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CONCENTRATIONS OF MINERALS IN SELECTED EDIBLE MUSHROOM SPECIES GROWING IN POLAND AND THEIR EFFECT ON HUMAN HEALTH*

Mirosław Mleczek[1]✉, Zuzanna Magdziak[1], Piotr Goliński[1], Marek Siwulski[2], Kinga Stuper-Szablewska[1]

[1]Department of Chemistry, Poznań University of Life Sciences
Wojska Polskiego 75, 60-625 Poznań, **Poland**
[2]Department of Vegetable Crops, Poznań University of Life Sciences
Dąbrowskiego 159, 60-594 Poznań, **Poland**

ABSTRACT

Introduction. Intake of wild growing edible mushroom in selected regions of Europe (especially East and Central Europe) is significant. Additionally, mushrooms are able to accumulation many times higher amounts of nutritional and toxic elements than plants, therefore knowledge on their concentration levels and changes in their content is important for human health.
Material and methods. Eleven biologically important (Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Zn) and five toxic elements (Al, Ba, Cd, Hg, Pb) were determined in twenty three fruiting bodies of edible wild growing mushroom species. The tested mushroom species: were collected from selected places located practically throughout Poland. Efficiency of element accumulation in mushrooms and soils were analysed by flame atomic absorption spectrometry (FAAS) and atomic emission spectrometry (AES).
Results. The highest concentrations for K, Mg, Na, Zn and Fe and significantly lower concentrations of Ba, Cd, Co, Hg, Ni, Pb and Sr were observed. Additionally, significant lower accumulations of elements by the lamellar were found in comparison to the tubular fungi.
Conclusion. Based on presented results in our opinion an occasional intake of the analysed mushrooms is not dangerous to humans. Of course, some toxic elements (Hg or Pb) are accumulated in human organs, but these elements are provided also with other foodstuffs (vegetables, fruits, meat) or drinks.

Key words: accumulation, edible mushroom, minerals, human health

INTRODUCTION

Fungi represent a large group of eukaryotic organisms that includes microorganisms (yeasts and moulds) and fleshy familiar mushrooms (macrofungi, macromycetes, higher fungi). These organisms, classified as the kingdom of Fungi, are separate from plants, animals, and bacteria. They are found in every environment and play important roles in most ecosystems. Along with bacteria, fungi are the major decomposers in soil, and

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✉mirekmm@up.poznan.pl

therefore they hold a key role in biogeochemical cycles [Gadd 2007], such as nutrient cycling (especially as saprotrophs and symbionts) and degradation of organic matter to inorganic molecules, which may be introduced again into metabolic pathways in plants or other organisms. In addition, from tens of thousands of fungal species worldwide, around 4000 are edible and they are very popular and readily used by people. Edible wild mushrooms are characterised by low calorie content, high contents of vegetable proteins, vitamins, and minerals, they are valuable health-promoting foods [Racz et al. 1996, Kula et al. 2011]. The consumption of wild edible mushrooms is high, even in the developed world, due to their unique taste, which is used extensively in cooking, in many traditional cuisines (notably Chinese, Korean, European and Japanese) [Chudzyński et al. 2011]. Wild mushroom species can be regarded as healthy foods in well-balanced diets due to their contents of functional minerals and nutrients. Mushrooms are good sources of protein and carbohydrates and their nutritional contents are comparable to most legumes and meat [Kalač 2009]. Moreover, they can also be used in low-calorie diets for their low contents of fat. It was reported that trace element concentrations in mushrooms are significantly higher than those in agricultural crop plants, vegetables or fruits [Kalyoncu et al. 2010]. Elements can be divided into two groups, i.e. major elements and trace elements. Major elements include Na, K, Ca, Mg, Cl, P and S and their recommended daily intake is more than 50 mg/day. Trace elements Fe, I, Fe, Zn, Se, Cu, Mn, Cr, Mo, Co, Ni are needed at less than 50 mg/day [Ismail et al. 2011].

