*Suillus luteus*	
B	5	*Leccinum scabrum*	5 km
	6	*Xerocomus badius*	
	7	*Xerocomus badius*	
	8	*Suillus luteus*	
C	9	*Suillus leteus*	10 km
	10	*Xerocomus badius*	
	11	*Leccinum scabrum*	
D	12	*Suillus luteus*	15 km
	13	*Xerocomus badius*	
	14	*Leccinum scabrum*	
	15	*Suillus luteus*	

Methods

The fruiting bodies of mushrooms were first manually cleaned from leaves, needles and soil and dried in warm room during 2 weeks. Dry material was milled and stored in laboratory until analysis. The solid samples (1g) were mineralized with 8 mL of nitric acid (65% pure- basic, POCh Gliwice, Poland) using microwave mineralization (Ultrawave, Milestone Ethos-One, Italy) during 30 min.The clear solution volume was made up to 50 mL for each sample using deionised water. The quantitative ($mg.kg^{-1}$d.m.) determination of 13elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb, Tl, Zn and Se) was carried out by Optical Emission Spectrometry with Inductively Induced Plasma (ICP-OES) using ThermoiCAP 6500 (Thermo Fisher Scientific Inc., USA).

Statistical analysis

Statistical calculations were performed using StatSoft Statistica, 9.0. Normality of distribution was checked with Shapiro-Wilk test. As a significant differences between the meansat $p < 0.05$ values were considered. For the verification nonparametric Kruskal-Wallis test was used. Pearson's correlation coefficients to assess metal-metal interaction were calculated.

RESULTS AND DISCUSSION

Among studied elements, for Al, Ca, Cu, Ni and Fe the higher contamination of mushrooms harvested in the immediate vicinity of the foundry was observed (**Table 2**). Moreover, between these elements high correlation (r>0.6) appeared (**Table 3**). For other studied elements the dependency of their concentrations in mushrooms on the distance from metallurgic plant was no occurred.

Table 2 The concentration of elements [mg. kg^{-1}d.m.] in mushrooms collected in the increasing distance from the aluminum foundry (A<B<C<D) Mean±standard deviation and coefficient of variation V [%] were shown.

Element	Distance from the metallurgic plant			
	0.2 km (A) (n=4)	**5 km (B)** (n=4)	**10 km (C)** (n=3)	**15 km (D)** (n=4)
Al	28.7 ± 9.3[a] 32.4%	17.8 ± 8.2[a] 45.9%	7.3 ± 5.1[b] 70.4%	8.6 ± 1.0[b] 11.5
Ca	94.4 ± 20.0[a] 21.2%	126.3 ± 53.2[a] 42.1%	11.7 ± 20.2[b] `173.2%	8.3 ± 1.4[b] 17.3%
Cd	2.1 ± 2.3 108.3%	3.8 ± 3.0 78.3%	3.6 ± 3.6 98.4%	1.0 ± 0.8 78.6%
Cu	117.8 ± 73.4 62.3%	170.5 ± 100.4 58.9%	44.9 ± 18.9 42.0%	68.1 ± 48.3 70.9%
Fe	198.8 ± 57.9[a] 29.1%	185.6 ± 59.9[a] 32.3%	35.0 ± 18.0[b] 51.5%	36.7 ± 22.7[b] 61.9%
K	29737.5 ± 8727.4 29.3%	34925.0 ± 9717.6 27.8%	31521.7 ± 6714.4 21.3%	28271.7 ± 4752.2 16.8%
Mg	916.3 ± 187.9 20.5%	1036.9 ± 222.3 21.4%	921.7 ± 176.5 19.2	920.8 ± 50.1 5.4
Mn	24.9 ± 7.1 28.7%	41.9 ± 29.8 71.3%	13.0 ± 1.3 10.2%	17.6 ± 6.0 33.9%
Ni	2.6 ± 1.9 73.6%	3.0 ± 1.2 41.4%	0.2 ± 0.3 118.4%	0.1 ± 0.1 173.2%
Pb	0.7 ± 0.3 47.9%	0.9 ± 0.5 51.0%	0.7 ± 0.3 44.3%	0.8 ± 0.9 113.1%
Zn	125.1 ± 62.9 50.3%	143.9 ± 46.6 32.4%	128.3 ± 34.7 27.0%	157.5 ± 55.2 35.0%
Tl	3.7 ± 1.3 35.4%	3.4 ± 1.2 35.3%	2.4 ± 2.0 81.9%	2.6 ± 1.4 54.5%
Se	0.7 ± 0.5 73%	0.8 ± 0.5 65.8%	0.9 ± 1.5 159.5%	0.8 ± 1.0 132%

