Geliş(Recevied) :27.02.2020
Kabul(Accepted) :01.07.2020

Araştırma Makalesi/Research Article
Doi: 10.30708.mantar.692644

Determination of Elemental Composition of Some Wild Growing Edible Mushrooms

Ali KELEŞ[1], Hüseyin GENÇCELEP[*2]

**Corresponding author:hgenccelep@omu.edu.tr*

[1]Yüzüncü Yil University, Faculty of Education, Department of Biology Education, Van, Turkey
Orcid ID:0000-0002-6087-0805/alikeles61@yahoo.com.tr
[2]Ondokuz Mayıs University, Engineering Faculty, Depart. of Food Engineering, Samsun, Turkey
Orcid ID:0000-0002-8689-7722/ hgenccelep@omu.edu.tr

Abstract: The aim of this study was to determine and elaborate the mineral contents and the some highly toxic elements of wild grown-edible mushrooms. The potassium (K), magnesium (Mg), calcium (Ca), manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd) and lead (Pb) contents of twenty edible mushrooms, collected from Gümüşhane province, Turkey, were analyzed. The studied mushrooms varied widely in their content of both essential and toxic deleterious elements. The minimum and maximum mineral contents of mushrooms were determined as mg/kg dw for K (4170-15747), Mg (295-2095), Ca (100-2778), Mn (3.82-170.25), Fe (50.25-1121.53), Zn (22.99-91.76), Cu (5.89-135.35), Ni (1.05-6.07), Cd (0.06-7.29) and Pb (0.02-32.31) were determined. The potassium content was found to be higher than those of the other minerals in all the mushrooms. Lead and cadmium were present but at concentrations that are not hazardous to human health except for *Armillaria ostoyae.* The K, Mg, Ca, Mn, Fe, and Ni concentrations were determined to be high in *Agrocybe dura.*

Key words: Minerals, Toxic element, Wild edible mushrooms

Yabani Büyüyen Bazı Yenilebilir Mantarların Element Bileşiminin Belirlenmesi

Öz: Bu çalışmanın amacı, yabani yetişmiş mantarların mineral içeriğini ve bazı yüksek derecede toksik elementlerini belirlemek ve detaylandırmaktır. Gümüşhane ilinden toplanan yirmi yenilebilir mantarın Potasyum (K), magnezyum (Mg), kalsiyum (Ca), manganez (Mn), demir (Fe), çinko (Zn), bakır (Cu), nikel (Ni), kadmiyum (Cd) ve kurşun (Pb) içeriği analiz edilmiştir. İncelenen mantarlarda, hem yararlı hem de toksik elementler çok geniş aralıkta değişiyordu. Mantarların minimum ve maksimum mineral içerikleri, K (4170-15747), Mg (295-2095), Ca (100-2778), Mn (3.82-170.25), Fe (50.25-1121.53) için mg/ g kurumadde olarak belirlendi. Örneklerde Zn (22.99-91.76), Cu (5.89-135.35), Ni (1.05-6.07), Cd (0.06-7.29) ve Pb (0.02-30.46 mg/kg kurumadde) aralığında belirlendi. Potasyum içeriğinin, tüm mantarlarda diğer minerallerden daha yüksek olduğu bulunmuştur. Mantarlarda kurşun ve kadmiyum *Armillaria ostoyae* dışındaki mantarlarda insan sağlığı için tehlikeli olmayan konsantrasyonlarda belirlenmiştir. Ayrıca *Agrocybe dura'da* K, Mg, Ca, Mn, Fe ve Ni konsantrasyonlarının yüksek olduğu belirlendi.

Anahtar kelimeler: Mineral, Toksik element, Yabani yenebilir mantarlar

Introduction

Wild edible mushrooms are valued for their unique taste, aroma, nutritional value, and medicinal potentials (Falandysz and Gucia, 2008). In the last few decades, the interest in services of urban ecosystems has greatly increased. Mushrooms have been a popular delicacy in many countries, particularly in central and east Europe. Wild mushrooms are also a popular food source in Turkey. Mushrooms have a long history of use in traditional Chinese medicine. Mushrooms have also been reported as therapeutic foods, useful in preventing diseases such as hypertension, hypercholesterolemia and cancer. These functional characteristics are mainly due to their chemical composition (Kalaĉ, 2016; Zsigmond *et al.,* 2018). The consumption of wild edible mushrooms is increasing, even in the developed world, due to their good contents of proteins and trace minerals (Kalaĉ, 2016). Nevertheless, mushrooms are also recognized as efficient trace metal accumulators (Rzymski *et al.,* 2017).