Despite the fact that mushrooms contain a wide spectrum of elements and organic substances, they also contain problematic heavy metals presented in environment. What is more, wild edible mushrooms are mainly collected from city lawns and parks, roadside forests and industrial sites [Falandysz et al. 2001], due to the fact that mushroom picking is an attractive form of recreation [Chudzyński et al. 2011]. Particularly the above mentioned areas are exposed to pollution with various elements, thus the mushrooms are unsuitable for human consumption [Falandysz et al. 2001, Chudzyński et al. 2011]. Furthermore, recently presented data showed that some mushrooms were found to be efficient accumulators and even hyperaccumulators of noble metals such as Au and Ag, as it was observed in *Amanitas* mushrooms (*Amanita submembranacea* and *Amanita strobiliformis*) or the *Agaricus* mushrooms [Borovička et al. 2005, 2009, Borovička and Ránda 2007]. Also certain species of mushrooms contain high concentrations of Pb, Cd, Cr, Ni, Mn, Fe, As and Hg, which is potentially harmful to human health. This fact is all-important, since previously presented data [Falandysz et al. 2003, Kula et al. 2011] indicated that although the degree of heavy metal pollution of soil is low, metal concentrations in mushrooms may be relatively high. However, the uptake and presence of heavy metals in fruiting bodies depend on genetic factors in individual species [Gadd 2003, 2004, Campos et al. 2009, 2011], environmental conditions and the region of growth [Chudzyński et al. 2011, Falandysz et al. 2012, Mleczek et al. 2013]. It should also be remembered that soil is a factor that highly determines the concentration of elements in sporocarps of fungi, especially metals. The concentrations of elements in fruiting bodies collected from polluted sites are considerably higher compared to other plants, due to their effective uptake and bioaccumulation of the toxic elements.

This study presents a comprehensive survey investigating selected elements in soil (the background on which they were growing) and 23 edible mushroom species. Presented data showed the concentrations of essential, non-essential and toxic elements presented in forest soil and in fruiting bodies, as well as bioconcentration factors. Such information may provide insight into the potential risk to human health.

MATERIAL AND METHODS

Mushroom sample collection

Fruiting bodies of 23 edible mushroom species were collected in 2011 from selected woods located practically throughout Poland. The analysed mushroom species were: *Boletus badius* (19), *Boletus calopus* (9), *Boletus chrysenteron* (9), *Boletus edulis* (25), *Boletus luridus* (8), *Boletus subtomentosus* L. (9), *Calocera viscosa* (6), *Cantharellus cibarius* (11), *Chlorophyllum rhacodes* (8), *Cortinarius violaceus* L. (16), *Gyroporus cyanescens* (14), *Hygrophoropsis aurantiaca* (19), *Lactarius salmonicolor* (8), *Leccinum versipelle* (12), *Lycoperdon perlatum* (6), *Macrolepiota procera* (13), *Rozites caperatus* (6), *Suillus bovinus* L. (15),

Suillus granulatus (10), *Suillus grevillei* (17), *Suillus luteus* L. (9), *Tylopilus felleus* (8) and *Xerocomus rubellus* (21). The digits in round brackets denote the number of samples for particular species. We analysed selected elements in the whole fruiting bodies (without separation into caps and stems) as regards thetotal intake of studied mushroom species as a whole. Mushrooms were collected to paper bags (100 cm^3) and transported to the laboratory within 24 hours.

Mushroom preparation

The mushrooms after collection were carefully washed with distilled water from the Milli-Q Advantage A10 Water Purification Systems (Merck Millipore), then dried in an electric drier at 105 ±2ºC for 48 h. Dry samples were ground to a powder for 2 min in a laboratory Cutting Ball Mill 200 by RETSCH company. The material as three representative samples (1 g each) was mineralized in a CEM Mars 5 Xpress microwave mineralization system (CEM Corp., Matthews, NC, USA) in a closed system (55 mL vessels) using 6 mL of 65% HNO_3 and 1 mL of 30% H_2O_2. Digestion of the mushroom materials was performed according to a microwave program composed of three stages: first stage – power 600 W, time 3 min, temperature 100°C; second stage – power 600 W, time 3 min, temperature 120°C; third stage – power 1200 W, time 8 min, temperature 200°C. Materials after digestion were filtered through 45-mm filters (Sartorius Stedim Biotech. Grade 1288), and then whole contents were made up to a final volume of 100 mL with distilled water.

Soil sample collection and preparation

Soil samples were collected from each location where mushrooms were growing, each time from the depth of 5 cm below the ground surface and at a distance of 5-20 cm from the collected mushroom fruiting bodies. Soil samples were collected using a soil auger (5 cm outside diameter × 1.5 m tube length), by transferring about 0.5 kg soil samples to air-tight polypropylene containers (Lacontainer) so that the soil filled them to the brim (to prevent changes in the chemical composition). After that soils were transported to the laboratory. The cobble (cb: $75 < d \leq 200$ mm) and gravel (g: $2 < d \leq 75$ mm) fractions present in the soil material were removed. The soil samples for analyses of studied elements were prepared in the same way as mushroom samples (drying, grinding and mineralization).

