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Assessment of Metal Contents in *Hydum rufescens, Macrolepiota procera* Mushrooms Collected from Turkey

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ABSTRACT

Wild-growing mushrooms have been considered as a delicious food in many countries for a long time. However, some of them can accumulate large concentrations of heavy metals, which can be dangerous to human health particularly, when the intake is high. Thanks to the climatic conditions, Turkey has also a great potential for wild edible mushroom species and several species have been consumed especially in rural areas. In this study, 13 metals (Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd) and 3 isotopes of Pb (^{206}Pb, ^{207}Pb and ^{208}Pb) contents in two different wild-growing edible mushroom species (*Hydum rufescens, Macrolepiota procera*) collected from Kastamonu forest in October of 2014, in Turkey were investigated. Mushroom samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that metal contents in *Macrolepiota procera* were higher than the metal contents in *Hydum rufescens* except Al and Mn. All of the toxic element concentrations (Cr, Cd, As) were low and below the world average in both mushroom species. Consequently, there was no any health risk associated with consumption of the analyzed wild edible mushroom species.

ÖZ

Anahtar Kelimeler:
Metal miktarı,
Yenilebilir yabani mantar,
ICP-MS,
Türkiye.

Yabani mantarlar, uzun zamandan beri birçok ülkede lezzetli bir yiyecek olarak kabul edilmiştir. Bununla birlikte, mantarların bazıları özellikle fazla tüketildiğinde insan sağlığına zararlı olabilecek kadar fazla ağır metal biriktirebilir. İklimsel koşullar sayesinde Türkiye yenilebilir mantar türleri için büyük bir potansiyele sahiptir ve özellikle kırsal alanlarda çeşitli mantar türleri tüketilmektedir. Bu çalışmada, 2014 yılı Ekim ayında Kastamonu ormanlarından toplanan, yenilebilir yabani mantar türlerinin (*Hydumr ufescens, Macrolepiota procera*) 13 metal (Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd) ve 3 Pb izotopu (^{206}Pb, ^{207}Pb ve ^{208}Pb) miktarları araştırılmıştır. Mantar örnekleri, indüktif olarak eşleştirilmiş plazma - kütle spektrometresi (ICP-MS) ile analiz edilmiştir. Sonuçlar *Macrolepiota procera*'daki Al ve Mn dışındaki tüm metal miktarının *Hydum rufescens*'deki metal miktarlarından daha yüksek olduğunu göstermiştir. Her iki mantar türünde de toksik element konsantrasyonları (Cr, Cd, As) düşük ve dünya ortalamasının altında bulunmuştur. Sonuç olarak, analiz edilen yenilebilir yabani mantar türlerinin tüketimi ile ilişkili herhangi bir sağlık riski olmadığı söylenebilir.

1. Introduction

Mushrooms are among the foods that consumption has been increasing day by day. The main reason for this increase may be due to the fact that the mushrooms are dietary nutrients [1]. They have high water content and low-fat ratio [2]. Additionally, having a high protein content is a great way to turn off the protein deficiency [3], especially for vegetarians. In recent years, thanks to the reports of many scientists studied on the bioactive properties of mushrooms such as antioxidant [4,5], antimicrobial [6,7], anticancer [8] etc., mushrooms have been the focus of more attention.

Some mushrooms were reported that they have ability to accumulate metals [9-11] in addition to their bioactive properties. They are also known as bio indicators for environmental monitoring [12-13]Undoubtedly, land is the best storage material and elements such as cadmium, mercury, arsenic, etc., are also absorbed many living organisms. This type of accumulation occurred in the mushrooms can be toxic to living organisms especially at high concentrations [14]. So, mushrooms not only include the metals necessary for our bodies but also accumulate toxic metals. To know the amount of the metal accumulation especially in the edible mushrooms is very important for learning the toxic effect on human health.

Thanks to the climatic conditions, Turkey has a great potential for wild edible mushroom and several species have been consumed especially in the rural areas. The aim of this study is to investigate the metal contents accumulated in two wild edible mushroom species (*Hydum rufescens* and *Macrolepiota procera*) collected from Kastamonu forest in Turkey.

2. Material and Methods

2.1. Mushrooms

Wild edible mushroom species were collected from Kastamonu province located in Black Sea region to the North of Turkey, (Figure 1), in October of 2014. The species of mushrooms (Figure 2 and 3), their habitats, locations (province, district and village), growing forms and regional name are given in Table 1.

Figure 1. Study area

Figure 2.*Hydum rufescens*

Figure 3.*Macrolepiota procera*

Table 1. Mushroom species, their habitats and locations, growing forms and regional name

No	Mushroom species	Habitat - Location	Edibility	Growing Form	Regional name
1	*Hydum rufescens*	On soil, Kastamonu	Edible	Wild	Geyik avurdu
2	*Macrolepiota procera*	On soil, Kastamonu	Edible	Wild	Dede bürük

2.2. Samples preparation and treatment

All the mushroom samples were sliced and dried at a drying mechanism until they were completely dehydrated. Then samples were crushed for passing a 40 mm mesh sieve.