Studies have shown that some mushroom species contain high concentrations of nutritional trace elements such that the fruiting bodies of higher mushrooms are generally considered rich sources of mineral constituents, including the heavy metals (Falandysz *et al*., 2001, 2003). Mushrooms are an important part of diet in many world regions. Wild edible species collected for culinary reasons have already been found to uptake several toxic elements easily (including Hg, Ni, Cd and Pb) from the ambient environment and accumulate them in aboveground parts (Falandysz *et al*., 2015). Therefore, the place from which they are collected is crucial if the specimen is to be safe for human health. Unfortunately, some mushroom species are able to accumulate relatively high levels of these elements which can pose a threat to human health. However, other elements can also be harmful for mushroom consumers (e.g. As, Cd, Cr (III), Hg or Pb). Trace metal contents in mushrooms are usually higher than those in agricultural crop plants, vegetables, fruits or even animal tissue (Falandysz *et al*., 2015; Kalaĉ, 2016).

Exposure to toxic elements in humans occurs through a variety of routes, including the inhalation of air pollutants or contaminated soil particles, and the consumption of contaminated foods. For non-occupationally exposed individuals, the most likely source of trace elements intake is the diet. Consumers of delicacies such as mushrooms, which may not have been extensively investigated for toxic metal contents, could be exposed via the diet. Information about heavy metal concentrations in foods and their consumers' dietary intake is very important for assessing their health risks to humans. Exposure to elevated levels of mineral elements, such as Cd, Hg, Pb, Cr, and Ni could lead to both acute and chronic health hazards (Falandysz *et al*., 2015).

The macrofungi are collected to make a substantial contribution to food intake. Therefore, it is necessary to know the levels of essential elements in edible mushrooms (Isıloğlu *et al*., 2001). The bioavailability of iron in mushrooms is therefore high and up to 90% of the iron present can be absorbed (Kalaĉ and Svoboda, 2000). The contents of trace metals are related to species of mushroom, collecting area of the sample, age of fruiting bodies and mycelium, and distance from any source of pollution. Metals, such as iron, copper, zinc and manganese are essential metals, since they play an important role in biological systems. Lead and cadmium are non-essential metals as they are toxic, even in traces. The essential metals can also produce toxic effects when the metal intake is excessively elevated (Tuzen *et al.,* 2007; Kalaĉ, 2016). Accurate and adequate food composition data are invaluable for estimating the adequacy of intakes of essential nutrients and assessing exposure risks from intake of toxic non-essential heavy metals (Soylak *et al.,* 2003; Mleczek *et al.,* 2018).

Mushrooms have become increasingly attractive as functional foods for their potential beneficial effects on human health. Due to the toxic minerals they carry, mushrooms should be taken into consideration during their consumption as human food. Also, mushrooms are important in the ecosystem because they are able to biodegrade the substrate, to collect heavy metal (Kalaĉ, 2016).

Turkey has a large edible mushroom potential and is becoming an important exporter of wild mushrooms. Trace metal levels in wild mushroom samples in Gümüşhane province have not yet been determined. The purpose of this study is to determine toxic and essential elements (K, Mg, Ca, Mn, Fe, Zn, Cu, Ni, Cd and Pb in fruit bodies of several mushroom species from Gümüşhane, Turkey.

Material and Method

Samples

The thirty macrofungi samples were collected during field trips in Gümüşhane province, Turkey. Colour slides of the macrofungal specimens were taken in their natural habitats during fields studies. After relevant notes were taken of their morphological and ecological features, they were put in private prepared boxes and brought to the laboratory. Their spore prints were taken and spore dimensions were measured using an ocular micrometer. Then, dried specimens were placed in locked polyethylene bags and kept in a deep freezer at -20 ^{0}C to protect against parasites.

Identification of the specimens was performed according to Breitenbach and Kranzlin (1984–2000), Bresinsky and Besl (1990), Buczacki (1989) and Dahncke and Dahncke (1989). All specimens are kept in the Herbarium of Yuzuncu Yıl University, Department of Biology (VANF). Table 1 shows the taxa of wild edible macrofungi.

Method

Atomic absorption spectrophotometer (Varian Techtron Model AAS 1000, Varian Associates, Palo Alto, CA) was used for the determination of the minerals (Ca, Mg, K, Fe, Zn, Cu, Mn, Pb, Ni and Cd) in dried fruit bodies of macrofungi. Each dried mushroom sample was weighed as 4-5 g and placed in a porcelain crucible and ashed at 550°C for 18-20 h.; then the ash was dissolved in 1ml concentrated HNO3, evaporated to dryness, heated again at 550°C for 4 h, treated successively with 1 ml HNO_3 and 1 ml H_2O_2 and then diluted with double deionized water up to a volume of 25 ml. Three blank samples were treated in the same way. The species, which were digested in an acid solution of HNO_3, were passed through the AAS system using different lamps, and calibrated with related minerals in different concentrations for different micronutrients (AOAC, 1990).

