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The content of copper, zinc, and nickel in the selected species of edible mushrooms

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Abstract
The aim of the research was to evaluate the accumulation level of copper, zinc and nickel in forest mushrooms – Bay Bolete (Xerocomus badius), Saffron Milk Cap (Lactarius deliciosus), Rough-Stemmed Bolete (Leccinum scabrum), Slippery Jack (Suillus luteus) and Parasol Mushroom (Macrolepiota procera). The analysed mushrooms were obtained from growth forests located in the Masovian Voivodeship in the following counties: Siedlce, Sokołów, Łosice and Łuków. Total content of metals was determined using the method of atomic emission spectroscopy with inductively coupled plasma, after the earlier mineralisation of materials 'by dry combustion' in a muffle furnace at the temperature of 450°C, and after melting of ash in a 10% solution of HCl. In the soil samples taken from the places where the tested mushrooms occur, pH in 1 mol KCl·dm-3 and total content of copper, zinc and nickel were determined by the ICP-AES method after earlier mineralization in mixture of concentration HCl and HNO3 (3:1) in a microwave system. Test results were statistically analysed with the use of software STATISTICA 12 PL (STATSOFT, TULSA, USA). The analysed mushrooms had diverse content of the determined metals. The highest total average content of copper and zinc was present in Bay Bolete: 34.83 mg · kg-1d.m. for Cu and 155.50 mg · kg-1d.m. for Zn, and the highest average content of nickel was contained in Rough-Stemmed Bolete – 2.98 mg · kg-1d.m.. The lowest average content of copper and zinc was determined in Rough-Stemmed Bolete: 11.98 mg · kg-1d.m. for Cu and 91.90 mg · kg-1d.m. for Zn, and lowest total average content of nickel was present in Bay Bolete – 1.05 mg · kg-1d.m.
No excessive accumulation of examined heavy metals was stated in the analysed mushrooms species.

1. INTRODUCTION

Mushrooms from natural sites are products rich in mineral substances, including valuable macro- and microelements. However, many researchers [Bielawski and Falandysz 2008, Chojnacka and Falandysz 2007, Soylaket et al. 2005, Gastet et al. 1988, Falandysz et al. 2002, Falandysz et al. 2006] pay attention to the fact that specific fungi species are able to take numerous metallic elements from soil and accumulate them in their fruiting bodies in concentrations considerably exceeding their amounts in soil. Pająk [2016] confirmed high accumulation of zinc in Bay Bolete (*Xerocomus badius*), coming from areas heavily contaminated with this metal, and at the same time indicated the possibility of using this species as a bioindicator of environmental contamination by zinc. Nevertheless, Kuusi [1981] believed that there are other mushroom species that are characterised by high resistance to excessive content of heavy metals in soil and have no tendency to accumulate them in their fruiting bodies. The process of taking metallic elements and metalloids from soil, their transport in the mycelium and fruiting body, distribution and accumulation is the result of many genetic and environmental factors, among which, the most important are soil pH, redox potential, content of organic matter, enzymatic activity, and chemical forms of metals [Falandysz et al. 2002, Falandysz et al. 2006].
Karmańska and Wędzisz [2010] stated that metals are accumulated in fruiting bodies of mushrooms as a consequence of binding with proteins and metallothioneins.
Considering the growing consumption of mushrooms from natural sites, both in Poland, as well as in Europe, research was undertaken in order to determine the

Table 1. Descriptive statistic of total content of copper, zinc and nickel ($mg \cdot kg^{-1}$ DM) in analysed mushrooms

Element	Mean	Minimum	Maximum	SD	RSD
Bay Bolete *(Boletus badius)*					
Cu	34.83^{d}	31.15	37.65	1.94	5.57
Zn	155.50^{c}	128.80	177.20	18.19	11.70
Ni	1.05^{a}	0.80	1.40	0.18	16.87
Saffron Milk Cap *(Lactarius deliciosus)*					
Cu	12.88^{a}	10.92	14.56	1.16	8.99
Zn	145.10^{c}	122.80	168.40	12.73	8.77
Ni	2.07^{b}	1.82	2.32	0.18	8.70
Rough-Stemmed Bolete (*Leccinum scabrum*)					
Cu	11.98^{a}	9.85	14.91	1.63	13.61
Zn	91.90^{a}	79.90	111.40	10.40	11.32
Ni	2.98^{c}	2.46	3.68	0.38	12.84
Slippery Jack *(Suillus luteus)*					
Cu	19.90^{c}	16.92	21.45	1.72	9.10
Zn	122.00^{b}	100.80	141.60	10.64	8.72
Ni	2.71^{c}	1.82	3.42	0.47	17.17
Parasol Mushroom (*Macrolepiota procera)*					
Cu	15.44^{b}	13.92	17.16	1.14	7.38
Zn	107.00^{ab}	92.60	126.40	9.75	9.11
Ni	2.84^{c}	2.46	3.46	0.29	10.36

