



J. Serb. Chem. Soc. 86 (10) 927–940 (2021)
JSCS–5473

Macroelements versus toxic elements in selected wild edible mushrooms of the Russulacea family from Serbia

MARIJA DIMITRIJEVIĆ^{1*}, VIOLETA MITIĆ², DRAGAN ĐORĐEVIĆ²,
GORDANA POPOVIĆ³, NENAD KRSTIĆ^{2#}, JELENA NIKOLIĆ²
and VESNA STANKOV JOVANOVIĆ²

¹University of Niš, Faculty of Medicine, Boulevard of dr Zorana Đinđića 81, 18000 Niš, Serbia, ²University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradaska 33, 18000 Niš, Serbia and ³University of Belgrade, Faculty of Pharmacy, Department of General and Inorganic Chemistry, Vojvode Stepe 450, 11000 Belgrade, Serbia

(Received 10 April, revised 19 May, accepted 24 May 2021)

Abstract: Three edible mushrooms of the Russulacea family (*Lactarius deliciosus*, *Lactarius sanguifluus* and *Lactarius semisanguifluus*), most frequently consumed in Serbia, were analyzed using the ICP-OES technique to evaluate the content of K, P, Ca, Mg, Na, Al, As, Cd and Pb, both in cap and stipe. Corresponding soils were analyzed, too. Based on the obtained values for the elemental composition of the mushrooms and the soil, bioaccumulation and translocation factors were calculated. All the examined mushrooms species were recognized as bioexclusors of analyzed toxic elements, but bioaccumulators of K, P and Ca. The studied mushrooms are good sources of macroelements. One portion of 300 g of fresh mushrooms had a significant contribution of K and P, exceeding 15 % of the recommended daily intake for the elements. On the contrary, mushrooms had a low potential to bioaccumulate toxic elements, and presented results indicated the regular consumption of wild edible mushrooms is safe for human health. Correlation analysis was applied to determine phosphorus's influence on the elements' content in the mushrooms and corresponding soils, demonstrating the most remarkable mushrooms' tendency to accumulate phosphorus.

Keywords: element composition; correlation analysis; bioaccumulation factor; translocation factor.

* Corresponding author. E-mail: marija.dimitrijevic@pmf.edu.rs

Serbian Chemical Society member.

<https://doi.org/10.2298/JSC210410038D>

INTRODUCTION

Nowadays, food is not just an energy source for human beings. It is required to be functional, to have medical properties, and thus to contribute to the well-being of the organism. The mushrooms are appreciated in diet due to their chemical and nutritional properties and their therapeutic and disease-preventing characteristics.¹ Although commercial mushroom species are used in the diet on a massive scale, the consumption of wild edible mushrooms is becoming increasingly popular in Serbia.

The elemental composition of mushroom represents a spectrum of macro and microelements. The abundance of macroelements such as P, K, Ca, Mg and Na is desired in the human diet, and their determination in edible wild-grown mushrooms is of great importance. Mushrooms can uptake large amounts of water and elements (*e.g.*, phosphorus, iron, potassium, cadmium, magnesium, copper and zinc) due to mycelium's extensive surface contact with the top layer of soil.² Mycelium is perfectly adapted to penetrate and access soil pore spaces. The fungal hyphae's vast surface area and physiology enable an effective absorption and bioconcentration of various metals, metalloids, and nonmetals.³ Despite many positive aspects of mushroom consumption, there are risks associated with their ingestion, such as poisoning with harmful elements, *e.g.*, mercury, lead, cadmium and arsenic, which might accumulate in mushrooms.⁴ These elements are considered hazardous because, with greater exposure, they can lead to increased health risks. A particular problem is the accumulation and deposition of certain elements in the human tissues, from which they are difficult to eliminate. The ability to accumulate heavy metals differs in certain types of mushrooms. Usually, element concentration in caps is higher than in other parts of fruiting bodies of mushrooms.⁵

A detailed review of the literature points to the lack of publication of the elements' content in the Russulacea family's mushrooms from Serbia. The aim of this paper was to identify the inorganic composition of three wild edible mushrooms: *L. deliciosus*, *L. sanguifluus* and *L. semisanguifluus*. Content of toxic elements (Al, As, Cd and Pb) and macroelements (K, P, Ca, Mg and Na) was determined in caps and stipes, as well as in corresponding soil substrates. The obtained values enabled a better understanding of the accumulation potential of the mentioned mushrooms because it was possible to calculate the translocation factor (TF) and bioaccumulation factor (BAF) for each element. Also, the nutritional value and possible risk of consuming wild edible mushrooms were determined.

EXPERIMENTAL

Chemicals and instrumentation for inorganic characterization

All reagents were analytical-reagent grade, purchased from Merck (Darmstadt, Germany). Multielement standard solutions for ICP analysis were purchased from Ultra Scientific (North Kingstown, RI, USA). Inorganic characterization (K, P, Ca, Mg, Na, Al, As, Cd and

Pb) of mushrooms and corresponding soil substrates were carried by an ICP-OES iCAP 6000, Thermo Scientific. In Table I are presented analytical parameters for ICP-OES that were used for all measurements.