Table 1. Taxa of wild edible macrofungi collected from Gümüşhane region of Turkey

No	Class, Family and taxa of macrofungi	Habitat	KHN no:
1.	*Agaricus bisporus* (J.E. Lange) Imbach	Gümüşhane, Torul, Köprübaşı district, meadow area (Agaric)	842
2.	*A. langei (F.H. Møller) F.H. Møller*	Gümüşhane, Torul, Zigana Mountein, Zigana tunnel around, conifer forest	865
3.	*Coprinus comatus* (O.F. Müll.) Pers.	Gümüşhane, Torul, Günay WİIlage, meadow area	1318
4.	*Hydnum repandum* L.	Gümüşhane, Torul, Zigana Mountein, Zigana tunnel around, conifer forest	879
5.	*Marasmius oreades* (Bolton) Fr.	Gümüşhane, Torul, Köprübaşı district meadow area	845
6	*Armillaria ostoyae* (Romagn.) Herink	Gümüşhane, Kürtün, Örümcek Mountein, mixed forest, on stumps of poplar tree	1221
7.	*Agrocybe dura* (Bolton) Singer	Gümüşhane, Torul, Köprübaşı district	1434
8.	*A. praecox* (Pers.) Fayod	Gümüşhane, Geçitkaya Willage, on stumps of poplar tree	1102
9.	*Pleurotus eryngii* (DC.) Quél.	Gümüğhane, Bozkır, On Heliz residues	874
10.	*P. ostreatus* (Jacq.) P. Kumm.	Gümüşhane, Near Akçahısar Castle, on stumps of poplar tree (Poplar mushroom)	3425
11.	*Cyclocybe cylindracea* (DC.) Vizzini & Angelini	Gümüşhane, Güvercinlik Willage, on stumps of poplar tree	1093
12.	*Cantharellus cibarius Fr.*	Gümüşhane, Torul, Zigana Mountein, Zigana tunnel around, conifer forest	889
13	*Clavulina cinerea* (Bull.) J. Schröt.	Gümüşhane, Kürtün, Örümcek Mountein, mixed forest	889
14.	*Leccinum scabrum* (Bull.) Gray	Gümüşhane, Günay Willage, conifer forest	1320
15.	*Suillus granulatus* (L.) Roussel	Gümüşhane, Günay Willage, conifer forest	1311
16.	*S. luteus* (L.) Roussel	Gümüşhane, Köse, conifer forest	1443
17.	*Cerioporus squamosus* (Huds.) Quél.	Gümüşhane, Torul, Köprübaşı district, on stumps of poplar tree	854
18.	*Lactarius deliciosus* (L.) Gray	Gümüşhane, Torul, Günay willage, meadow area	1321
19.	*L. salmonicolor* R. Heim and Leclair	Gümüşhane, Torul, Zigana Mountein, Zigana tunnel around, conifer forest	885
20.	*Russula delica* Fr.	Gümüşhane, Torul, Zigana Mountein, Zigana tunnel around, conifer forest	882

To check for possible contamination by reagents or glassware, blanks containing 4ml of ultrapure concentrated HNO_3 and 4 ml H_2O_2 were run together with analytical samples and every batch of analytical samples was run together with the standard matrix. The values of Ca, Mg, K, Fe, Zn, Cu, Mn, Pb, Ni and cadmium Cd were calculated as mg/kg dw. Detection limit is defined as the concentration corresponding to three times the Standard deviation of ten blanks. Detection limit values of elements as mg/kg in AAS were found to be 0.012 for K, 0.003 for Mg, 0.015 for Ca, 0.029 for Mn, 0.060 for Fe, 0.013 for Zn, 0.041 for Cu, 0.063 for Ni, 0.032 for Cd and 0.10 for Pb. The results were within limits of quantification for above minerals (calculated as 10-fold of standard deviation from ten replicates of the instrumental blank solution) 0, 2, 4, 8 and 16 mg/g or mg/kg, respectively. Correlation coefficients of the mineral result were determined between r=0.9932 and 0.9999. Mushrooms were selected normally harvested for consumption (pileus+stipe). For all the mushroom species, at least three samples were analysed.

Results and Discussion

Data on potassium and nine metals most frequently determined in mushrooms from Gümüşhane, Turkey are given for 20 species in Table 2. All the metal concentrations were determined on a dry weight basis.

The most abundant element was found to be potassium, (ranging from 4170 to 15747 mg/kg dw), followed by magnesium, calcium and iron while the most variable mineral was calcium. Mushrooms contained a wide range of minerals, particularly manganese and magnesium. The lowest Mg, Zn and Ni contents were observed in *Russula delica* (Table 2). Wild-grown mushrooms are able to accumulate in their fruiting bodies large amounts of both macro- and micro-elements that are essential to fungi and its consumers. Mushrooms can also be specifically enriched with toxic elements such as As, Hg, Cd and Pb. Potassium (K) and phosphorus (P) are two prevailing elements in fruiting bodies and are usually followed by Ca, Mg, Na and Fe (Falandysz and Borovicka, 2013; Okoro and Achuba, 2012).