Analytical method and calculation

Concentrations of studied elements in mushrooms and soils were analysed by flame atomic absorption spectrometry (Al, Ba, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sr, Zn) and atomic emission spectrometry (Ca, K, Mg, Na), using an Agilent Technologies AA Duo – AA280FS/AA280Z spectrometer (Agilent Technologies, Mulgrave, Victoria, Australia) equipped only with one-elemental Varian hollow-cathode lamps (HCLs). Total Hg concentration was analysed by cold vapour atomic absorption spectrometry (CVAAS) using the same spectrometer AA Duo with the VGA-77 (wave length – 253.7 nm; slit width – 0.5R nm; lamp current – 4 mA) and the 1 g/L mercury standard (SpectraPure, Arlington, Texas). Calibration curves were prepared every time before the analysis with four replicates per each element concentration (Table 1).

Efficiency of element accumulation was characterized using the bioconcentration factor (BCF) calculated according to Gast et al. [1988] as the ratio of element concentration in a mushroom fruiting body to the concentration of the same element in the soil, where the mushroom was growing.

Statistical methods

Results recorded in the course of the conducted chemical analyses were subjected to statistical analyses with the use of STATISTICA v 8.0 software (StatSoft Polska). In order to compare contents of elements in samples Tukey's multiple comparison procedure was used, with identical letters in rows or columns denoting a lack of differences at the significance level $\alpha = 0.05$. Cluster analysis of elements was conducted using the Ward method. Cases were grouped based on Euclidean distances. Moreover, values of Pearson's correlation coefficients were calculated for correlations between concentrations of the metal in mushrooms and in soil.

RESULTS

The concentration of minerals in mushrooms was generally dependent on the mushroom species and soil. A graphical presentation of results by the Ward method indicated two groups of elements accumulated in a similar way (similar values of Euclidean distances). The first group comprises Ba, Cd, Co, Ni, Hg, Pb,

Table 1. Experimental conditions of used methods and statistical parameters of the calibration lines

Element	Al	Ba	Ca	Cd	Co	Cu	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
Technique	FAAS	FAAS	AES	FAAS	FAAS	FAAS	AES	AES	FAAS	AES	FAAS	FAAS	FAAS	FAAS
Wavelength nm	309.3	553.6	422.7	228.8	240.7	324.8	766.5	285.2	279.5	589.0	232.0	217	460.7	213.9
Slit width nm	0.5	0.5	0.5	0.5	0.5	0.5	0.2	0.5	0.2	0.2	0.2	1.0	0.5	1.0
Lamp current, mA	9	20	–	4	7	4	–	–	5	–	4	9	10	5
Model	Quadratic – provides a second order least squares line forced through zero													
Sensitivity, B(x)	0.021	0.006	0.013	0.17	0.07	0.02	0.002	0.003	0.002	0.004	0.04	0.03	0.06	0.07
LOD, $mg \cdot kg^{-1}$	0.052	0.013	0.016	0.01	0.21	0.19	0.004	0.002	0.003	0.016	0.15	0.14	0.10	0.03
Minimum concentration $C_{min}/mg \cdot kg^{-1}$	12.441	0.247	3.977	0.29	0.27	2.94	13 700	123.405	12.476	15.844	0.21	0.66	0.11	1.79
Maximum concentration $C_{max}/mg \cdot kg^{-1}$	103.214	3.465	376.553	2.67	3.98	19.54	32 900	608.155	75.104	142.781	4.89	18.82	1.99	20.86
Correlation coefficient r	0.9992	0.9994	0.9999	0.9995	0.9997	0.9989	0.9999	0.9998	0.9992	0.9999	0.9996	0.9992	0.9993	0.9988

FAAS – flame atomic absorption spectrometry.
AES – atomic emission spectrometry.
LOD – limit of detection.

Sr, Cu, Mn, Zn and Ca, whereas the other group of elements is composed of those with significantly higher concentrations, i.e. K, Mg, Na, Zn and Fe (Fig. 1).

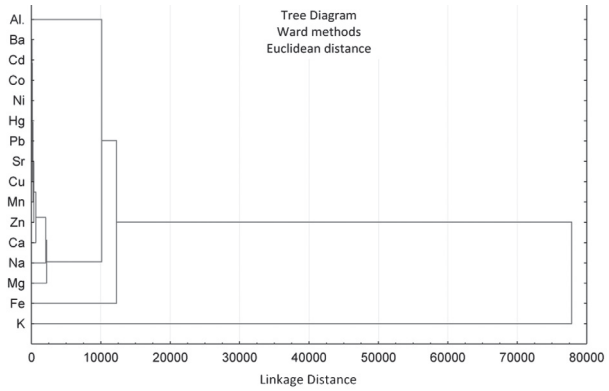

Fig. 1. Horizontal hierarchical tree plot for all elements and for all mushrooms species

The average concentrations and standard deviation (SD) for each of tested elements within a individual species was calculated. The low value of the standard deviation in most cases shows a limited variation in the concentrations of the analysed elements determined for particular mushroom species. Among the analysed elements the greatest variability was observed for Hg concentration in all tested mushroom species. A significantly higher value than the standard deviation was also shown for Cd in mushroom samples of *B. radius*, *B. chrysenteron*, *B. edulis*, *B. subtomentosus* L., *M. procera* and for Cu in mushroom samples of *B. radius*, *B. edulis*, *B. subtomentosus* L., *M. procera* and *T. felleus*.