a, b samples statistically different

With increasing distance from the plant, the Al content in mushrooms statistically ($P<0.05$) decreases in a species-specific manner (**Figure 1**). Samples *Leccinum scabrum* in the vicinity of the factory show a higher concentration of aluminum than *Suillus luteus* or *Xerocomus badius*. The highest value 39.6 mg.kg^{-1}d.m. was recorded in the case of sample 2 (*Leccinum scabrum*), while the average for the distance A was 28.7 ± 9.3 mg.kg^{-1}d.m. The mean level for sample collecting in point D amounted 8.6 mg.kg^{-1}d.m (**Table 2**). The lowest content 2.8 mg.kg^{-1}d.m. was recorded in the sample No. 10 (*Xerocomus badius*). Obtained results showed that the aluminum content in tested samples in comparison to those available in literature was relatively low. Tests carried out on *Xerocomus badius* from the western Poland showed aluminum content in levels from 22.20 ± 4.57 to 28.08 ± 5.81 mg.kg^{-1}d.m. **(Mleczek *et al.*, 2013)**, which are comparable to the average level of this element reported in mushrooms from tested area. Studies conducted by **Rudawska and Leski (2005)** showed significantly higher Al concentration in mushrooms as compared to our findings. The biggest differences were found for *Leccinum scabrum*, where the aluminum content in the cited work amounted to 365 ± 62.5 mg.kg^{-1}d.m., which is a value almost 10 times higher than in own results.

Table 3 The Pearson correlation coefficient (r) between the concentration of analyzed elements in mushrooms

	Al	*Ca*	*Cd*	*Cu*	*Fe*	*K*	*Mg*	*Mn*	*Ni*	*Pb*	*Se*	*Tl*	*Zn*
Al	1												
Ca	0,769	1											
Cd	-0,02	0,407	1										
Cu	0,643	*0,965*	0,317	1									
Fe	*0,917*	*0,961*	0,245	0,884	1								
K	0,079	0,651	0,893	0,651	0,442	1							
Mg	0,106	0,715	0,59	0,816	0,493	0,889	1						
Mn	0,495	*0,919*	0,393	*0,983*	0,79	0,739	*0,907*	1					
Ni	0,839	*0,992*	0,367	*0,932*	*0,986*	0,58	0,624	0,866	1				
Pb	-0,15	0,403	0,126	0,619	0,185	0,528	0,84	0,728	0,294	1			
Se	-0,77	-0,63	0,448	0,038	-0,73	0,119	-0,2	-0,57	-0,66	-0,29	1		
Tl	*0,967*	0,882	0,02	0,809	*0,972*	0,225	0,328	0,688	*0,924*	0,103	-0,85	1	
Zn	-0,48	-0,22	-0,47	0,038	-0,35	-0,15	0,248	0,132	-0,31	0,732	-0,18	-0,3	1