Mushroom samples (0.5 g) were digested in a mixture of 5 mL of HNO_3 (65%), 2 mL of HCl (37%) in a microwave digestion system for 31 min and diluted to 50 mL volume with deionized water and samples were filtered through 0.45 micron filters. These samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS,A Bruker 820-MS).

2.3. Statistical analysis

The data were presented as means ± standard deviations of ten replicates for metal composition and analyzed by using Statistical Package for Social Sciences (SPSS version 23.0). The data were analyzed by ANOVA and tests of statistical significance were performed using Duncan's multiple range tests.

3. Results and Discussions

The metal contents of mushrooms are presented in Table 2. Magnesium acts as a catalyst in enzymatic reactions such as the transfer, storage and use of energy. It is called 'antistress mineral' because it helps to calm down [15]. In this study, magnesium content of *Hydum rufescens* and *Macrolepiota procera* was found 1037.2±120.5 and 1052.3±110.2 mg/kg respectively. Among the all metal contents only magnesium was not found statistically significant. In a study, magnesium content of 10 wild mushrooms has reported between 755.1±7.33-1150.7±41.45mg/kg [16]. In this study aluminum content of *M. procera* (37.1±2.7mg/kg) was found higher than aluminum content of *H. rufescens* (25.2±2.5 mg/kg). In the literature, the aluminum content in wild mushrooms (n = 271, 19 species) and in cultivated *Agaricus bisporus* (n = 15) was reported from 14±6.8 to 123±55 mg/kg dried weight [17]. So, it can be said that the species of mushrooms affect the amount of aluminum.

Table 2. Metal contents of mushrooms (mg/kg, dry weight)

Mushroom	Mg	H.G.*	Al	H.G.	Ca	H.G.	Mn	H.G.	Fe	H.G.
Hydum rufescens	1037.2 (120.5)**	a	25.2 (2.5)	a	602.0 (45.8)	b	7.8 (0.7)	b	145.8 (15.0)	a
Macrolepiota procera	1052.3 (110.2)	a	37.1 (2.7)	b	295.3 (8.7)	a	2.6 (0.2)	a	277.8 (20.31)	b

	Co	H.G.	Ni	H.G.	Cu	H.G.	Zn	H.G.	Se	H.G.
Hydum rufescens	0.63 (0.051)	b	41.2 (11.3)	b	52.7 (4.4)	a	57.7 (4.3)	a	2.76 (0.06)	a
Macrolepiota procera	0.23 (0.010)	a	9.0 (1.5)	a	96.3 (6.9)	b	86.4 (6.1)	b	3.13 (0.10)	b

	Pb-206	H.G.	Pb-207	H.G.	Pb-208	H.G.	Cr	H.G.	As	H.G.	Cd	H.G.
Hydum rufescens	0.17 (0.016)	a	0.15 (0.008)	a	0.16 (0.014)	a	0.093 (0.003)	b	0.029 (0.002)	a	0.26 (0.011)	a
Macrolepiota procera	0.36 (0.033)	b	0.33 (0.030)	b	0.34 (0.033)	b	0.038 (0.002)	a	0.026 (0.002)	a	0.61 (0.035)	b

*: H.G: Homogeneity groups mean having the same superscript letter(s) are not significantly different ($p>0.05$) by
Duncan's multiple range tests.
**: Standard deviation values are given in parentheses.

The various biological roles of calcium are necessary for processes such as structural support, cell adhesion, mitosis, blood coagulation, muscle contraction, and glandular secretion [17]. In this study, calcium content of *H. rufescens* (602.0±45.8 mg/kg) was found approximately two times higher than calcium content of *M. procera* (295.3±8.7 mg/kg). Michelot et al. [18] have reported the calcium content of 92 wild specimens of mushrooms collected in France was between 174 and 7230 mg/kg.

Manganese involved in bone formation, protein, fat, and carbohydrate metabolism [19]. Like calcium, manganese content of *H. rufescens* (7.8±0.7 mg/kg) was found approximately two times higher than manganese content of *M. procera* (2.6±0.2 mg/kg). Our manganese values were found lower than eight different species of wild edible mushrooms collected from Greek (11.3±0.6-100±5.0 mg/kg) [20].

Iron is one of the indispensable trace elements for people. Taking an excessive amount of iron has toxic effect [21]. In this study, iron content of *M. procera* (145.8±15.0 mg/kg) was found lower than the iron content of *H. rufescens* (277.8±20.31 mg/kg). Our results are in agreement with the literature that reported the iron content in 92 wild specimens of mushrooms collected from France (21.7- 639 mg/kg) [18].