The mean contents of elements detected in the mushrooms of all the investigated species (Table 2) generally decreased in the following order: K > Mg > Ca > Fe > Mn > Zn > Cu > Ni > Cd > Pb. These elements can be divided according to their level in dry matter into five groups: i) those exceeding 1000 mg/kg (K, Mg and Ca); (ii) ranging from 100 to 1000 mg/kg (Mn, Fe and Zn); (iii) ranging from 10 to 100 mg/kg (Cu); (iv) ranging from 1 to 10 mg/kg (Ni); and (v) below 1 mg/kg (Cd and Pb).

Potassium content was higher than other minerals in all mushrooms in this study, varying between 4170 (*Lactarius salmonicolor*) and 15747 mg/kg dw (*Cantharellus cibarius*). In general, most of the mushrooms studied contained considerably high amounts of potassium. The levels of essential elements in mushroom species were higher than those of toxic elements. Gençcelep *et al.* (2009) reported the potassium contents of wild edible mushrooms as being between 12600 and 29100 mg/kg dw. Wang *et al*. (2014) found that potassium content was between 16000 (*S. rugoso-annulata*) and 37000 (*C. cornucopioides*) mg/kg in dry matter. Sanmeea *et al.* (2003) reported that potassium accumulation in mushrooms could rise up to 45200 mg/kg. Liu *et al.* (2012) reported that the lowest potassium value (1300 mg/kg dw) was measured in *Melanoleuca gigantea* and *Melanoleuca arcuata*, the highest potassium value (4600 mg/kg dw) was found in *Boletus griseus*. The greatest concentrations of K were obtained in C. *cibarius* (41823 mg/kg), whereas the lowest was in *Boletus edulis* (11269 mg/kg) (Cvetkovic, 2015). Usually potassium content in mushrooms varies between 20000 and 40000 mg/kg dw. The overall data indicates that mushrooms may contain elevated levels of potassium. In this study, potassium levels were lower than reported values in the literature. Showing that mushrooms are an excellent source of potassium in the human diet.

Magnesium content was 295 mg/kg dw in *Russula delica* and 2095 mg/kg dw in *Agaricus bisporus*. The level of magnesium reported in this study was relatively low compared to earlier published reports (Demirbaş, 2000) which was magnesium content ranged from 330 mg/kg dw in *Tricholoma anatolicum* to 6560 mg/kg dw in *Morchella deliciosa*. In our previous study, the concentration levels of Mg in *Morchella vulgaris* 1920 mg/kg, *Helvella lacunosa* 1190 mg/kg, *Lepista nuda* 3410 mg/kg were found (Gençcelep *et al.,* 2009). Liu *et al.* (2002) reported that the magnesium contents of the mushrooms ranged from 84 mg/kg dw in *Leucopaxillus giganteus* to 550 mg/kg dw in Macrocybe *gigantea*. Previously reported magnesium contents in mushrooms varied between 800 and 1800 mg/kg dw (Kalaĉ, 2010). The lowest magnesium value, 248 mg/kg dw *Bolereus tomentipes*, was found by Li *et al.* (2011). Sanmeea et al. (2003) reported that mature *Astraeus hygrometricus* had 1600 mg/kg of Mg concentrations. In this study, magnesium concentrations of the same fungus species were found to be lower than the other studies. As a result, environmental factors are very important to amount of metal concentrations in mushrooms.

Magnesium levels in this study are in agreement with the value reported in the literature.

In the present study, the calcium contents of the mushrooms ranged from 100 mg/kg dw in *Armillaria ostoyae* to 2778 mg/kg dw in *Coprinus comatus*. In our previous study, the concentration levels of Ca in *Morchella vulgaris* 870 mg/kg, *Helvella lacunosa* 470 mg/kg, *Lepista nuda* 8800 mg/kg were found (Gençcelep *et al.,* 2009). Previously reported calcium contents of mushrooms varied from 100 to 500 mg/kg dw (Kalaĉ, 2010). The calcium contents in our mushroom samples are higher than the values reported in the literature. The accumulation of metals in mushrooms has been found to be affected by environmental and fungal factors.

Table 2. Taxa of wild edible macrofungi collected from Gümüşhane region of Turkey (mg/kg dw)