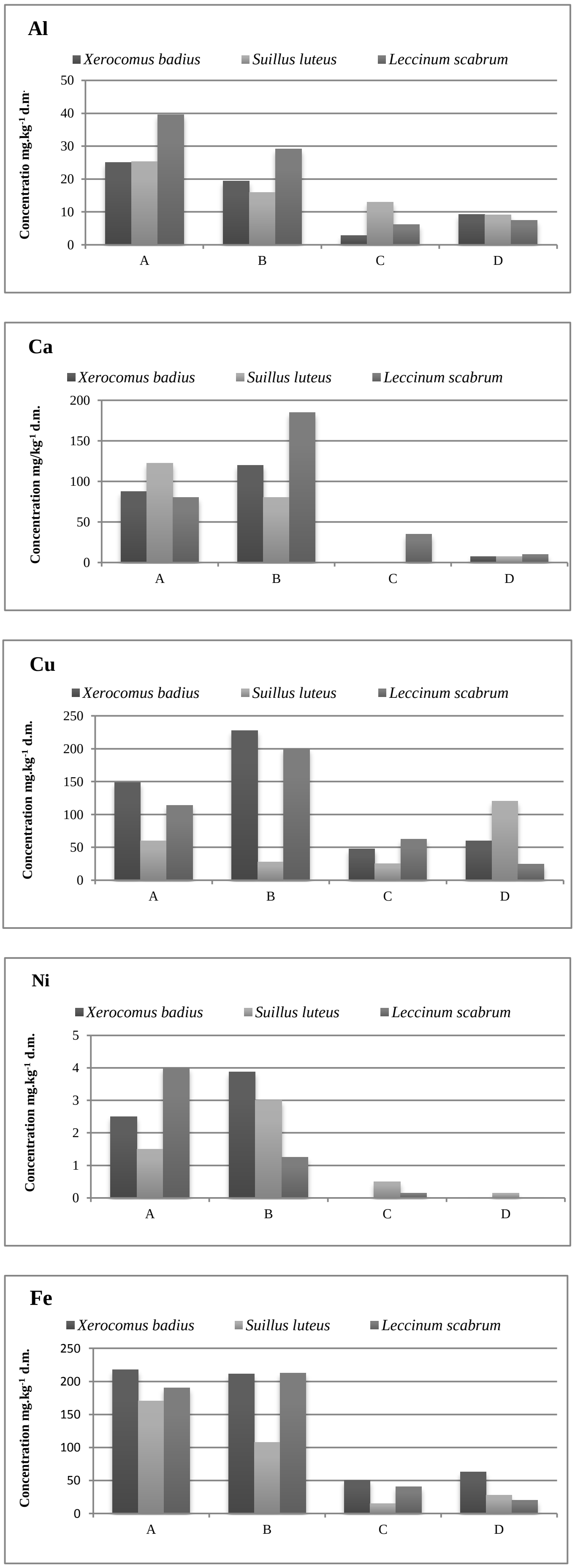

Figure 1 Changes in tested elements content in the fungi samples correlated with increasing distance from the point of emission

Tested samples contain significant amounts of copper, iron, nickel and calcium at a distance up to 5 km inclusive (**Figure 1**). The concentrations of these elements often exceed the values presented in the literature and were significantly higher than mean levels for samples collected from further distance. The average copper content in the samples from a distance of 5 km was 144.1± 86.2 mg.kg^{-1}d.m. The highest content was characterized by *Xerocomus badius* (188.8 ± 80.7 mg.kg^{-1}d.m.), and the lowest by *Suillus luteus* (43.6± 22.9 mg.kg^{-1}d.m). However, literature show that in the clear area of Europe, concentrations of copper in *Xerocomus badius* are in the range 25-75 mg.kg^{-1}d.m. **(Kalač, 2010)**. For *Leccinum scabrum* from eastern Poland, the concentrations of copper in the hat of mushroom was determinated as 24 ± 7 mg.kg^{-1}d.m. **(Bielawski and Falandysz, 2008).** For other elements (K, Mg, Zn, Mn, Se) the impact of pollutants emitted by foundry for their concentrations in the studied fungi were not observed. The level of macronutrients such as K and Mg was 20 000 - 40 000 mg.kg^{-1}d.m. and 800 - 1 800 mg.kg^{-1}d.m., respectively. Similar results were obtained by **Rudawska and Leski (2005)**, who recorded the concentration of K and Mg 21 300 mg.kg^{-1}d.m. and 400 mg.kg^{-1}d.m. for *Leccinum scabrum*, 29 700 mg.kg^{-1}d.m. and 800 mg.kg^{-1}d.m. for *Suillus luteus* and 34 900 mg.kg^{-1}d.m. and 900 mg.kg^{-1}d.m. for *Xerocomus badius*, respectively. In our study the observed level of selenium was significantly higher in the case of *Suillus luteus*. The highest concentration of this element (2.6 m.kg^{-1}d.m.) was recorded in sample of *Suillus luteus* collected 10 km away from polluted area indicating no effect of plants on the level of this element in mushrooms.