Cobalt is an important co-factor in Vitamin-B12, which is essential element for human health [22]. In this study, cobalt content of *H. rufescens* and *M. procera* was found 0.63±0.051 and 0.23±0.010 mg/kg. Our cobalt values were found lower than eight wild edible mushroom species collected from forests of West Macedonia, Greece (0.65–5.74 mg/kg) [23].

Nickel is a moderately toxic element [24]. In our study, nickel content of *H. rufescens* (41.2±11.3 mg/kg) was found approximately 4.5 times higher than manganese content of *M. procera* (9.0±1.5 mg/kg). In a previous study, nickel content of eight mushroom species of Turkish origin has been reported to be between 8.2 and 26.7 mg/kg [25].

Copper is a necessary element in many chemical reactions for both plants and animals. This mineral, which is found in many important enzymes, has a vital importance [26]. Copper content of *H. rufescens* (52.7±4.4 mg/kg) was found lower than that of copper content in *M. procera* (96.3±6.9 mg/kg). It was reported that the copper content of 12 different mushroom samples collected from polluted and unpolluted locations (in Tokat, Turkey) was between 12 and 181 mg/kg [27].

Zinc is an essential for the structure and function of myriad proteins, including regulatory, structural and enzymatic' [28]. In this study, zinc content of *H. rufescens* and *M. procera* was found as 57.7±4.3 and 86.4±6.1 mg/kg, respectively. The zinc content of 28 species of edible mushrooms from different sites in the province of Lugo (NW Spain) was reported between 30.00 and 309.8 mg/kg [29].

Selenium is a vital element for human because it is required in biosynthesis of important selenoenzymes [30]. Selenium content of *H. rufescens* (2.76±0.06 mg/kg) was found lower than selenium content of *M. procera* (3.13±0.10 mg/kg). Selenium content of 142 mushroom samples in Finland was ranged from 0.05 to 37 mg/kg [31].

^{206}Pb is the end of the decay chain of ^{238}U, the uranium series or radium series. ^{207}Pb is the final step of the Actinium series from ^{235}U. ^{208}Pb is the end of the Thorium series from ^{232}Th [32]. In a previous study, lead content of 238 samples of 28 species of edible mushrooms collected from different sites in the province of Lugo (NW Spain) was reported between 0.35 and 4.1 mg/kg [33]. In our study, all lead isotopes (Pb-206, Pb-207, Pb-208) content of *M. procera* were found higher than the lead isotopes content of *H. rufescens*.

Trivalent chromium, found in most foods and nutrient supplements, is an essential nutrient with very low toxicity [34]. In literature, chromium content of eight different species of wild edible mushrooms growing in Epirus (Ioannina) and West Macedonia (Grevena, Kastoria), regions of Greece were reported between 0.41 and 13.1 mg/kg [23]. However, in our study, chromium content of *H. rufescens* and *M. procera* was found very low levels (0.093±0.003 and 0.038±0.002mg/kg, respectively).

Arsenic is a chemical element which raises much concern in terms of the environmental effect [35]. Arsenic content of *H. rufescens* and *M. procera* was found very close to the each other (0.029±0.002 and 0.026±0.002mg/kg, respectively) and the arsenic content of mushrooms was not significantly different ($p>0.05$) from each other by Duncan's multiple range test. In a previous study, the arsenic contents of 162 fruit body samples of 37 common edible mushroom taxa were analyzed and it was reported that very low [lower than 0.05 mg/kg dry matter (DM)] concentrations were found in the samples of 13 taxa, while higher (or very high) contents were quantified in other common taxa (the highest arsenic content was recorded in the fruit body of *Laccaria amethysthea* at 146.9 mg/kg DM) [36].

Cadmium is extremely toxic to humans as well as plants. Cadmium flow to humans is more through cereals, fruits, vegetables and other edible plant parts than through meat (muscles) [36]. However, like arsenic, cadmium content of our mushrooms (*H. rufescens* and *M. procera*) was found very low level (0.26±0.011 and 0.61± 0.035 mg/kg, respectively). In a previous review study, cadmium contents of 88 samples of mushrooms were reported ranged in 0.28–86mg/kg [37].

Consequently; all of the toxic element concentrations (Cr, Cd, As) were low and below the world average in both mushroom species [38].

4. Conclusions

In this study; 14 different metal (Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, ^{206}Pb, ^{207}Pb and ^{208}Pb) contents in two different wild-growing edible mushroom species (*H. rufescens*, *M. procera*), collected from Kastamonu forest (in Turkey) in October of 2014 were investigated. The results showed that metal contents in *M. procera* were higher than the metal contents in *H. rufescens* except Al and Mn. In this case, it can be said that metal accumulation changes with respect to mushroom species. All the toxic element concentrations (Cr, Cd, As) were low and below the world average in both mushroom species. This result has been found satisfactory. Consequently, there was no any health risk associated with the consumption of the analyzed wild edible mushroom species. In order to explain the effect of environmental factors more sophisticated studies should be performed.

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