Comments: SD – standard deviation, RSD – relative standard deviation (%)
$^{a, b, ab, c}$ – homogeneous groups of means at a < 0.05

accumulation level of copper, zinc and nickel in forest mushrooms – Bay Bolete (*Xerocomusbadius*), Saffron Milk Cap (*Lactariusdeliciosus*), Rough-Stemmed Bolete (*Leccinumscabrum*)**,** Slippery Jack (*Suillusluteus*) and Parasol Mushroom (*Macrolepiota procera*).

2. MATERIAL AND METHODS

The analysed mushrooms came from the growth forests located in the Masovian Voivodeship in the following counties: Siedlce, Sokołów, Łosice and Łuków. They were classified as edible mushrooms according to the Regulation of the Minister of Health of June 12, 2018 [Journal of Laws 2018, item 1281].
The samples were obtained in months September–October 2017; 20 samples were taken for each fungi species, and 5 fruiting bodies comprised the sample unit. The total content of metals was determined using the method of atomic emission spectroscopy with inductively coupled plasma, after the earlier mineralisation of materials 'by dry combustion' in a muffle furnace at the temperature of 450°C, and after dissolution of ash in a 10% solution of HCl. In the soil samples taken from the places where the tested mushrooms occur, pH in 1 mol $KCl \cdot dm^{-3}$ and total content of copper, zinc and nickel were determined by the ICP-AES method after the earlier mineralization in mixture of concentration HCl and HNO_3 (3:1) in a microwave system. In order to verify the obtained results, an analysis of standard reference material (IC-INTC-CS-M-1 Mushroom (*Suillus bovinus*) – Trace elements) produced by the Institute of Nuclear Chemistry and Technology in Warsaw) analysis was carried out. The percentage recovery of the content of the investigated metals was for Cu-94%, Zn-104%. Test results were statistically analysed with the use of software STATISTICA 12PL (STATSOFT, TULSA, USA). In order to verify the significance of differences between the average content of the elements determined in the specific mushroom species, one-factor analysis of variance and Tukey's HDS test were carried out. The average values were combined into homogeneous groups at the level of significance $\alpha < 0.05$. An analysis of linear correlation of total content of elements determined in mushroom samples was additionally performed.

3. RESULTS AND DISCUSSIONS

The examined soils were characterized by the acid reaction (value of pH in 1 mol $KCl \cdot dm^{-3}$ ranged from 4.4 to 5.6) and contained 5.12–7.82 mg $Cu \cdot kg^{-1}$, 17.45–46,04 mg $Zn \cdot kg^{-1}$ and 4.00–7.26 mg $Ni \cdot kg^{-1}$. The tested species of edible mushrooms had diverse content of copper, zinc and nickel, which demonstrates that their chemical composition depends not only on soil characteristics, but is a genetically predetermined specific property (Table 1). The mushrooms contained on average from 11.98 to 34.83 mg $Cu \cdot kg^{-1}$ d.m., from 91.90 to 155.50 mg $Zn \cdot kg^{-1}$ d.m., and from 1.05 to 2.8 mg $Ni \cdot kg^{-1}$ d.m.

Table 2. Linear correlation coefficients between the content of Cu, Zn and Ni in the analysed mushrooms and soil properties

Selected species	Soil properties	Content in analysed		
		Cu	Zn	Ni
Bay Bolete	pH metal content	-0.734* 0.756*	0.106 0.734*	0.472 0.596
Saffron Milk Cap	pH metal content	0.0464 0.646*	-0.067 0.855*	-0.223 0.849*
Rough-Stemmed Bolete	pH metal content	0.662* 0.806*	-0.115 0.844*	0.408 0.831*
Slippery Jack	pH metal content	0.284 0.713*	-0.514 0.912*	0.072 0.277
Parasol Mushroom	pH metal content	-0.199 0.615	0.323 0.806	-0.564 -0.389

Comments: * - significant at a < 0.05

Kalać et al. [1996], Kalac and Svoboda [2000], Bielawski and Falandysz [2008], Sas-Golak et al. [2011], as well as Adamiak et al. [2013] indicated in their research variability of the content of metallic elements and metalloids depending on the species of wild edible mushrooms. Among the analysed species, the highest total average content of copper and zinc was determined in Bay Bolete, respectively (mg·kg^{-1} d.m.): Cu – 34.83 (range from 31.15 to 37.65), Zn – 155.50 (range from 128.80 to 177.20) and of nickel in Rough-Stemmed Bolete – 2.98 (range from 2.46 to 3.68).

