MINERAL CONTENT OF WILD EDIBLE MACROFUNGI *LAETIPORUS SULPHUREUS* AND *SUILLUS FLURYI* FROM MACEDONIA

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Abstract
The aim of this study was to determine the contents of mineral elements and heavy metal accumulation in two edible macrofungi species Laetiporus sulphureus and Suillus fluryi. Specimens were analyzed for six elements (iron, copper, zinc, selenium, cadmium and lead) contents using atomic emission spectroscopy with inductively coupled plasma (AES-ICP). Suillus fluryi demonstrated much higher contents of selenium (0.85 mg/kg dry weigh), zinc (47.7 mg/kg dry weigh) and copper (44.97 mg/kg dry weigh), essential trace elements that are related to the antioxidant potential of the specimen. Only small amounts of toxic metals, such as cadmium and lead, were found in both tested species. The results confirmed that the investigated wild macrofungi Suillus fluryi may be a functional component of the human diet.

Keywords: *edible macrofungi, ICP-AES, mineral elements, Laetiporus sulphureus, Suillus fluryi*

Introduction

The fungal kingdom includes many species with diverse morphological and ecological characteristics that support their survival in the environment. Mushrooms are macrofungi that are characterized by the production of visible fruit bodies which generate and distribute their spores [1]. Wild-growing mushrooms are valued due to their taste and aroma, as well as their nutritional quality (rich protein and low fat contents) and they are considered as sources of a wide range of biologically active secondary metabolites [1-6].

Mushrooms also accumulate high concentrations of metallic elements, metalloids and non-metals even when growing above soils with low concentrations of these elements [7]. The genotype of the mushrooms and the soil conditions where the mushrooms are found are main factors influencing the bioaccumulation of elements in macrofungi [6,7].

Human organism requires trace amounts of some essential elements, including iron, copper, zinc and selenium, which play an important role in biological processes. Since macrofungi have ability to bioaccumulate the essential trace elements from the growth medium into the fruiting body, their consumption can make an important contribution to nutrition intake and overall health. Apart from the abundance of essential minerals in mushrooms, potentially toxic elements including Cd and Pb also occur sometimes at elevated concentrations [7]. It is known that the concentration of essential or non-essential trace elements above threshold concentration levels can cause morphological abnormalities, reduce growth and increase mortality and mutagenic effects in humans [8].

In the present paper focus is given to the elements that are of health promoting and toxicological importance: Se, Zn, Cu, Fe, Cd and Pb in two edible mushroom species growing widely throughout the Balkan region, *Laetiporus sulphureus* and *Suillus fluryi*. The data derived would serve as a useful basis to assess the nutritional value of the selected mushrooms, along with the limits of toxic metals.

Materials and Methods

Fruiting body selection. Wild fruiting bodies of the samples *Laetiporus sulphureus* and *Suillus fluryi* were collected in autumn 2011. Geographical location and natural habitat of the mushroom specimens are shown in Table 1. Taxonomic identification was made in the Mycological Laboratory at the Institute of Biology, Faculty of Natural Sciences and Mathematics in Skopje, by implementing standard methods of microscopic and chemical techniques (coloring of fruit bodies and spores), as well appropriate literature [9-14]. The representative voucher specimens were deposited at the Macedonian Collection of Fungi (MCF) at the Institute of Biology.

The fruiting bodies were cleaned to remove any residual compost/soil and subsequently air-dried in the oven at 40 ^{o}C. Dried mushrooms were ground to fine powder and stored in airtight plastic bags in the dark, at room temperature for further analysis.

Table 1. Geographical location and natural habitat of the mushroom species

Mushroom species	Natural habitat	Geographical location
Laetiporus sulphureus	saprotrophic (on stump of deciduous trees)	park Kozle, Skopje
Suillus fluryi	mycorrhizal (on ground in pineforest)	Suva Gora Mt.

Determination of minerals. All the element concentrations were determined on the basis of dried weight (dw) of mushrooms.

After drying process 1 g of the mushroom material was incinerated at a temperature of 400 ^{0}C and then 8 ml nitric acid was added and heated to dissolve. After it, hydrogen peroxide (2 ml) was added to each tube and was heated. Digests were diluted with water and mixed well before they were transferred into individual 25 ml volumetric flasks and made up to volume.