TABLE I. ICP-OES instrumental parameters

Flush pump rate	100 rev. min ⁻¹
Analysis pump rate	50 rev. min ⁻¹
Nebulizer gas	0.7 L min ⁻¹
Coolant gas flow	12 L min ⁻¹
Auxiliary gas flow	0.5 L min ⁻¹
Plasma view	Axial
Flush time	30 s

The accuracy of method was determined using the European Reference Materials “ERM-CD281: K, Ca, Na, As, Cd and Pb.” The referenced value is reported in Table II.

TABLE II. Comparison of found element concentrations and certified values, and obtained recoveries (concentration±SD)

Element	Certified concentration, mg kg ⁻¹	Found concentration, mg kg ⁻¹	Recovery, %
K	34000	33000	97.0
P	2800	2700	96.4
Ca	6300	6000	95.2
Mg	1600	1550	96.9
Na	4000	3900	97.5
As	0.04±0.01	0.04±0.01	95.2
Cd	0.120±0.007	0.11±0.03	96.7
Pb	1.7±0.1	1.6±0.1	96.4

Quantification of wavelengths for each element, the detection limits (*LOD*), the limits of quantification (*LOQ*), and the correlation coefficients (*r*²) are represented in Table III.

TABLE III. Emission wavelengths, correlation coefficient of calibration curves, limit of detection (*LOD*) and limit of quantification (*LOQ*) for each element analyzed

Element	λ / nm	<i>r</i> ²	<i>LOD</i> / $\mu\text{g L}^{-1}$	<i>LOQ</i> / $\mu\text{g L}^{-1}$
K	766.5	0.9914	39.43	131.44
P	213.6	0.9995	6.93	23.10
Ca	393.4	0.9999	0.09	0.32
Mg	279.6	0.9999	0.12	0.41
Na	588.9	1	0.46	1.53
Al	308.2	0.9998	4.52	15.07
As	189.0	0.9995	2.76	9.19
Cd	226.5	0.9994	0.19	0.63
Pb	220.353	0.99966	2.42	8.05

All the experimental results were the mean ± standard deviation of three parallel measurements.

Sample collection

The mushroom samples (*Lactarius deliciosus*, *Lactarius sanguifluus* and *Lactarius semisanguifluus*) were identified as edible mushrooms belonging to the family Russulaceae. The samples of the species mentioned above were collected during 2020, in the rural, unpolluted part of the Sićevo gorge, in the forests dominated by pine, away from the road. The specimen vouchers were deposited in the Herbarium Moesiacum Nis (HMN), Department of Biology and Ecology, Faculty of Science and Mathematics, University of Niš, under the acquisition numbers 17, 18 and 19. The mushrooms were collected at three experimental points to overcome variability, taking approximately 200 g of each examined mushroom species. Mushroom samples were cleaned, cut, and separated into two parts: cap and stipe; for each mushroom species sampled, the soil, down to the depth of 10 cm, after removing the superficial organic layer.

Digestion of mushroom samples

The element content of mushrooms was determined by the wet mineralization using a modified procedure of Tüzen.⁶ One gram of each mushroom species was mixed with 15 mL oxi-acidic mixture consisting of HNO₃:H₂SO₄:H₂O₂ (4:1:1), heated up to 150 °C for 4 h, and diluted to 25 mL with deionized water. A blank sample was prepared in the same way.

Digestion of soil samples

According to Method 3050B,⁷ the pseudo total element contents of soils were determined. Weighted soil sample mass (1 g) was placed into an Erlenmeyer and treated with 10 mL of concentrated HNO₃ for 24 h and then heated to a small volume. A mixture of 30 % H₂O₂ and H₂O (3:2, volume ratio) was added and evaporated to a small volume. After cooling, 3 mL of 30 % H₂O₂ was added and evaporated. Then added 10 mL of concentrated HCl and samples were left overnight. Obtained digestates were filtered and diluted with distilled water to 25 mL.

RESULTS AND DISCUSSION

The element composition of fruiting bodies of three wild edible mushrooms in the caps, stipes, and surrounding soils are presented in Table IV. All element concentrations were determined on a dry weight (DW) basis. Still, for intake calculations, 300 g of fresh weight (FW) mushroom samples (containing 30 g of dry matter)⁸ were presented, assuming the average portion per person (average body weight 65–70 kg).⁹ The intake calculations were done on the average element content in mushrooms. The intake of each element was calculated by consuming a portion of 300 g. The results are presented in Table V.

Worth mentioning is that elements are accumulated in different quantities comparing the cap and the stipe, depending on the species and the element concentrations in the substrate that the mushroom grew on.

