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EVALUATION OF TRACE METAL CONTENTS IN MUSHROOM SAMPLES FROM AZDAVAY DISTRICT, KASTAMONU, TURKEY

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Abstract

Mushrooms are a popular food because they are an important source of essential amino acids, proteins and dietary fibers, but they have a great capacity to accumulate metals from substrate. Due to this reason, the content of 5 trace metals (Fe, Cr, Zn, Pb, Se) of fruit bodies of 21 fungi species originally found in Azdavay, Kastamonu Region, Turkey were analyzed by atomic absorption spectroscopy. The contents of investigated trace metals in mushroom samples were found to be in the range of 4.6–3478.7 mg kg^{-1} for Fe, 5.1–19.9 mg kg^{-1} for Cr, 10.4–138.6 mg kg^{-1} for Zn, 5.8–28.0 mg kg^{-1} for Pb and 0.65–1.47 mg kg^{-1} for Se. The relative standard deviations (R.S.D.) were found below 10%. The accuracy of procedure was confirmed by CRMs (BCR 191 Brown bread, ERM-BD 151 Skimmed milk powder).

Keywords: Azdavay, mushroom, trace metals

AZDAVAY (KASTAMONU, TURKEY) YÖRESİ MANTARLARI ESER METAL İÇERİĞİNİN BELİRLENMESİ

Özet

Mantarlar, önemli bir amino asit, protein ve lif kaynağı oldukları için popüler bir besindir, ancak substrattan metal biriktirme kapasiteleri yüksektir. Bu çalışmada Kastamonu Bölgesi, Azdavay'da orijinal olarak bulunan 21 mantar türünün 5 eser metal (Fe, Cr, Zn, Pb, Se) içeriği atomik absorpsiyon spektroskopisi ile analiz edilmiştir. Çalışılan mantar numunelerindeki eser metal içerik aralıkları demir için 4.6–3478.7 mg kg^{-1}, krom için 5.1–19.9 mg kg^{-1}, çinko için 10.4–138.6 mg kg^{-1}, kuşun için 5.8–28.0 mg kg^{-1} ve selenyum için 0.65–1.47 mg kg^{-1} olarak tespit edilmiştir. Bağıl standart sapma %10'nun altında bulunmuştur. Yöntemin doğruluğu sertifikalı referans malzemeler (BCR 191 Brown bread, ERM-BD 151 Skimmed milk powder) ile kontrol edilmiştir.

Anahtar Kelimeler: Azdavay, mantar, eser metal

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1. Introduction

In biological systems, all metals are considered toxic at a certain level of exposure, and many metals play a vital but important role [1]. In this context, metals are divided into two main groups: Copper, zinc, iron, cobalt, etc. essential metals for human health. Essential metals can also produce toxic effects if metal use is excessive. Non-essential metals are metals that do not have a positive role in a biological system and are toxic even at low levels of exposure [2]. Edible mushrooms are a valuable health food, because they are rich in many nutrients (amino acids, proteins, vitamins, minerals, dietary fibers, and antioxidants) [3]. Although edible mushrooms are favorite food, they can also accumulate potentially harmful metals [4]. In some instances, the accumulation of trace elements in mushroom can reach toxic level, depending on the concentration of trace metals in the growing environment [5].

Trace metal concentrations in mushroom are significantly higher than in crop plants, vegetables and fruits [6]. Mushrooms are known to uptake and accumulate various chemical elements [7].

This study is aimed to determine the level of trace metals (Fe, Cr, Zn, Pb, Se) in the fruit bodies of 21 fungi species originally found in Azdavay, Kastamonu Region, Turkey. Mushroom samples were collected in 2020 and determination of the trace metal concentrations has been evaluated by Atomic absorption spectroscopy (AAS).

These scientific data are important in the fields, mushroom science, food science and health science.

2. Materials and Methods

2.1. Collection and identification of mushroom samples

Mushroom samples were collected on October 25, 2020 from Azdavay district, Kastamonu- Turkey (900 m., 41 38 N and 33 17 E). The mushrooms on which they were grown (substrate), the place of collection, whether they are edible or not, and the herbarium numbers were given in Table 1. Samples were authenticated by Dr. Ilgaz AKATA from and stored at the Ankara University, Science Faculty Herbarium Laboratory (Turkey).