No	Taxa	K	Mg	Ca	Mn	Fe	Zn	Cu	Ni	Cd	Pb
1	*Agaricus bisporus*	7624	2095	936	33.07	217.99	61.06	69.19	4.89	0.42	4.97
2	*Agaricus langei*	5386	1273	238	13.98	104.18	47.19	46.85	3.30	0.54	1.94
3	*Coprinus comatus*	9548	1553	2778	20.18	277.66	48.34	47.26	6.07	1.18	1.39
4	*Hydnum repandum*	6334	481	103	16.82	1121.53	34.68	11.55	2.09	0.28	4.56
5	*Marasmius oreades*	12124	888	761	30.78	262.92	91.76	58.48	1.91	0.15	0.02
6	*Armillaria ostoyae*	8636	732	100	32.89	242.11	57.13	31.11	2.27	7.29	32.31
7	*Agrocybe dura*	12066	1507	1542	170.25	395.66	40.06	17.60	3.67	1.98	1.76
8	*Agrocybe praecox*	7786	979	573	14.69	133.54	38.34	24.00	1.87	0.52	0.56
9	*Pleurotus eryngii*	7839	1838	205	8.15	103.86	56.69	9.39	2.68	0.17	1.13
10	*Pleurotus ostreatus*	9975	1514	465	10.57	242.09	55.29	5.89	2.03	0.57	1.18
11	*Cyclocybe cylindracea*	9264	544	160	21.31	259.91	30.10	19.09	2.11	0.23	0.91
12	*Cantharellus cibarius*	15747	686	439	18.73	174.42	82.22	46.91	2.91	1.65	6.51
13	*Clavulina cinerea*	15737	412	184	35.84	355.20	49.75	135.35	3.88	3.92	30.46
14	*Leccinum scabrum*	8040	752	178	3.82	98.14	48.57	34.59	2.91	0.06	0.92
15	*Suillus granulatus*	5618	593	277	5.18	166.02	40.31	16.72	1.71	0.13	0.75
16	*Suillus luteus*	6449	736	184	7.53	113.96	52.30	14.84	1.67	0.12	1.10
17	*Cerioporus squamosus*	7384	1574	102	4.70	50.25	44.47	15.16	2.61	1.99	1.05
18	*Lactarius deliciosus*	7121	579	222	12.45	144.01	57.12	8.85	1.61	0.88	1.39
19	*Lactarius salmonicolor*	4170	529	237	17.45	73.93	34.50	13.70	1.38	1.22	3.19
20	*Russula delica*	5198	295	119	8.13	106.39	22.99	26.90	1.05	2.55	4.17
	Mean *±SD*	8602 ±3212	978 ±529	490 ±646	24.32 ±35.75	232.18 ±229.52	49.64 ±16.30	32.67 ±30.08	2.63 ±1.23	1.29 ±1.79	5.01 ±9.18
	Minimum	4170	295	100	3.82	50.25	22.99	5.89	1.05	0.06	0.02
	Maximum	15747	2095	2778	170.25	1121.53	91.76	135.35	6.07	7.29	32.31

But, it seems to be higher when compared to the concentrations obtained by Sanmeea *et al.* (2003) (100-2400 mg/kg dw). Andreea *et al.* (2018) suggest that the Ca has a considerable role in the integrity of the cell and the vacuolar membranes, and it slows enzymatic browning reactions.

Manganese was also determined in all mushrooms. The manganese content of the mushrooms studied in the present work ranged from 3.82 mg/kg dw in *Leccinum scabrum* to 170.25 mg/kg dw in *Agrocybe dura*. The reported manganese values in the literature for mushrooms were 14.2-69.7 mg/kg, 21.7-74.3 mg/kg and 7.1-81.3 mg/kg, 5.54-135 mg/kg dw (Gençcelep *et al.,* 2009; Soylak *et al.* (2005), respectively. The manganese values in this study are found lower than in the literature.

The iron content of the mushrooms ranged from 50.25 mg/kg dw in *Cerioporus squamosus* to 1121.53 mg/kg dw in *Hydnum repandum*. Iron values in mushroom samples (as reported) ranged from 31.3-1190 mg/kg (Sesli and Tüzen, 1999), 56.1-7162 mg/kg (Işıloğlu *et al.,* 2001), 50.1-842.0 mg/kg (Gençcelep *et al.,* 2009), respectively. Wang *et al.* (2014) found that iron (Fe) content in *Thelehhora ganhajun* was 1500 mg/kg dw, which is particularly higher than in other mushrooms. The iron values in the present study are in lower than with reported values in the literature. It is known that adequate iron in a diet is very important in order to decrease the incidence of anemia.

Mushrooms are known as zinc accumulators and the sporophore: substrate ratio for Zn ranges from 1 to 10 mg/kg (Işıloğlu *et al.,* 2001). The zinc content was the lowest (22.99 mg/kg dw) in *Russula delica*, whereas it was highest (91.76 mg/kg dw) in *Marasmius oreades* (Table 2). The reported literature zinc content ranged between 22.10 and 185 mg/kg dw (Gençcelep *et al.,* 2009; Kalaĉ, 2001; Kaya and Bağ, 2001). Sarıkürkçü *et al.* (2012) found the highest Zn values in *Helvella leucopus* and *Tricholoma auratum* (354 and 356 mg/kg, respectively). In this study, some mushroom species have higher zinc content more than 50 mg/kg (*Agaricus bisporus, Pleurotus eryngii, Lactarius deliciosus, Suillus luteus, Pleurotus ostreatus, Cantharellus cibarius* and *Armillaria ostoyae*). These mushrooms species were collected from locations near the downtown of Gümüşhane. Therefore, metal accumulation may be more owing to soil pollution. Zn is an essential nutrient that has an important role in biological systems. Zinc is necessary for the functioning of various enzymes and plays an essential role in DNA, RNA, and protein synthesis. The major symptoms of zinc deficiency are delayed growth and slow maturation (WHO, 1996).