Daily, the human body requires specific amounts of elements for the organism's proper functioning and development. Elements which in large quantities can be found in the body, such as K, Na, Mg, Ca and P, are required for many essential processes in human metabolism, such as fluid balance, proper formation of bones and teeth, muscle contraction, and the functioning of the nervous system. Mushrooms can be considered an essential source of biologically important

elements, suggesting the existence of a very effective mechanism enabling them to take up elements from the substrate more readily.¹⁰

TABLE IV. Element composition in studied mushroom species of the Russulaceae family in caps, stipes and in corresponding soil substrates, and the bioaccumulation (BAF) and translocation factor (TF) for the analyzed samples

Element/Content	Origin	<i>L. deliciosus</i>	<i>L. sanguifluus</i>	<i>L. semisanguifluus</i>
K Content \pm SD mg kg ⁻¹ DW	Cap	14143 \pm 498	13337 \pm 450	134923 \pm 452
	Stipe	11074 \pm 430	116556 \pm 441	12387 \pm 451
	Soil	84412 \pm 801	10552 \pm 512	9242 \pm 501
	BAF	3	2.4	2.8
	TF	1.3	1.1	1.1
P Content \pm SD mg kg ⁻¹ DW	Cap	8212 \pm 199	6510 \pm 193	6386 \pm 193
	Stipe	5117 \pm 181	4778 \pm 180	4939 \pm 182
	Soil	1094 \pm 112	1045 \pm 109	927 \pm 99
	BAF	12.2	10.8	12.2
	TF	1.6	1.4	1.3
Ca Content \pm SD mg kg ⁻¹ DW	Cap	261 \pm 13	266 \pm 12	332 \pm 22
	Stipe	232 \pm 13	245 \pm 12	340 \pm 22
	Soil	311 \pm 21	520 \pm 32	379 \pm 25
	BAF	1.6	1	1.8
	TF	1.1	1.1	1
Mg Content \pm SD mg kg ⁻¹ DW	Cap	718 \pm 52	630 \pm 50	697 \pm 45
	Stipe	519 \pm 21	517 \pm 31	578 \pm 32
	Soil	4791 \pm 180	5104 \pm 191	5144 \pm 190
	BAF	0.3	0.2	0.2
	TF	1.4	1.2	1.2
Na Content \pm SD mg kg ⁻¹ DW	Cap	2.3 \pm 0.1	8.4 \pm 0.8	7.1 \pm 0.6
	Stipe	12 \pm 1	10 \pm 1	8 \pm 1
	Soil	17 \pm 1	18 \pm 1	19 \pm 1
	BAF	0.8	1	0.8
	TF	0.2	0.8	0.8
Al Content \pm SD mg kg ⁻¹ DW	Cap	73 \pm 6	98 \pm 8	87 \pm 7
	Stipe	82 \pm 7	105 \pm 9	159 \pm 9
	Soil	57871 \pm 600	64563 \pm 655	64436 \pm 654
	BAF	0.003	0.003	0.004
	TF	0.886	0.93	0.548
As Content \pm SD mg kg ⁻¹ DW	Cap	0.55 \pm 0.05	0.58 \pm 0.05	0.44 \pm 0.05
	Stipe	0.40 \pm 0.04	0.49 \pm 0.05	0.48 \pm 0.05
	Soil	22 \pm 2	24 \pm 2	24 \pm 2
	BAF	0.044	0.045	0.039
	TF	1.345	1.191	0.928
Cd Content \pm SD mg kg ⁻¹ DW	Cap	1.1 \pm 0.1	0.58 \pm 0.05	0.45 \pm 0.05
	Stipe	0.53 \pm 0.04	0.36 \pm 0.04	0.34 \pm 0.04
	Soil	8.13	8.78	9.98
	BAF	0.196	0.004	0.09
	TF	2.028	1.604	1.306

TABLE IV. Continued

Element/Content	Origin	<i>L. deliciosus</i>	<i>L. sanguifluus</i>	<i>L. semisamguuiufulus</i>
Pb Content \pm SD mg kg ⁻¹ DW	Cap	0.75 \pm 0.09	1.3 \pm 0.1	1.0 \pm 0.1
	Stipe	0.67 \pm 0.05	1.1 \pm 0.1	0.56 \pm 0.06
	Soil	45 \pm 3	49 \pm 3	48 \pm 3
BAF		0.031	0	0.032
TF		1.126	1.24	1.82

TABLE V. Content of nutritionally important macroelements and toxic elements in selected mushroom species calculated on 300 g of fresh mushrooms; daily intake of element relative to RDI; DIE – daily intake of element relative to RDI

Species	K		P		Ca		Mg		Na	
	Content mg/300 g FW	DIE %	Content mg/300 g FW	DIE %	Content mg/300 g FW	DIE %	Content mg/300 g FW	DIE %	Content mg/300 g FW	DIE %
	<i>L. deliciosus</i>	378.3	18.9	199.9	36.4	7.4	0.9	18.6	5.8	0.22
<i>L. san- guifluus</i>	374.9	18.7	169.3	30.8	7.7	1.0	17.2	5.4	0.28	0.018
<i>L. semisam- guuiufulus</i>	388.2	19.4	169.9	30.9	10.1	1.3	19.1	6.0	0.23	0.016
	Al		As		Cd		Pb		Content, mg/300 g FW	
<i>L. deliciosus</i>	2.3		0.014		0.024		0.021			
<i>L. san- guifluus</i>	3.1		0.016		0.014		0.036			
<i>L. semisam- guuiufulus</i>	3.7		0.014		0.012		0.024			