2.2. Digestion and elemental analysis of mushroom samples

The mushroom samples were dried at 105°C for 24 h. Dried samples were homogenized using an agate homogenizer and stored in polyethylene bottles until analysis. Deionized water from a Milli-Q system (Millipore 18.2 MΩ/cm resistivity) was used to prepare all aqueous solutions. HNO_3 and H_2O_2 were of suprapure quality (E. Merck, Darmstadt). All the plastic and glass-ware were cleaned by soaking in dilute HNO_3 (10%) and were rinsed with deionized water prior to use. For the elemental analysis, an Agilent 240 FS AA (Atomic Absorption Spectrometer) was used.

For digestion, a CEM Mars 6 microwave digested system was used. 0.25 gram of sample was digested with 9 mL of HNO_3 (65%) and 1 mL of H_2O_2 (30%) in microwave digestion system and diluted to 50 mL with deionized water. A blank digestion was carried out in the same way. For the digestion procedure, the heat was run up to 180°C in 10 min and kept constant for 10 min.

The concentrations of Fe, Cr, Zn and Pb were determined by using atomic absorption spectroscopy. Selenium level in the mushroom samples were determined using a HGAAS with argon as inert gas.

The studied species, the family of samples, Herbarium no, Habitat, Substrate and edibility have been presented in Table 1. The trace metal content of each mushroom samples were measured in triplicate and all relative standard deviations for replicates were less than 10%.

3. Results and Discussion

The results on fruit bodies of the mushroom samples (mushroom dry weight) used in this study are presented in Table 2. Acidic and organic matter contents in the ecosystems and soils of mushrooms are directly affected the heavy metal concentration of mushrooms [14].

Heavy metal accumulation in mushrooms is a complex process that is affected by both environmental (soil pH, metal content, amount of organic matter, etc.) and internal (taxon, growth stage and mycelium age) factors [15].

Table 1. Families, habitats, substrates, edibility, and herbarium numbers of mushroom species

Mushrooms	Family	Herbarium no	Substrate	Edibility	Reference
Stropharia caerulea Kreisel	Strophariaceae	AKATA 7397	on soil	Inedible	[8]
Lepiota cristata (Bolton) P. Kumm.	Agaricaceae	AKATA 7398	on soil	Inedible	[9]
Mycena epipterygia (Scop.) Gray	Mycenaceae	AKATA 7399	on soil	Inedible	[10]
Hydnum repandum L.	Hydnaceae	AKATA 7400	on soil	Edible	[8]
Clavariadelphus truncatus Donk	Clavariadelphaceae	AKATA 7401	on soil	Edible	[10]
Tricholomopsis rutilans (Schaeff.) Singer	Tricholomataceae	AKATA 7402	on stump	Edible	[11]
Russula chloroides (Krombh.) Bres.	Russulaceae	AKATA 7403	on soil	Edible	[12]
Oudemansiella melanotricha (Dörfelt) M.M. Moser	Physalacriaceae	AKATA 7404	on soil	Edible	[8]
Tricholoma bufonium (Pers.) Gillet	Tricholomataceae	AKATA 7405	on soil	Inedible	[11]
Trichaptum abietinum (Pers. ex J.F. Gmel.) Ryvarden	Polyporaceae	AKATA 7406	on stump	Inedible	[8]
Hygrophorus pudorinus (Fr.) Fr.	Hygrophoraceae	AKATA 7407	on soil	Edible	[8]
Pholiota squarrosa (Vahl) P. Kumm.	Strophariaceae	AKATA 7408	on root	Inedible	[8]
Chalciporus piperatus (Bull.) Bataille	Boletaceae	AKATA 7409	on soil	Edible	[10]
Tricholoma pardinum (Pers.) Quél.	Tricholomataceae	AKATA 7410	on soil	Inedible	[11]
Cystoderma amianthinum (Scop.) Fayod	Agaricaceae	AKATA 7411	on soil	Edible	[8]
Pseudoclitocybe cyathiformis (Bull.) Singer	Pseudoclitocybaceae	AKATA 7412	on soil	Edible	[8]
Lactarius aurantiacus (Pers.) Gray	Russulaceae	AKATA 7413	on soil	Edible	[12]
Lactarius deliciosus (L.) Gray	Russulaceae	AKATA 7414	on soil	Edible	[12]
Chroogomphus rutilus (Schaeff.) O.K. Mill.	Gomphidiaceae	AKATA 7415	on soil	Edible	[8]
Pleurotus dryinus (Pers.) P. Kumm.	Pleurotaceae	AKATA 7416	on tree	Edible	[13]
Pycnoporus cinnabarinus (Jacq.) P. Karst.	Polyporaceae	AKATA 7417	On branch	Inedible	[8]