Minimum and maximum values of copper were 5.89 and 135.35 mg/kg dw in *Pleurotus ostreatus* and *Clavulina cinerea*. Copper contents of mushroom samples in the literature have been reported to be in the range of 4.71-51.0 mg/kg (Tüzen *et al.,* 1998) and 10.3-145 mg/kg (Sesli and Tüzen, 1999). Copper contents found in this study parallel those reported in the literature.

In the present study, the Cu concentrations detected in mushrooms were lower than previously reported in the literature but only one mushroom (*Clavulina cinerea*, 135.35 mg/kg) higher than 100mg/kg in Table 2. Keleş *et al.* (2017*)* found that copper values in *Leccinum versipelle* (102.40 mg/kg) and *Russula delica* (128.94 mg/kg) were collected near the downtown of Erzincan, Turkey, therefore copper contents of these samples were found higher than the others. In our previous study, the concentration levels of Cu in *Pleurotus ostreatus* 47.1 mg/kg and *Lepista nuda* 26.6 mg/kg were found (Gençcelep *et al.,* 2009). Cu is an essential element. Enzymes containing copper are important for the body to transport and use iron. In previous studies, Cu concentrations in edible mushrooms were found to be between 100 and 300 mg/kg, which was not considered a health risk (Kalaĉ and Svoboda, 2000). In 1996, a joint FAO/International Atomic Energy Agency/ WHO official report set an upper limit for the safe range of population mean exposures for adults of 0.2 mg/kg body weight per day (WHO, 1996).

Nickel was determined all mushrooms. *Coprinus comatus* contained high nickel content with an amount of 6.07 mg/kg dry matter. The reported Ni values for wild-growing mushrooms were 0.4-15.9, 0.4-2, 1.72-24.1 mg/kg (Işıloglu, 2001; Kalaĉ and Svoboda, 2000, Soylak *et al.,* 2005), respectively. The Ni levels are generally in agreement with previous studies. The obtained Ni levels in some mushrooms (*Coprinus comatus*, *Agaricus bisporus, Clavulina cinerea, Agaricus langei* and *Agrocybe dura)* are higher than the allowed amount (0.05-5 mg/kg) of National Academy of Sciences (1975) for plants and foods (NAS, 1975) (Table 2). Nickel has been linked to lung cancer and the tolerable upper intake level for this toxic element is reported as 1 mg/day (FNB, 2001).

Cadmium is known as a principal toxic element, since it inhibits many life processes. Cadmium has been associated with renal damage; cancer and childhood aggression (JECFA, 2011). Mushroom, in particular, can be very rich in cadmium. Cadmium was measured as the lowest detected in *Leccinum scabrum* (0.06 mg/kg dw) and it was the highest in *Armillaria ostoyae* (7.29 mg/kg dw) which is relatively high compared to reported literature data (Mendil et al., 2005) Cd levels were found generally lower than 2.0 mg/kg for the other mushrooms species, in this study. Long-term exposure to high levels of Cd may lead to considerable accumulation in the liver and kidneys, particularly the renal cortex, resulting in kidney damage (WHO,1989). Thus, cadmium seems to be the most deleterious one among heavy metals in mushrooms. It is acceptable daily or weekly intake may be easily reached by consumption of an accumulating mushroom species (Kalaĉ *et al.,* 2004). In the case of this element the JECFA authority has established a provisional tolerable monthly intake (PTMI) at a level of 0.025 mg/kg bodyweight (JECFA, 2011), which accounts for 1.5 mg per month for a 60-kg adult.

Pb concentrations of mushroom samples were generally low, except *Armillaria ostoyae* and *Clavulina cinerea* with an amount of 32.31 and 30.46 mg/kg dw. The Pb levels of all other samples were not higher compared to the reported Pb values for mushrooms by Tüzen *et al.,* (1998) (2.35 mg/kg), Kalaĉ and Svoboda (2000) (0.5-20 mg/kg) and Kaya and Bag (2010) (2.166 mg/kg). Sarikürkcü *et al.,* (2012) found the lowest Pb value in *Lyophyllum decastes* (0.5 ± 0.19 mg/kg). This is followed by *Morchella esculenta* (0.9 ± 0.29 mg/kg). In *Rhizopogon roseolus, Volvoriella gloiocephala* and *Cyclocybe cylindracea*, Pb contents were found equal or above 4.0 mg level (6.2 ± 0.44, 5.9 ± 0.11 and 4.0 ± 0.50 mg/kg), respectively. Pb is used for a number of industrial, domestic, and rural purposes for example, in lead batteries and in leaded petrol. A significant source of exposure to lead is via the diet. Lead is a cumulative toxin that can primarily affect the blood, nervous system, and kidneys. In the blood at high concentrations, lead inhibits red blood cell formation and eventually results in anemia (Çayır *et al.,* 2010). The provisional tolerable weekly intake (PTWI) of Pb was set at 0.025 mg/kg bodyweight (the equivalent of 0.0036 mg/kg body weight per day) (JECFA, i.e., 1.5 mg weekly (and 0.21 mg daily) for an adult weighing 60 kg.