For all tested elements, the lowest and the highest concentration values (mg/kg d.m.) were determined for: Al: 12.50 (*C. violaceus* L.) – 42.84 (*L. perlatum*), Ba: 0.25 (*S. luteus* (L.) – 2.81 (*T. felleus*), Ca: 3.98 (*T. felleus*) – 185.09 (*L. perlatum*), Cd: 0.91 (*B. badius*) – 22.72 (*B. chrysenteron*), Co: 1.82 (*B. badius*) – 8.47 (*L. salmonicolor*), Cu: 8.89 (*B. calopus*) – 80.45 (*B. badius*), Fe: 46.78 (*B. badius*) – 589.39 (*B. badius*), Hg: 0.87 (*H. aurantiaca*) – 6.83 (*B. badius*), K: 10 287.77 (*B. badius*) – 91 904.56 (*B. badius*), Mg: 421.70 (*S. granulatus*) – 1119.74 (*B. chrysenteron*), Mn: 8.74 (*B. badius*) – 66.85 (*B. badius*), Na: 31.51 (*B. chrysenteron*) – 1252.09 (*B. badius*), Ni: 0.82 (*B. badius*) – 7.88 (*B. badius*), Pb: 0.04 (*B. chrysenteron*) – 1.73 (*B. badius*), Sr: 0.14 (*B. badius*) – 3.87 (*M. procera*) and Zn: 40.55 (*B. badius*) – 166.03 (*B. chrysenteron*).

The applied Garbiel procedure of objects division made it possible for particular metals to identify the groups, which was the edible mushroom species with similar element concentrations in fruiting bodies. For the following elements the numbers of species in groups were as follows: 3 for: Ba, 4 for: Al, Co, Cu, Fe, Hg, Pb and Sr, 5 for: Ca, Cd, K, Mn, Na, Ni and Zn, 6 for Mg. Table 2 and 3 present the highest average concentration values for studied elements in tested mushroom species.

All presented concentrations were included in the first objects group – mushroom species with the highest concentration of a particular element. Additionally, for a comparison of accumulation efficiencies for the analysed elements between particular mushroom species, the Tukey test was used and values presented in Tables 2 and 3 show the highest accumulation of a majority of the elements by *C. rhacodes*, *L. perlatum*, *G. cyanescens* and *Lactarius salmonicolor* mushroom species. On the other hand, the lowest concentration was observed in *M. procera* and *C. cibarius*. The accumulation efficiency for the tested elements was also examined in 2 groups, i.e. lamellar and tubular mushrooms. Significantly lower accumulation rates for the elements were found in the lamellar mushrooms in contrast to the tubular fungi.

The Pearson's coefficient of correlation (Table 4) between metal concentrations in mushrooms and in soil showed that the metal concentrations were influenced by the species and by the soil characteristics. The correlation was significant for all tested mushroom species. Additionally, the accumulation efficiency of selected elements by tested mushroom species was estimated using the bioconcentration factor (BCF). BCF > 1 was recorded for a majority of mushroom species in case of: Cd (4.62-0.17), Co (2.56--0.86), Cu (9.89-0.73), Hg (140.28-2.09), K (1.59--0.09), Na (2.29-0.14), Ni (1.48-0.10), Pb (1.67-0.19), Sr (1.18-0.02) and Zn (7.30-1.52). Generally, for the other elements: Al (0.05-0.01), Ba (0.15-0.01), Ca (0.61-0.03), Fe (0.58-0.02), Mg (0.89-0.11), BCF values were below 1, which indicates no accumulation of these elements.