Table 2. Heavy metal contents of the mushroom species (mg kg^{-1}) (mean ± S.D., N =3)

	Mushrooms	Fe	Cr	Zn	Pb	Se
1	*Stropharia caerulea*	50.2±0.3	13.1±2.5	138.6±1.2	20.4±4.8	1.08±0.01
2	*Lepiota cristata*	56.9±4.0	17.3±2.4	94.6±2.9	21.8±2.3	1.33±0.17
3	*Mycena epipterygia*	250.1±16	10.8±4.6	81.1±1.2	17.3±1.4	0.97±0.01
4	*Hydnum repandum* L.	17.1±0.6	15.6±5	48.6±1.0	22.2±3.4	0.72±0.01
5	*Clavariadelphus truncatus*	162.1±11.7	18.9±2.1	135.1±0.4	27.6±2.7	0.98±0.00
6	*Tricholomopsis rutilans*	989.0±7.7	18.1±2.4	62.2±0.7	27.4±1.7	1.14±0.01
7	*Russula chloroides*	334.9±7.4	10.4±1.5	45.6±0.4	18.2±4.8	0.68±0.01
8	*Oudemansiella melanotricha*	387.8±4.2	15.7±4.3	10.4±0.2	28.0±0.7	0.77±0.01
9	*Tricholoma bufonium*	4.6±0.5	19.9±0.9	13.6±0.4	20.7±6.9	1.23±0.03
10	*Trichaptum abietinum*	23.0±1.0	9.8±2.0	13.6±0.2	21.3±3.8	0.81±0.01
11	*Hygrophorus pudorinus*	754.0±7.9	12.6±0.7	48.7±1.2	19.5±2.6	1.00±0.02
12	*Pholiota squarrosa*	127.8±5.1	11.5±3.9	52.1±0.8	22.4±6.9	1.18±0.02
13	*Chalciporus piperatus*	79.4±4.1	13.1±3.6	25.4±1.1	23.6±3.9	0.79±0.04
14	*Tricholoma pardinum*	327.2±5.2	11.6±4.2	43.5±0.4	23.6±5.0	0.65±0.01
15	*Cystoderma amianthinum*	2.9±0.1	17.0±3.5	67.8±0.7	24.2±5.0	1.09±0.01
16	*Pseudoclitocybe cyathiformis*	224.4±4.4	9.2±2.0	55.0±0.3	18.1±0.9	1.47±0.01
17	*Lactarius aurantiacus*	129.8±6.1	16.0±2.9	25.7±0.1	17.1±2.2	1.15±0.00
18	*Lactarius deliciosus*	3478.7±7.2	18.0±1.8	46.6±0.3	16.0±0.2	1.20±0.01
19	*Chroogomphus rutilus*	22.9±1.9	5.1±0.7	43.1±1.0	17.8±1.6	0.88±0.02
20	*Pleurotus dryinus*	7.7±0.5	11.8±3.4	90.4±0.3	8.9±0.5	0.80±0.00
21	*Pycnoporus cinnabarinus*	2670.6±12	19.1±0.6	71.1±1.6	5.8±0.7	0.97±0.02

Iron is one of the most important metals and monitoring its concentration in biological systems is also important [16]. Excessive accumulation of Fe concentration can cause tissue damage, so its concentration should be carefully controlled [17]. The concentration of Fe was also high and this is probably a result of the high soil concentration [18]. In this study, Fe concentrations of mushroom samples are obtained from 2.9 to 3478.7 mg kg^{-1}. The highest Fe level was determined in *Lactarius deliciosus*. In the literature, Fe concentrations for mushroom samples have been determined in the range of 49.0-1713.0 mg kg^{-1} [14] 3690.7-9455.2 mg kg^{-1} [16], 568-3904 mg kg^{-1} [19], 102-1580 mg kg^{-1} [20], 50.1-842 mg kg^{-1} [21], and 112.0-5079.0 mg kg^{-1} [22]. Obtained Fe values are compatible with those reported studies in the literature.