Aiming to assess the health risks associated to the consumption of the mushrooms with regard to the toxic metal content, we used the PTWI (Provisional Tolerable Weekly Intake) values given by the Food and Agriculture Organization/World Health Organization Joint Expert Committee on Food Additives (JECFA) (FAO/WHO, 2011). The PTWI is the maximum amount of a contaminant to which a person can be exposed per week over a lifetime without an unacceptable risk of health effects. The level is provisional, because it is subject to review when new information becomes available. According to the FAO/WHO the PTWI values given in mg/kg body weight (bw) are the followings: 0.015 for As, 0.007 for Cd and 0.025 for Pb. In 2011 the values for As and Pb were withdrawn by the Committee because of the need for further research, the level of Cd was changed to 0.025 PTMI (Provisional Tolerable Monthly Intake). In our evaluation, we used the values given in 2009 for As and Pb, and the values given in 2011 for Cd. We have also calculated the recommended weekly amount (RWA) as the maximum safe intake in kg of fresh mushroom considering the PTWI value as one.

Present human health risk assessments of elements like toxic metals or metalloids are traditionally based on the total content in foods and food consumption, although, the amount of an ingested element in the diet does not always reflect the amount that is accessible to the consumer. The terms bioaccessibility and bioavailability are often used indiscriminately although their meaning is slightly different. Bioaccessibility defines the fraction of a contaminant ingested with food that is released from its matrix into the digestive juice and has the potential to be absorbed by the intestines during the digestion. Bioavailability, however, refers to the proportion of a contaminant ingested with food that is absorbed by the intestine with the subsequent potential to reach the systemic circulation and exert toxic effects (Versantvoort *et al.,* 2005; Zsigmond *et al.,* 2018).

The results of nutritionally valuable minerals show that twenty mushroom species contained high amounts of potassium, calcium, magnesium and iron. Most of them contain little lead, nickel, cadmium or copper. Minerals in the diet are required for metabolic reactions, transmission of nerve impulses, rigid bone formation and regulation of water and salt balance (Kalaĉ and Svoboda*,* 2000).

Mushrooms collected from urban and industrial areas polluted with toxic compounds (Ni, As, Hg, Cd and Pb) usually show highly elevated content of such constituents in flesh (Falandysz and Borovicka, 2013). The content of toxic elements in the studied mushrooms was generally low and safe, although all investigated species contained a relatively high content of rare-earth elements (REEs), particularly of Cd ve Pb.

Finally, Principal Component Analysis (PCA) was used to display the differences among all the observations (all mushroom species characterized by all elements) (Figure 1). The results of PCA of the mean values of minerals of wild mushroom samples are depicted in a 3-dimensional plot (Figure 1). Results from the PCA showed that principal components (PC) 1, 2 and 3 described about 68.71% of the total variation of sample: 31.12% PC1, 23.80% PC2 and 13.79% PC3. Principal component 1 was heavily loaded on Ca, Ni and Mg, component 2 was loaded on Cd, Pb and Cu whereas PC3 was loaded Zn, K, Fe and Mn. The PCA analysis showed that Mn, Ni, Ca and Mg were positively correlated to each other, and the correlation was very high. Figure 1 also presents the positive low correlation between Fe and Zn. Results also showed that there is negative significant relationship among Zn and K attributes (Figure 1).

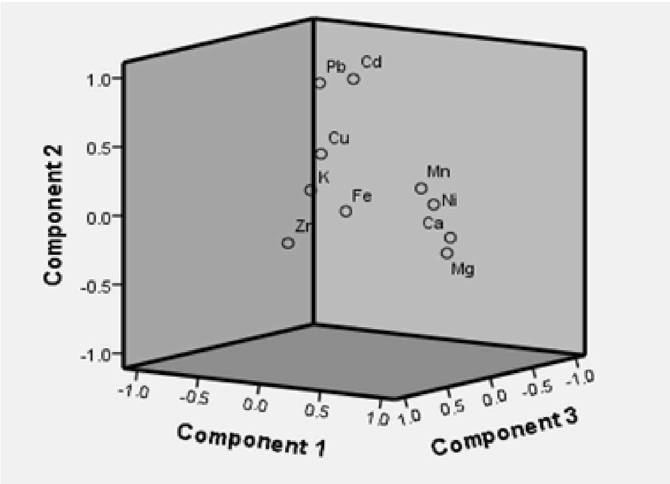

Figure 1. Principal component analysis threeplot of minerals contents of wild mushrooms.