The concentration of lead in the tested samples ranged from 0.25 mg.kg^{-1}d.m. (*Xerocomus badius*, 15 km) to 1.825 mg.kg^{-1}d.m. (*Suillus leteus*, 15 km). The results show any relationship between the level of lead and the distance from the plant or species of fungi. The concentration of cadmium in the tested samples was in the range of 0.175 mg/kg d.m. (*Suillus luteus*, 200 m) to 7.5 mg.kg^{-1}d.m. (*Leccinum scabrum*, 10 km). Concentrations of lead in the tested samples are within the limits set for the samples from uncontaminated areas **(Kalač, 2010)**. However, some samples of *Xerocomus badius* and *Leccinum scabrum* have exceeded the maximum levels of cadmium from uncontaminated areas reported in the literature **(Kalač, 2010)**. The presented results clearly indicate a reduced content of cadmium in *Suillusluteus* in comparison to other species. A similar levels of cadmium have been found by other authors in Poland **(Falandysz *et al.*, *1993;* Falandysz and Chojnacka, 2007)** and Europe (**Kalač, 2010).**

The studied mushrooms *Xerocomus badius*, *Suillus leteus* and *Leccinum scabrum* contain minerals required in human diet, such as Ca, Cu, Fe, K, Mg, Mn, Zn and Se as well as toxic elements, such as Al, Cd, Pb and Tl. The level of toxic elements was lower that minerals. Since for some metals, their concentration in mushrooms harvested in the immediate vicinity of plants are even several times higher, it appears that mushrooms harvested within about 5 km should not be used for human consumption. What is true, calculations show that even excessive intake (100 g) of fresh mushrooms per week is not associated with a risk of exceeding the allowable limits of weekly intake (calculated as % of PTWI) recommended by **WHO/FAO (2011)**, which amounted for Al (0.1-0.41), Cu (0.18-0.70), Fe (0.09-0.51), Zn (0.26-0.32), Pb (2.11-2.90) and Cd (5.86-21.71% of PTWI). The results shown that high accumulation of cadmium in the analyzed fungi harvested near metallurgical plant may pose health risk especially in the case of enhanced consumption. Consequently, secure zone in which mushrooms will be free from this heavy metal is located within a radius> 15 km from the aggregation of metallurgical plants.

CONCLUSION

It was confirmed that heavy metal emission by metallurgic plants caused environmental pollution which resulted in enhanced accumulation of some metals in fruiting bodies of mushrooms. The high accumulation existed mainly in the distance up to 5 km from the border of plant. However, in most cases the average consumption of polluted mushrooms did not pose the risk for human health, excluding cadmium intake. As expected, metal uptake seems to be species dependent: *Leccinum scabrum* accumulated more Al and *Xerocomus badius* acumulate a large amount of Cu. The least susceptible to pollution turned out to be *Suillus luteus*, which was simultaneously rich in Se. Those some species are the most susceptible biomarkers of environmental pollutionwith heavy metals.

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