The lowest total average content of copper and zinc was present in Rough-Stemmed Bolete, respectively (mg·kg^{-1} d.m.): Cu – 11.98 (range from 9.85 to 14.91), Zn – 91,90 (range from 79.90 to 111.40), whereas the lowest total average content of nickel was present in Bay Bolete – 1.05 (range from 0.80 to 1.40). Karmańska and Wędzisz [2010] determined the average content of copper in Bay Bolete at the level from 36.8 to 43.6 mg·kg^{-1} d.m., of zinc within the limits of 44.0 to 47.1 mg·kg^{-1}d.m., whereas the amount of copper in Slippery Jack was in the range of values from 15.2 to 18.30 mg·kg^{-1} d.m., and zinc – 48.9 mg·kg^{-1} d.m. on average.

In the research carried out by Adamiak et al. [2013], regarding the heavy metal content in fruiting bodies of the selected forest fungi species from the Upland of Siedlce (the Wodynie municipality), the average content of copper, zinc and nickel in Bay Bolete amounted to respectively (mg·kg^{-1} d.m.): Cu – 23.4 (range from 22.3 to 25.4); Zn – 126 (range from 121.0 to 131.0) and Ni – 1.66 (range from 1.44 to 2.14), hence was close to the results obtained in own research.

Bielawski and Falandysz [2008] tested the content of the selected elements in the fruiting bodies of Rough-Stemmed Bolete, from the surrounding area of the city of Starachowice, and in that area, determined the content of copper in the range from 17.0 to 42.0 mg · kg^{-1} d.m. (21.0 on average), of zinc from 180.0 to 300.0 mg·kg^{-1} d.m. (200.0 on average) and of nickel from 0.28 to 0.64 mg·kg^{-1} d.m. (0.44 on average).

In the research carried out by Pająk [2016], regarding the level of accumulation of heavy metals in Bay Bolete picked in a heavily contaminated forest complex of the Świerklaniec Forest District, the Brynica sub-district, which is located in direct vicinity of the Zinc Mine 'Miasteczko Śląskie', the average zinc content was increased and amounted to 185.6 mg·kg^{-1} d.m. (range from 142.1 to 305.4). It confirms direct relationship between the amount of this metal in soil and its accumulation in the fruiting bodies of the tested species, and therefore, indicates the possibility of using Bay Bolete as the bioindicator of the environmental pollution level of zinc. The results obtained during own research have lower values than the ones gathered by Pająk [2016], whereas they are close to the results published by Bielawski and Falandysz [2008], Adamiak et al. [2013] and the results obtained in the research that was carried out earlier [Kuziemska et al. 2018].

Statistical calculation showed that the average content of metals in the analysed mushrooms was correlated with the selected soil properties (reaction and Cu, Zn, Ni content). Particularly noteworthy is the positive correlation between the content of zinc and copper in the fruiting bodies of all the mushrooms examined species and their content in the soil as well as between the content of nickel in the fruiting bodies of Saffron Milk Cap and Rough Stemmed Bolete and content of this metal in the soil (Table 2).

In the summary of the carried out research, it must be stated that the content of copper, nickel and zinc in the fruiting bodies of the analysed edible fungi species obtained from natural sites modifies their species, as well as the properties and chemical composition of the soil.

4. CONCLUSIONS

1. The analysed fungi species contained a varied amount of copper, zinc and nickel depending on their species.
2. The highest total average content of copper and zinc was determined in Bay Bolete, and the highest total average content of nickel in Rough-Stemmed Bolete.

3. The lowest total average content of copper and zinc was contained in Rough-Stemmed Bolete, and the lowest total average content of nickel was present in Bay Bolete.
4. The contents of copper and zinc in the fruiting bodies of the analysed fungi species were significantly correlated with their content in the soil.

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