The elements standard calibration plots were made for quantification of the elements in the mushroom samples. The mass of an element in a sample was obtained from the element calibration plot using the sample element peak height. The calculation of the element content in terms of dried weight of mushroom took into account dilution factor of the sample and dried weight of the mushroom used in preparing the sample. Mineral contents were determined using atomic emission spectroscopy with inductively coupled plasma (PerkinElmer Optima 2000^{TM} DV ICP).

Results and Discussion

The element concentrations of selected mushrooms in this study, expressed as milligrams of element per kilogram of dry mushroom (mg/kg dw), are shown in Table 2.

The results from our study showed that the mushrooms species *Suillus fluryi* has fairly higher concentration of selenium than the species *Laetiporus sulphureus*, 0.850 and 0.001 mg/kg dw, respectively. It is known that edible mushrooms are selenium-rich food, but species vary in their Se content [7, 15]. Selenium and zinc are established as essential trace elements of fundamental importance to the human health. Selenium is an integral part of a group of biologically important selenoproteins, including Se-dependent glutathione peroxidases. There is evidence that several of that selenoproteins have antioxidant activity, controlling peroxide levels in cells by degrading hydroperoxides [16]. The recommended daily intake (RDA) for selenium that provides normal physiological function is approximately 55 μg/day and it can be incorporated into the body by ingesting selenium containing foods.

Zinc can also be categorized as a site-specific antioxidant using different mechanisms including protein sulfhydryl group protection against oxidation and competition with redox-active metals that contribute to oxidative stress, Fe and Cu [16]. In our study, the zinc content in the fruit body of the species *L. sulphureus* was found to be almost ten times lower than the content of the species *S. fluryi* (4.700 and 47.700 mg/kg dw, respectively). According to the contents of selenium and zinc in the fruiting bodies of tested mushrooms seems that *S. fluryi* is species with a greater antioxidant potential.

Similar levels of iron content in the analysed mushrooms were found, 58.700 and 56.700 mg/kg dw for *L.sulphureus* and *S. fluryi*, respectively. Our results are in accordance with reported Fe levels of some species of wild mushrooms from unpolluted areas ranged between 50-300 [6] and 46.3-317 mg/kg dw [17]. Copper contents found in this study are also comparable with those reported in literature. Copper contents found in the studied mushrooms *L. sulphureus* and *S. fluryi* were 5.600 and 44.970 mg/kg dw, respectively. The obtained low Cu concentration of the species *L. sulphureus* is in accordance with previous data reported by Ayaz et al., who pointed out the lowest copper content in *L. sulphureus* (2.8 mg/kg dw) among the tested species in their study [18]. Reported Cu levels of wild mushrooms from unpolluted areas ranged between 20-200 [6] and 3.8-32.6 mg/kg dw [17], which is not considered a health risk.

Table 2. Mineral contents of selected mushroom species

Mushroom species	Content (mg/kg dw)					
	Se	Zn	Cu	Fe	Pb	Cd
Laetiporus sulphureus	*0.001*	*4.700*	*5.600*	*58.700*	*0.150*	*0.200*
Suillus fluryi	*0.850*	*47.700*	*44.970*	*56.700*	*0.475*	*0.162*

Cadmium and lead are among the toxic substances of concern in edible wild mushrooms. The maximum concentrations of cadmium and lead permitted by European Union regulation in mushrooms are 1.0 mg/kg fresh weight (equivalent to 10 mg/kg dw, assuming 90% moisture) and 0.1 mg/kg fresh weight (equivalent to 1.0 mg/kg dw), respectively [19]. Results from our study showed that studied species *L. sulphureus* and *S. fluryi* had low cadmium (0.200 and 0.162 mg/kg dw, respectively) and lead (0.150 and 0.475 mg/kg dw respectively) levels, which are not considered to be a health risk.

Conclusion

The results presented in our study show that the contents of trace elements in analyzed mushroom species are acceptable for human consumption at nutritional and toxic levels. Toxic metal contents of the studied mushrooms were found at relatively low levels compared to the contents of the essential trace elements. Our results suggest that the wild edible mushrooms *Laetiporus sulphureus* and *Suillus fluryi*, collected from unpolluted areas can be used as safe and high-quality components in well balanced diet. In addition, *Suillus fluryi* was found favorable among the investigated mushrooms in terms of its selenium and zinc contents that are related to mushroom antioxidant potential.

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