A portion of mushrooms' contribution is considered to be significant if it provides 15 % of the recommended daily intake (RDI) of nutritionally valuable elements.¹¹

Macroelements, namely potassium and phosphorus, can be found in the most considerable quantities in mushrooms. Potassium levels are between 20- and 40-fold higher in fruiting bodies than in underlying substrates.¹² Among the analyzed mushroom species, the content of K is higher in the caps than in the stipes, and mushroom *L. deliciosus* stood out with the highest potassium content, 14143 mg kg⁻¹. Seeger reported that the potassium content in 410 wild fungi species ranges from 1.5–117 g kg⁻¹.¹³ Therefore, mushrooms can be used in the diet of patients with chronic potassium deficiency, but care must be taken in people with renal insufficiency. The RDI of potassium for adults is 2000 mg.¹⁴ From Table V, it can be seen that all analyzed mushroom samples have a significant contribution of potassium, from a portion of 300g of fresh mushrooms, because it exceeds 15 %.

Phosphorus is the second most abundant element in edible and wild mushrooms that can bioaccumulate in large quantities from the substrate. The concentration of P in the analyzed mushrooms ranges from 4778 mg kg⁻¹ (stipe of *L. sanguifluus*) to 8212 mg kg⁻¹ (cap of *L. deliciosus*). Also, it can be observed that the bioaccumulation of phosphorus in the caps is higher than in the stipes. The *RDI* for phosphorus is 550 mg.¹⁵ Based on the results, it can be noticed that all analyzed samples of mushrooms have a significant contribution to the daily intake of phosphorus (> 15 %), and the species *L. deliciosus* has the highest value, 36.4 %.

Calcium and magnesium are determined in mushrooms in lower amounts than phosphorus and potassium. Calcium occurs in very similar concentrations in caps and stipes in all the analyzed mushrooms. The species *L. semisanguifluus* was separated with a slightly higher calcium content, 332 mg kg⁻¹ in cap and 340 mg kg⁻¹ in stipe. The *RDI* for calcium is 800 mg,¹⁴ and the highest Ca concentration found in this study is 10.07 mg/300 g of fresh mushrooms, which is 1.3 % of the average daily intake. It can be concluded that mushrooms represent a small source of Ca in the diet. However, as calcium is generally not classified as an element deficient in the human diet, this deficiency can be ignored.

Magnesium content in fruiting bodies were even lower than those in substrates.¹² It seems either evenly distributed in caps and stipes, or somewhat higher levels are observed in caps than in stipes,¹⁶ which is the case with these mushroom samples. Among the tested mushroom samples, *L. deliciosus* has the highest content of magnesium, 718 mg kg⁻¹, and consuming a portion of 300 g of fresh mushrooms can provide a maximum of 6 % of magnesium daily intake.

Sodium is a macroelement found in small amounts in mushrooms, which is very important because sodium excess in nutrition can lead to high blood pressure. This element differs from other macroelements due to its more significant presence in stipe than in the caps. All analyzed mushrooms showed lower sodium levels than average, ranging from 50-750 mg kg⁻¹.¹⁶ Mushrooms *L. deliciosus* is different in terms of the highest sodium content in the stipe (12 mg kg⁻¹) and the lowest in the cap (2.3 mg kg⁻¹). The *RDI* for sodium is 1500 mg.¹⁷ Consuming a portion of 300 g of fresh mushrooms provides about 0.018 % of sodium per day, which qualifies mushrooms as food recommended for consumption without the risk of hypertension.

Since mushrooms have been viewed from a nutritional point of view and have been found to accumulate macronutrients in appropriate amounts, toxicological testing is necessary to determine that they are safe to consume.

Previous research showed a wide range of aluminium content in wild-growing species (<25 to 500 mg kg⁻¹ DW).¹⁶ The Al concentration in the mushroom caps is 73 to 98 mg kg⁻¹, and these concentrations are lower than in the stipe in all analyzed species. This metal concentration in the stipe was the highest in *L.*

semisanguifluus, 159 mg kg⁻¹, while *L. deliciosus* had the lowest, 82 mg kg⁻¹. Zsigmond *et al.*¹⁸ obtained similar results examining the inorganic composition of many mushrooms, among which the species *L. deliciosus*, and the obtained results are similar to the results of this study, except that the concentration of aluminium in the cap (52.4 mg kg⁻¹) is higher than in the stipe (31.3 mg kg⁻¹). Sarikurkcu *et al.*²⁰ reported lower concentrations of Al in *L. sanguifluus* (63 mg kg⁻¹ DW).¹⁹

According to the literature analysis, provisional tolerable weekly intake (*PTWI*) was determined most frequently, but the Joint FAO/WHO Expert Committee on Food Additives (JECFA) gives tolerable intake levels for contaminants, expressed on either a daily or a weekly basis.²⁰ In view of the cumulative nature of aluminium in the organism after dietary exposure, the Panel considered it more appropriate to establish a tolerable weekly intake (*TWI*) for aluminium rather than a tolerable daily intake (*TDI*) and based on the combined evidence from the abovementioned studies, the Panel established a *TWI* of 1 (mg Al/kg bw)/week.²¹ If 70 kg is taken as the consumer's average weight, the *TWI* for Al is 70 mg per week. By consumption 300 g portions of fresh studied mushrooms weekly, percentage of entered quantity Al ranges between 3.3 and 5.3 %.