Table 2. Highest concentration values of elements (mg·kg^{-1} d.w.) in the tested mushroom species (mean ±SD and range)

Species	Al	Ba	Ca	Cd	Co	Cu	Fe	Hg
B. calopus		2.34 ±0.07[a]						
		(2.28-2.44)						
B. chrysenteron				9.07 ±5.06[a]				
				(3.98-22.72)				
C. viscosa						53.34 ±0.50[a]		
						(52.64-53.81)		
C. rhacodes	38.94 ±0.65[a]	1.76 ±0.03[a]	140.7 ±0.43[a]	8.83 ±0.14[a]	7.49 ±0.03[a]	79.87 ±0.1[a]	481.87 ±5.40[a]	
	(38.14-39.73)	(1.72-1.80)	(140.27-141.29)	(8.64-8.95)	(7.45-7.53)	(79.75-79.99)	(475.79-488.91)	
G. cyanescens				9.41 ±0.08[a]			434.37 ±1.31[a]	6.90 ±0.04[a]
				(9.35-9.52)			(432.99-436.14)	(6.85-6.94)
H. aurantiaca	38.37 ±0.79[a]	1.47 ±0.03[a]						
	(37.26-38.95)	(1.43-1.51)						
L. salmonicolor					8.44 ±0.03[a]			
					(8.37-8.47)			
L. versipelle		1.80 ±0.05[a]						
		(1.75-1.86)						
L. perlatum	42.29 ±0.50[a]	1.91 ±0.04[a]	184.58 ±0.56[a]		6.89 ±0.05[a]	64.62 ±1.54[a]	417.42 ±3.28[a]	
	(41.64-42.84)	(1.85-1.95)	(183.79-185.09)		(6.83-6.94)	(62.57-66.30)	(412.87-420.48)	
S. gravillei		1.87 ±0.25[a]					325.82 ±145.92[a]	
		(1.61-2.19)					(177.99-478.44)	
T. felleus		1.52 ±0.94[a]						
		(0.49-2.81)						
X. rebellus				10.58 ±1.04[a]				
				(9.46-11.76)				

d.w. – dry weight.

Table 3. Highest concentration values of elements (mg·kg^{-1} d.w.) in the tested mushroom fruiting bodies (mean ±SD and range)

Species	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
B. calopus						1.39 ±0.03[a]		
						(1.35-1.42)		
B. edulis					5.15 ±0.97[a]			
					(4.24-6.94)			
B. luridus	17 996.82 ±38.8[a]			803.69 ±3.79[a]				
	(17 953.04--18 047.37)			(798.67-807.84)				
C. rhacodes				747.28 ±2.34[a]	5.81 ±0.07[a]	1.31 ±0.00[a]		141.27 ±1.63[a]
				(745.08-750.53)	(5.73-5.89)	(1.30-1.32)		(139.00-142.77)
G. cyanescens	17 836.71 ±5.02[a]		38.45 ±0.33[a]	576.59 ±10.16[a]				
	(17 830.56--17 842.86)		(37.99-38.75)	(562.40-585.61)				
L. salmonicolor				900.23 ±3.03[a]	5.01 ±0.03[a]	1.15 ±0.01[a]		
				(896.36-903.74)	(4.97-5.04)	(1.12-1.15)		
L. perlatum		1495.82 ±3.45[a]		706.25 ±332.94[a]	5.88 ±0.02[a]	1.30 ±0.01[a]		164.83 ±1.25[a]
		(1491.35-1499.75)		(703.56-707.98)	(5.85-5.91)	(1.30-1.32)		(163.10-166.03)
R. caperata	19 034.20 ±111.59[a]							
	(18 878.56--19 134.57)							
S. bovinus (L.)							2.25 ±1.78[a]	
							(0.44-4.08)	
S. gravillei						1.23 ±0.20[a]		
						(1.02-1.44)		

d.w. – dry weight.

Table 4. Correlation between tested elements concentration in particular mushroom fruiting bodies species and soil

Mushroom species	r
B. badius	0.90771**
B. calopus	0.95139***
B. chrysenteron Bull.	0.93253***
B. edulis Bull.	0.86897**
B. luridus	0.95090***
B. subtomentosus L.	0.91719**
C. viscosa	0.90699**
C. cibarius	0.91057**
C. rhacodes	0.71198*
C. violaceus (L.)	0.93512***
G. cyanescens	0.90837**
H. aurantiaca	0.95762***
L. salmonicolor R.	0.74487*
L. versipelle	0.95566***
L. perlatum	0.75594*
M. procera	0.92874**
R. caperata	0.96711***
S. bovinus (L.)	0.95792***
S. granulatus	0.92424**
S. gravillei	0.88699**
S. luteus (L.)	0.91968**
T. felleus	0.89837**
X. rebellus	0.92087**

*Correlation significant at the 0.1 level.
**Correlation significant at the 0.01 level.
***Correlation significant at the 0.001 level.