Chromium can be considered trace element, but it is toxic for health in excessive doses [23]. It plays a role in balancing glucose tolerance in the body [24]. The minimum Cr level was measured as 5.1 mg kg^{-1} dry matter in *Chroogomphus rutilus* and maximum levels of Cr were measured as 19.9 mg kg^{-1} dry matter in *Pleurotus dryinus*. The highest concentration of Cr in the literature were 21.6 mg kg^{-1} [25], 13.7 mg kg^{-1} [26] and 16 mg kg^{-1} [27]. The values of Cr in the mushrooms agree with previous studies.

Low amounts of Zn are essential for the growth of plants and animals, including humans [28]. It serves as a cofactor in the structure of many enzymes. Therefore, these enzymes need zinc to function. It also has important roles in cell division and protein synthesis [29]. The highest Zn level observed was 138.6 mg kg^{-1} in *Stropharia caerulea*. Zn levels in other mushrooms are ranged from 10.4 to 135.1 mg kg^{-1}. Concentration of Zn for mushrooms in the literature are ranged from 16 to 134 mg kg^{-1}[14], 30 to 150 mg kg^{-1} [30], 21.94 to 100.17 mg kg^{-1} [24], and 35 to 136 mg kg^{-1} [31].

The main sources of Pb contamination to humans are consumption of the food and drinks. Pb has a toxic effect on biological system. The presence of Pb in foods is due to soil-related environmental contamination, atmospheric precipitation, pesticides, and materials used in its manufacture. Regular exposure to small amounts of Pb can cause serious health injuries such as encephalopathy, kidney damage, nervous system and various effects on the body [17,20]. The lowest Pb content was determined in *Pycnoporus cinnabarinus* (5.8 mg kg^{-1}) whereas the highest Pb content was determined in *Oudemansiella melanotricha* (28 mg kg^{-1}). The concentration of Pb were determined for mushrooms in the literature between 0.5-20 mg kg^{-1} [14, 25, 32]. The content of Pb in many mushroom species growing in uncontaminated areas is below 2.0 mg kg^{-1} of dry matter. However, Pb concentrations level up to 5 mg kg^{-1} dry matter has been observed for many species. Pb concentrations are quite high in mushrooms growing around highways. Exceedingly high Pb concentrations in dry matter over 100 mg kg^{-1} was found in the nearby surroundings of lead smelters [33].

Selenium is necessary micronutrient for biological systems. It is vital for the synthesis of 25 selenoproteins, including glutathione peroxidase, thioredoxin reductase and iodothyronine deiodinases [34]. Se has a very important role for the synthesis of 25 selenoproteins, including glutathione peroxidase, thioredoxin reductase and iodothyronine deiodinases [35]. It is vital in the functioning of the structural and enzymatic system in the body, including its positive effect on the immune system, anti-carcinogenic effect, balancing redox reactions [36]. Higher and lower Se levels compared to the required amounts for living organisms have some health risks, and the required amount of Se in humans has a narrow window [37]. The range of Se levels were between 0.65 (*Tricholoma pardinum*) and 1.47 mg kg^{-1} (*Pseudoclitocybe cyathiformis*) in mushroom species. The average Se concentration of the mushroom samples was 0.99 mg kg^{-1}. The concentrations of Se in the mushrooms agree with literature values [38, 39].

Accuracy of the method was also evaluated by analyzing BCR 191 (Brown bread) and ERM-BD 151 (Skimmed milk powder). The achieved results were in good agreement with certified values. The results for this study are given in Table 3.

Table 3. Found and certified values of trace metals in CRMs, N=3

Metal	Certified value (BCR-191) (mg kg^{-1})	Found value (mg kg^{-1})	Recovery	Certified value (ERM-BD 151) (mg kg^{-1})	Found value (mg kg^{-1})	Recovery
Fe	40.7±2.3	39±3.3	95.8	53±4	51.9±3.9	97.9
Zn	19.5±0.5	18.8±0.9	96.4	44.9±2.3	44.1±1.0	94.7
Pb	187±14	185.9±11	99.4	0.207±0.014	0.219±0.058	105.2
Se	-	-	-	0.19±0.04	0.214±0.03	112.6

4. Conclusion

This study provides significant data on trace metal concentration of the studied species from the region, and thus indicate environmental contamination. Trace metal concentration levels in the studied mushrooms were compared with the literature values. The results of this study were observed to be generally in good agreement with previous studies.

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