Arsenic in mushrooms can be present in organic and inorganic forms.¹⁶ The average content of arsenic in wild mushrooms are usually less than 1 mg kg⁻¹ DW.¹² In the present study, arsenic concentrations are similar in caps and stipes for all analyzed mushroom species and ranged from 0.4 to 0.58 mg kg⁻¹. There are no significant differences observed between species. However, the *L. sanguifluus* possessed a slightly more elevated mean concentration, 0.58 mg kg⁻¹ in cap and 0.49 mg kg⁻¹ in the stipe, than the other species. Xu *et al.*²² reported that *L. deliciosus* had average arsenic concentration of 0.75 mg kg⁻¹, which is slightly higher than the result in this paper. Genetic and environmental factors determine the concentration of arsenic in mushrooms. The role of genetic factors in As regulation can be stated based on the remarkably high arsenic contents of the same genus' mushroom species (*Agaricus*, *Clitocybe*, *Lepista*, *Macrolepiota*).²³ JEFCA noted that the previously established *PTWI* of 15 µg/kg body weight (equivalent to 2.1 µg kg⁻¹ body weight per day) for inorganic arsenic was in the region of the benchmark dose lower confidence limit (*BMDL*_{0.5}) and therefore was no longer appropriate. This *PTWI* was therefore withdrawn by the Committee.²⁴ The CONTAM panel found *BMDL*₀₁ values between 0.3 and 8.0 (µg/kg bw)/day for an increased risk of lung, skin, and bladder cancer, as well as skin lesions.²⁴ Calculated at 70 kg body weight, it amounts to 0.021 to 0.56 mg arsenic per day. A portion of 300 g of fresh mushrooms maximum contains 16 µg of arsenic, which does not exceed the regulations' acceptable daily intake.

Cadmium is one of the most frequently determined elements in mushrooms due to its harmful effects on human health.¹⁶ Cd is often found in soil and enters

the food chain through plants.²⁵ Most significant concentrations of Cd were obtained among analyzed species in *L. deliciosus* (1.1 mg kg⁻¹ in cap and 0.53 mg kg⁻¹ in stipe). Literature data reveal normal cadmium levels between <1–5 mg kg⁻¹ DW in wild-growing species, whereas contents >1 mg kg⁻¹ DW are sparse within cultivated mushrooms.¹⁶ Commonly, cadmium contents are higher in caps than in stipes,¹⁶ as is the case with results presented in this research. In previous studies, content of Cd in *L. deliciosus* was 0.54 mg kg⁻¹,²⁶ 1.91 mg kg⁻¹,²² and in *L. sanguifluus* was 0.43 mg kg⁻¹.¹⁹ Aloupi *et al.*²⁷ reported Cd concentrations at 0.06–0.25 mg kg⁻¹ in *L. deliciosus*, 0.08–0.59 mg kg⁻¹ in *L. sanguifluus*, and 0.06–0.61 mg kg⁻¹ in *L. semisanguifluus*, which is similar to results for the same mushrooms presented in this research.

The CONTAM Panel established *TWI* for cadmium of 2.5 µg/kg bw, which for a 70 kg consumer is 0.175 mg per week and 0.025 mg per day.²⁸ So, consuming a portion of 300 g *L. deliciosus*, 95.6 % of the cadmium could be ingested daily.

Like most toxic elements, lead can be accumulated in the body for a long time, and it is necessary to monitor its even low concentration in potential sources.²⁹ Obtained results (Table IV) point to lead evenly distribution in caps and stipes. *L. sanguifluus* showed a slightly higher lead content compared to the other two species, 1.3 (cap) and 1.1 mg kg⁻¹ (stipe). The analysis of the lead concentration in species *L. deliciosus* and *L. sanguifluus* was previously reported from other researchers which indicated a lower content of this element in the mentioned species.²⁶ Regarding lead, the CONTAM panel concluded that the provisional *PTWI* of 25 µg/kg body weight, set by JECFA and adopted by the Scientific Committee on Food (SCF) is no longer appropriate.^{30,31} The respective *BMDL*s derived from blood lead levels in µg L⁻¹ (corresponding dietary intake values in µg/kg bw per day) were: developmental neurotoxicity *BMDL*₀₁, 12 (0.50, corresponding to 35 µg per day for the average consumer); effects on systolic blood pressure *BMDL*₀₁, 36 (1.50, corresponding to 105 µg per day for the average consumer); effects on prevalence of chronic kidney disease *BMDL*₁₀, 15 (0.63, corresponding to 44.1 µg per day for the average consumer).³⁰ A portion of 300 g of fresh *L. sanguifluus* may pose a risk to the health of consumers because it contains 0.036 mg arsenic.