DISCUSSION

Accumulation of elements in mushrooms growing in Poland

Efficiency of elements accumulation in wild growing edible mushrooms collected from Poland has been repeatedly described in the available literature. Our results point at a significant accumulation of selected elements (especially Cd, Hg, K and Zn) by majority of tested mushroom species, but to provide the actual estimation of mushroom potential to elements accumulation, some of the most interesting literature source should be compared. Gucia et al. [2012] analysed the accumulation efficiency of 20 elements in Parasol Mushroom (*M. procera*) fruiting bodies collected from Northern Poland. The presented results were generally higher than those in our study for all analysed elements except Ni. What is more, results presented by Gucia et al. [2012] were focused on accumulation efficiency in mushrooms collected from only one place (located in Northern Poland), while in our study the selected locations were scattered practically throughout Poland, where significantly wider concentration ranges were recorded. Additionally, we analysed the amount of elements in fruiting bodies with no division into the cap and stipe, which in part can explain the differences in both results.

Obtained results were compared with data described by Falandysz et al. [2004], where Hg cobcentration in 15 wild growing mushroom species collected near the city of Koszalin (North Poland) were analysed. When comparing both sets of data, for the same 3 mushroom species (*S. bovinus* (L.), *S. grevillei* and *S. luteus* (L.)), the higher Hg accumulation was observed in our study. These differences are a result of significant differences in mushroom sample collection times (1997-1998 and 2011). Also, similar differences were observed in our study and in the results described by Chudzyński et al. [2011], where the authors analysed the concentration of Hg in *S. luteus* mushrooms (caps and stipes), collected from eight spatially scattered sites in Northern Poland in 2002-2007.

The Hg content in *S. luteus* caps and stipes were 0.16 ±0.04 and 0.09 ±0.02 mg/kg DW, respectively, while in our study the average concentration of Hg in the whole fruiting bodies was 2.79 ±1.27 mg/kg DW. The ranges of Hg concentrations in mushrooms collected from similar locations and BCF values were also different and generally higher in our studies (C_{Hg} from 1.28 to 4.74 mg/kg DW and BCF from 27.88 to 115-67) than those presented by Chudzyński et al. [2011] (Hg_{cap} from 0.1 to 0.23 mg/kg DW, Hg_{stipe} from 0.062 to 0.13 mg/kg DW and BCF_{cap} from 7.6 to 23 and BCF_{stipe} from 3.6 to 10).

Significant differences in Hg accumulation efficiency were also confirmed by our results and by Falandysz and Gucia [2008], who tested *M. procera* caps and stalks, collected from 15 sites in Poland between

1995 and 2003. Concentration of Hg in our *M. procera* fruiting bodies was significantly higher at 1.64 ±0.31 (1.3-2.0) mg/kg DW than that presented by Falandysz and Gucia [2008], but simultaneously BCF values were similar in our study (C_{Hg}: 29.83 ±3.86 and range: 26.37--35.86) and presented by Falandysz and Gucia [2008]: (Hg_{cap} 19 ±12 and Hg_{stipe} 15 ±11; BCF_{cap} from 7.9 to 42 and BCF_{stipe} from 5.6 to 37), which indicates a significant relationship between Hg concentrations in soil and its accumulation in mushrooms. The greatest differences were observed between our results and those described by Falandysz et al. [2012] who analysed Hg concentration in *C. cibarius* fruiting bodies collected in Poland between 1998 and 2008. Generally for all the described areas of sample collection, Hg concentration (0.029 ±0.007 mg/kg DW) and calculated BCF values (1.3-0.5) were significantly higher in our study (C_{Hg}: 1.77 ±0.27 mg/kg DW and BCF: 28.34-52.67).

On the basis of results presented in literature, it is difficult to state the same relationship between mushroom species and particular elements or elements accumulation efficiency for all elements jointly. Falandysz and Bielawski [2001] analysed Hg concentration in edible mushroom species collected near the town of Augustów. The same analysed mushroom species were: *B. edulis*, *C. cibarius*, *L. versipelle*, *R. caperatus* and *S. luteus* (L.). The concentration of Hg in our study was generally higher (especially for *C. cibarius* and *S. luteus* (L.)) and similar in particular mushroom species, whereas Falandysz and Bielawski [2001] pointed at significant differences between tested mushroom species. On the other hand, our observations indicate changes in the accumulation efficiency of elements by selected mushroom species. For example, Rudawska and Leski [2005] analysed 8 mushroom species collected from the Notecka forest (west-central Poland) in 1999/2000. Significantly lower concentrations of Al, Cd, Fe, Mn and Zn and higher Pb concentrations in *S. luteus* fruiting bodies were reported by those authors in relation to our study. Some places described by Rudawska and Leski [2005] were the same, where we collected our experimental materials, with our observation indicating higher accumulation levels of tested elements by *S. luteus* fruiting bodies 11 years later.