The logs of woods decomposed agro- and animal-wastes and soil are the mushrooms' natural substrates. Nutrients from the soil are available through external digestion and absorption by the mycelium. The concentration of elements in the mushrooms and corresponding soils, served for each element's bioaccumulation factor calculation (*BAF*). The *BAF* is precious tool for estimation of the accumulation efficiency of elements in mushrooms from growing media. For a plant or mushroom to be an efficient for the polluted soil bioremediation, the bioaccumulation factor has to be higher than 1.³²

The *BAF* values for most macroelements are higher than 1, meaning these mushrooms can be considered as accumulators of these elements. Of all the analyzed elements, phosphorus showed the highest value of *BAF* in all three species of mushrooms, which means that mushrooms can be considered accumulators and hyperaccumulators of this element. The determined content of toxic elements in all mushroom species was very low ($BAF < 1$). The extremely low *BAF* values for analyzed toxic elements in all the mushrooms suggest that none of the species act as an accumulator of hazardous elements to human health. Based on the bioaccumulation factor, all the analyzed species were found to be bioexclusors of toxic elements. Due to the low content of toxic elements, their intensive consumption cannot lead to exceeding the tolerable levels of toxic elements intake.

The ratio cap/stipe expresses the translocation factor (*TF*) in the fruiting body of mushrooms.³³ For all macroelements, except Na, the *TF* value is greater than 1, which means that the macroelements' concentration is higher in cap than in stipe for all of these species.

The translocation factor of toxic elements had high values, which means that the concentration level for these elements was more elevated in the cap than the stipe of mushroom.

Correlation analysis

The obtained results show that mushrooms contain the highest potassium concentration, but based on the bioaccumulation factor, they offer the most increased tendency to accumulate phosphorus. Consequently, P influences, or is influenced by, the availability or utilization of many other elements, both essential and nonessential.³⁴ For that reason, the impact of the concentration of phosphorus in soil on the concentration of other elements in soil and parts of mushrooms was monitored.

Correlation coefficients among elements of the fruiting body (caps and stipes) and corresponding soil substrates are presented in Fig. 1. Regarding correlation coefficients, it can be noticed that the concentration of macro and toxic elements in the soil depends on the concentration of phosphorus in the soil. The concentration of phosphorus is negatively correlated with all determined elements in the soil, which suggests that the concentration of macro and toxic elements decreases with this element's increase. This fact is significant from the toxicology point of view because it indicates that soil rich in phosphorus results in a lower concentration of toxic elements in mushrooms. The concentration of phosphorus in soil has the greatest influence on cadmium and sodium concentration, according to the high correlation coefficient ($r = -1$ and 0.97 , respectively, $p < 0.05$).

The other elements concentration (in the stipe and cap) was strongly affected by phosphorus concentration.

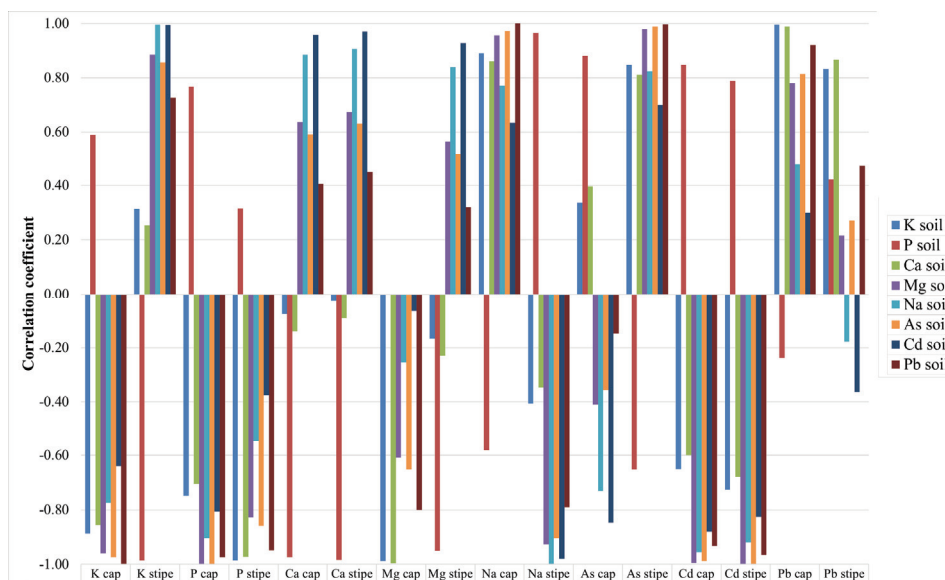


Fig. 1. Correlation of content of elements in soil and different parts of mushrooms.

The highest positive correlation was recorded between P in soil and Na in the stipe, $r = 0.95$ ($p < 0.05$), which indicates that mushrooms grown on P-rich soil accumulate more Na in the stipe than in the cap. This is confirmed by the translocation factor, which is the lowest for sodium, $TF = 0.2$. The strongest negative correlations were between phosphorus in the soil and potassium in the stipe, $r = -0.99$ ($p < 0.05$).

CONCLUSION

Results of this study confirm that mushrooms are a good source of macro-elements, providing a balanced diet. The study results pointed to high K and P contents surpassing more than 15 % of the recommended daily intake elements. It was found that the consumption of these mushrooms does not represent a toxicological risk. Regarding the content of toxic elements, the studied mushrooms are safe to consume and do not pose a risk to human health if consumed in the prescribed portions.

Depending on mushroom species, BAF values varied highly depending on the chemical element and were >1 for K, P, and Ca, while they were <1 for Mg, Na, Al, As, Cd and Pb. The translocation factor depends on the studied elements and their mobility in the mushroom's fruiting body and the mushroom species. The highest mobility in the fruiting body was shown by cadmium, $TF = 2$ for *L. deliciosus* species.

Correlation analysis showed that phosphorus concentration in the soil affects other elements' concentration in the soil and mushrooms.

Acknowledgement. Financial support of the Ministry of Education, Science and Technological Development of Serbia (Grant Nos. 451-03-68/2020-14/200124 and 451-03-68/2020-14/200113) is gratefully acknowledged.

ИЗВОД

ПОРЕЂЕЊЕ САДРЖАЈА МАКРО- И ТОКСИЧНИХ ЕЛЕМЕНАТА У ОДАБРАНИМ САМОНИКЛИМ ПЕЧУРКАМА КОЈЕ ПРИПАДАЈУ ПОРОДИЦИ RUSSULACEA

МАРИЈА ДИМИТРИЈЕВИЋ¹, ВИОЛЕТА МИТИЋ², ДРАГАН ЂОРЂЕВИЋ², ГОРДАНА ПОПОВИЋ³, НЕНАД КРСТИЋ², ЈЕЛЕНА НИКОЛИЋ² И ВЕСНА СТАНКОВ ЈОВАНОВИЋ²

¹Универзитет у Нишу, Медицински факултет, Булевар др Зорана Ђинђића 81, 18000 Ниш,

²Универзитет у Нишу, Природно-математички факултет, Дејарман за хемију, Вишеградска 33, 18000 Ниш и ³Универзитет у Београду, Фармацеутски факултет, Дејарман за општу и неорганску хемију, Војводе Сіше 450, 11000 Београд

Циљ овог рада било је одређивање садржаја К, Р, Са, Мг, На, Аl, Аs, Cd и Pb у три јестиве, самоникле печурке (*Lactarius deliciosus*, *Lactarius sanguifluus* и *Lactarius semisanquifluus*) које припадају породици Russulaceae. Такође, одређен је и садржај поменутих елемената у земљишту на коме су расле анализиране печурке. На основу добијених резултата, за сваки елемент је израчунат биоакумулациони и транслокациони фактор. Будући да је утврђено да печурке акумулирају одговарајуће макроелементе, резултати су приказани и као унос (%) одговарајућих елемената на основу препоручене дневне дозе, прерачунато на порцију од 300 g свежих печурака. За токсичне елементе израчунат је садржај уноса елемената на основу прихватљивог недељног уноса. Корелациона анализа је коришћена како би се утврдио утицај фосфора на садржај елемената у печуркама и одговарајућим земљиштима, обзиром да је фосфор показао најзначајнију тенденцију акумулације.

(Примљено 10. априла, ревидирано 19. маја, прихваћено 24. маја 2021)

REFERENCES

1. D. Agrahar-Murugkar, G. Subbuakshmi, *Food Chem.* **89** (2005) 599 (<https://doi.org/10.1016/j.foodchem.2004.03.042>)
2. X. M. Wang, J. Zhang, T. Li, Y.Z. Wang, H.G. Liu, *J. Anal. Methods Chem.* **2015** (2015) 1 (<https://doi.org/10.1155/2015/165412>)
3. J. Falandysz, M. Drewnowska, M. Chudzinska, D. Barańkiewicz, *Ecotoxicol. Environ. Saf.* **137** (2017) 265 (<https://doi.org/10.1016/j.ecoenv.2016.12.014>)
4. I. Širić, A. Kasap, D. Bedeković, J. Falandysz, *J. Environ. Sci. Health., B* **52** (2017) 156 (<https://doi.org/10.1080/03601234.2017.1261538>)
5. W. Reczyński, B. Muszyńska, W. Opoka, A. Smalec, K. Sułkowska-Ziaja, M. Malec, *Biol. Trace Elem. Res.* **153** (2013) 355 (<https://doi.org/10.1007/s12011-013-9670-3>)
6. M. Tüzen, *Microchem. J.* **74** (2003) 289 ([https://doi.org/10.1016/S0026-265X\(03\)00035-3](https://doi.org/10.1016/S0026-265X(03)00035-3))
7. *US EPA: Method 3050B: acid digestion of sediments, sludges, and soils*, 1996
8. P. Kalač, L. Svoboda, *Food Chem.* **69** (2000) 273 ([https://doi.org/10.1016/S0308-8146\(99\)00264-2](https://doi.org/10.1016/S0308-8146(99)00264-2))
9. EFSA Scientific Committee, *EFSA J.* **10** (2012) 2579 (<https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2012.2579>)
10. E. Sesli, M. Tüzen, *Food Chem.* **65** (1999) 453 ([https://doi.org/10.1016/S0308-8146\(98\)00194-0](https://doi.org/10.1016/S0308-8146(98)00194-0))