It is of interest to compare our results and those reported by Falandysz et al. [2001], who analysed the concentration of 38 elements in 18 mushrooms species collected from Northern Poland in 1994. The same tested mushroom species were: *B. edulis*, *C. cibarius*, *M. procera*, *S. bovinus* and *S. luteus*. What is more, lower concentrations of Ca, K and Mg and higher Fe concentrations were observed in our mushrooms fruiting bodies in comparison to results presented by Falandysz et al. [2001]. For the other analysed elements their accumulation efficiency – especially Pb and Sr – was similar. It should also be noted that their accumulation strictly depends to the investigated mushroom species. It should also be noted that the lamellar mushrooms accumulate fewer metal ions as compared to the tubular mushrooms. It is related to the fact that there is less mycelium in the substrate, and it is characterised by a more rapid growth and shorter life span [Cocchi et al. 2006] as a results of the specific mycelium structure, the exposed surface of vegetative cells and the large surface hyphae. At the same time, the ability to metals accumulation by fungi is associated with specific proteins – metallothionein [Malinowska et al. 2004].

Accumulation of elements in mushrooms collected worldwide

To discuss the problem of the presence of elements in mushroom not only in Poland, we would like to compare our results with data presented by authors who tested mushrooms collected from other countries. Kalač [2010] showed an interesting review of trace element concentrations in selected mushroom species (*B. edulis*, *M. procera* and *S. grevillei*) between 2000 and 2009, reporting similar results to ours with the exception of Fe and Mn contents (generally lower and higher than in our study, respectively). When comparing results of both works (concerning mushroom species), it is not possible to indicate species with the highest accumulation of all elements jointly. The particular mushroom species were selective in terms of their accumulation of elements (both macro- and micro-elements), which was presented by Cocchi et al. [2006], who analysed 60 species of common mushroom species collected in Italy. The same mushroom species were: *B. edulis*, *C. cibarius*, *L. perlatum*, *M. procera*, *R. caperatus*, *S. luteus* (L.) and *X. rubellus*. In our study, concentrations of Cd, Hg and Pb were similar to those presented by Cocchi et al. [2006] except for *R. caperatus* and *X. rebellus*.

Moreover, for some elements such as Cd, Co, Hg, Ni, Pb and Sr, the differences between tested mushroom species were not significant, what is similar to date presented by Campos et al. [2009] or Campos and Tejera [2011], who compared respectively 4 and 19 elements accumulation in 12 and 15 edible and non-edible mushroom species collected from central Spain. Additionally in many cases, the differences between varieties of the same mushroom specie are greater than differences between different species. It can suggest that edible mushrooms can be used as the indicators of environment pollution level but only as the whole, not concrete mushroom specie.

Mushroom intakes and consequence of their presence in human diet

Elements examined in our study may be divided into two groups: biologically important elements (Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Sr and Zn) and toxic elements (Al, Ba, Cd, Hg and Pb). In case of the first group, at concentration levels (range), the human organism immediately starts to develop a specific response (defense mechanisms), therefore amounts of these elements analysed in this work suggest that the consumption of one meal containing above 30 g dry mass of mushrooms per day, of whichever edible mushroom species, is safe for human health.

Commission Regulation (EC) No 1881/2006 of 19 December 2006, establishing maximum levels for certain contaminants in foodstuffs, points to legal restrictions relating to the maximum permissible concentrations of heavy metals (toxic) in plant foods. The regulations apply to Pb (vegetables and cereal products at 0.1-0.2 mg/kg), Cd (vegetables at 0.1-0.2 mg/kg), and Hg in fish and seafood products (1.0-0.1 mg/kg). In the case of fungi the regulations concern mainly pollution in cultivated mushrooms only if 1.0 mg/kg is allowed in fungi other than cultivated mushrooms.

Humans are likely to require at least 25 mineral elements for their well-being [Stein 2010]. Plants are the dietary sources for most of these elements. Regrettably, mineral malnutrition is prevalent in both developed and developing countries and it is estimated that up to two-thirds of the world's population might be at risk of deficiency of one or more essential mineral element [White and Broadley 2009]. The mineral elements most commonly lacking in human diets are Fe, Zn, I, Se, Ca, Mg and Cu [White and Broadley 2009, Stein 2010].