11. V. Stefanović, *Determination of the contents of macroelements and microelements in samples of Macrolepiota procera mushrooms and soil substrates from Rasina district*, University of Belgrade, 2016 (in Serbian)
12. P. Kalač, *Food Chem.* **113** (2009) 9 (<https://doi.org/10.1016/j.foodchem.2008.07.077>)
13. R. Seeger, *Z. Lebensm. Unters. Forsch.* **167** (1978) 23 (<https://doi.org/10.1007/BF01122881>)
14. EEC, *Amending Council Directive 90/496/EEC on nutrition labelling for foodstuffs as regards recommended daily allowances, energy conversion factors and definitions. Official Journal of the European Union, Commission Directive 2008/100/EC*, 2008
15. EFSA Scientific Committee, *EFSA J.* **2017** e15121 (<https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/sp.efsa.2017.e15121>)
16. P. Kalač, *Mineral Composition and Radioactivity of Edible Mushrooms*, Academic Press is an imprint of Elsevier, Amsterdam, 2019 (<https://doi.org/10.1016/C2018-0-02278-1>)
17. EFSA Scientific Committee, *EFSA J.* **17** (2019) 57782019 (<https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2019.5778>)
18. R. Zsigmond, K. Varga, S. Harangi, E. Baranyai, I. Urák, *Acta Univ. Sapient. Agric. Environ.* **7** (2015) 98 (<https://doi.org/10.1515/ausae-2015-0009>)
19. C. Sarikurku, J. Popović-Djordjević, M. H. Solak, *Ecotoxicol. Environ. Saf.* **190** (2020) 110058 (<https://doi.org/10.1016/j.ecoenv.2019.110058>)
20. P. Świsłowski, A. Dołhańczuk-Śródka, M. Rajfur, *Environ. Sci. Pollut. Res.* **27** (2020) 22235 (<https://doi.org/10.1007/s11356-020-08693-5>)
21. EFSA Scientific Committee, *EFSA J.* **754** (2008) 1 (<https://doi.org/10.2903/j.efsa.2008.754>)
22. Z. Xu, L. Fu, S. Feng, M. Yuan, Y. Huang, J. Liao, L. Zhou, H. Yang, C. Ding, *Molecules* **24** (2019) 1357 (<https://doi.org/10.3390/molecules24071357>)
23. M. J. Melgar, J. Alonso, M. A. Garcia, *Food Chem. Toxicol.* **73** (2014) 44 (<https://doi.org/10.1016/j.fct.2014.08.003>)
24. *FAO and WHO, Safety evaluation of certain contaminants in food. WHO Food Additive Series 63/FAO JECFA Monographs 8*, WHO Press, Geneva, 2011
25. H. Karami, N. Shariatifar, S. Nazmara, M. Moazzen, B. Mahmoodi, A. M. Khaneghah, *Biol. Trace Elem. Res.* **99** (2021) 389 (<https://doi.org/10.1007/s12011-020-02130-x>)
26. M. Kosanić, B. Ranković, A. Rančić, T. Stanojković, *J. Food Drug Anal.* **24** (2016) 477 (<https://doi.org/10.1016/j.jfda.2016.01.008>)
27. M. Aloupi, G. Koutrotsios, M. Koulousaris, N. Kalogeropoulos, *Ecotoxicol. Environ. Saf.* **78** (2012) 184 (<https://doi.org/10.1016/j.ecoenv.2011.11.018>)
28. EFSA Scientific Committee, *EFSA J.* **980** (2009) 1 (<https://doi.org/10.2903/j.efsa.2009.980>)
29. M. V. Dimitrijevic, V. D. Mitic, J. S. Cvetkovic, V. P. Stankov Jovanovic, J. J. Mutic, S. D. Nikolic Mandic, *Eur. Food Res. Technol.* **242** (2016) 1 (<https://doi.org/10.1007/s00217-015-2512-0>)
30. EFSA Scientific Committee, *EFSA J.* **8** (2010) 1570 (<https://doi.org/10.2903/j.efsa.2010.1570>)
31. EFSA Scientific Committee, *EFSA J.* **10** (2012) 2831 (<https://doi.org/10.2903/j.efsa.2012.2831>)
32. A. Scragg, *Environmental Biotechnology*, Oxford University Press, New York, 2005

33. C. C. Elekes, G. Busuioc, I. Dumitriu, *Adv. Biomed. Res.* 464 (<http://www.wseas.us/e-library/conferences/2010/Cambridge/MABIPH/MABIPH-61.pdf>)
34. F. Adams, *The Role of Phosphorus in Agriculture*, American Society of Agronomy, Madison, WI, 1980 (<https://doi.org/10.2134/1980.roleofphosphorus>).