Despite the fact that wild edible mushrooms may be important sources of macro- and microelements, we should pay attention to the elements provided to the human diet, namely heavy metals. In case of this group, the actual problem with the presence of these elements in vegetables, fruit and described in fungi on a large scale, is connected with their toxicity for human health. Average amounts of Al, Ba, Cd, Hg and Pb in one 30 g DW portion of mushrooms supply to the human body about 0.79, 0.03, 0.15, 0.07 and 0.03 mg, respectively. Compared to green plants, mushrooms can build up large concentrations of some heavy metals, particularly cadmium, mercury, copper and lead [Isiloglu et al. 2001, Turkekul et al. 2004). Mushrooms are valuable health foods, low in calories, high in vegetable proteins, iron, zinc, chitin, fibre, vitamins and minerals, but we have to bear in mind the fact that due to their ability of heavy metal accumulation they may also pose a potential human health risk.

However, knowledge on the nutritional value of wild growing mushrooms is limited when compared with other vegetables. It seems that mushrooms have still much more to offer, but it is necessary to focus all studies on establishing a real metabolic profile for one species with the view to promote it as a hyperaccumulator or bioindicator for one metal element. Different heavy metals such as As, Cd, Ni and Hg, when accumulated at high concentrations in mushrooms, are toxic to humans; on the other hand, many elements are essential for the human metabolism, such as Fe, Zn, Mn, Cu, Cr and Se, but at low concentrations, because they are enzyme activators. These essential elements become toxic in case of their excessive concentrations. It is well known that the content of heavy metals is related to the species of mushrooms, the sample collection area, the age of fruiting bodies and the distance from any source of pollution. For this reason all mushroom species tested in this study may be consumed, but only sporadically.

CONCLUSION

Human diet is enriched by an addition of mushrooms especially in Central European countries, where it is common to consume high amounts of mushrooms. For this reason, knowledge on the composition of elements in mushroom fruiting bodies is important.

In our study the highest concentrations of K, Mg, Na, Zn and Fe were confirmed. These elements (especially K, Mg and Na as macroelements) generally are not toxic for humans, therefore even if the mushrooms were consumed continuously, they cannot cause health problems. Additionally, we observed significantly lower concentrations of Ba, Cd, Co, Hg, Ni, Pb and Sr. These elements are microelements and some of them are toxic for humans, especially at higher doses, therefore in our opinion an occasional intake of the analysed mushrooms is not dangerous for humans. Of course, some toxic elements (Hg or Pb) are accumulated in human organs (liver, bones, kidneys), but these elements are provided also with other foodstuffs (vegetables, fruits, meat) or drinks.

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ZAWARTOŚCI PIERWIASTKÓW W WYBRANYCH GATUNKACH GRZYBÓW JADALNYCH ROSNĄCYCH W POLSCE I ICH WPŁYW NA ZDROWIE CZŁOWIEKA

STRESZCZENIE

Wprowadzenie. Spożycie dziko rosnących grzybów w wybranych regionach Europy (szczególnie wschodniej i centralnej) jest znaczące. Ponadto grzyby są zdolne do pobierania znacząco większych ilości pierwiastków zarówno odżywczych, jak i toksycznych, dlatego wiedza dotycząca poziomu ich stężeń oraz zmian w ich zawartości jest ważna dla ludzkiego zdrowia.

Materiał i metody. W owocnikach 23 dziko rosnących gatunków grzybów jadalnych oznaczano 11 pierwiastków biologicznie istotnych (Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Zn) oraz 5 toksycznych (Al, Ba, Cd, Hg, Pb). Badane grzyby pobierano z wybranych miejsc zlokalizowanych na terenie niemalże całej Polski. Efektywność akumulacji pierwiastków w grzybach oraz w glebach analizowano metodami atomowej spektrometrii absorpcyjnej z atomizacją w płomieniu (FAAS) oraz atomowej spektrometrii emisyjnej (AES).

Wyniki. Największymi stężeniami wyróżniały się: K, Mg, Na, Zn i Fe, natomiast istotnie mniejszymi: Ba, Cd, Co, Hg, Ni, Pb oraz Sr. Ponadto stwierdzono istotnie mniejszą akumulację pierwiastków przez grzyby blaszkowate względem owocników grzybów rurkowych.

Wnioski. Biorąc pod uwagę prezentowane wyniki, można stwierdzić, że sporadyczne spożywanie badanych gatunków grzybów nie jest niebezpieczne dla człowieka. Oczywiście metale ciężkie, jak choćby Pb czy Hg są gromadzone w ludzkich organach, ale wymienione pierwiastki są także dostarczane z innym pożywieniem (warzywa, owoce, mięso) czy napojami.

Słowa kluczowe: akumulacja, grzyby jadalne, pierwiastki śladowe, zdrowie człowieka

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