Ideally, mushrooms used for human consumption should be characterized by the lowest possible level of toxic elements, and contain relevant mineral content in their fruiting bodies. In summary, the present research investigated the elemental composition of mushrooms from the wild edible mushrooms for dietary purposes in Turkey over the last few years. The studied mushrooms were found to vary widely in their elemental composition. Some mushrooms demonstrated a lower variability in element content and the lowest content of toxic or potentially toxic elements when compared with other tested species. This would seem to indicate that wild edible mushrooms (as well as other mushrooms investigated previously) may constitute an important dietary source of these elements for humans. The studied mushrooms were found to be generally safe with respect to the content of potentially toxic elements, although increased contents of Ni, Cd and Pb in some of the studied species requires further attention as regards the bioavailability of these elements from mushrooms. Further studies are, however, necessary to elucidate any potential risks arising from the presence of rare-earth elements (REEs) in these foodstuffs.

References

Andreea, R., Zsigmonda, K.V., Izolda, K., István, U., Zoltán, M., Károly, H. (2018). Elemental composition of wild growing Agaricus campestris mushroom in urban and peri-urban regions of Transylvania (Romania). *Journal of Food Composition and Analysis,* 72 15–21.

Breitenbach, J., Kranzlın, F. (1984-2000). Fungi of Switzerland (Vol. 1–5). Switzerland: Verlag Mykologia Lucerne.

Bresinsky, A., Besl, H. (1990). A Colour Atlas of Poisonous Fungi (pp. 295). Stuttgart: Wolfe Publishing Ltd.

Buczacki, S. (1989). Fungi of Britain and Europe (pp. 320). Glasgow: William Collins Sons and Co Ltd.

Dahncke, M. R., Dahncke, S. M. (1989). 700 Pilze in Farbfotos (pp. 686). Stuttgart: AT Verlag Aarau.

AOAC, 1990. Official Methods of Analysis of AOAC International (17.Edition). USA.

Cvetkovic, J.S., Mitic, V.D., Stankov-Jovanovic, V.P., Dimitrijevic, M.V., Nikolic-Mandic, S.D. (2015). Elemental composition of wild edible mushrooms from Serbia. *Analitical Letter,* 48(3): 2107–2121.

Çayir, A., Coşkun, M., Coşkun, M. (2010). The heavy metal content of wild edible mushroom samples collected in Canakkale Province, Turkey. *Biological Trace Element Research,* 134(2):212–219.

Demirbaş, A. (2000). Accumulation of heavy metals in some edible mushrooms from Turkey. *Food Chemistry,* 68: 415-419.

Falandysz, J., Borovicka, J. (2013). Macro and trace mineral constituents and radionuclides in mushrooms-health benefits and risks. *Applied Microbiology and Biotechnology,* 97: 477–501.

Falandysz, J., Gucia, M. (2008). Bioconcentration factors of mercury by Parasol mushroom (Macrolepiota procera). *Environmental Geochemistry and Health,* 30: 121–125.

Falandysz, J., Kawano, M., Swieczkowski, A., Brzostowski, A., Dadej, M. (2003). Total mercury in wild-grown higher mushrooms and underlying soil from Wdzydze Landscape Park, Northern Poland. *Food Chemistry,* 81: 21–26.

Falandysz, J., Szymczyk, K., Ichihashi, H., Bielawski, L., Gucia, M., Frankowska, A., Yamasaki, S. (2001). ICP/MS and ICP/AES elemental analysis (38 elements) of edible wild mushrooms growing in Poland. *Food Additives and Contamination,* 18: 503–513.

Falandysz, J., Zhang, J., Wang, Y., Krasinska, G., Kojta, A., Saba, M., Shen, T., Li, T., Liu, H. (2015). Evaluation of the mercury contamination in mushrooms of genus Leccinum from two different regions of the world: accumulation, distribution and probable dietary intake. *Scientific Total Environments,* 537: 470–478.

Gençcelep, H., Uzun, Y., Tunçtürk, Y., Demirel, K. (2009). Determination of mineral contents of wild-grown edible mushrooms. *Food Chemitry*, 113: 1033–1036.

Isıloğlu, M., Yilmaz, F., Merdivan, M. (2001). Concentrations of trace elements in wild edible mushrooms. *Food Chemistry*, 73: 163–175.

JECFA, (2011). Safety Evaluation of Certain Contaminants in Food, Prepared by the Seventy-second Meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) WHO Food Additives Series, No. 959.

JECFA, (2012). Safety Evaluation of Certain Food Additives/Prepared by the Seventy Fourth Meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) WHO Food Additives Series, No. 65.

Kalaĉ, P., Svoboda, L. (2000). A review of trace element concentrations in edible mushrooms. *Food Chemistry,* 69: 273–281.

Kalaĉ, P. (2016). Edible Mushrooms: Chemical Composition and Nutritional Value. Elsevier, Amsterdam, Netherlands.

Kalaĉ, P., Svoboda, L., Havlickova, B. (2004). Content of cadmium and mercury in edible mushroom. *Journal Applied Biomedicine*, 2: 15-20.

Kaya, A, Bağ, H. (2010). Trace Element Contents of Edible Macrofung Growing in Adıyaman (Turkey). Asian Journal of Chemistry 22: 1515-1521.

Keleş, A., Gençcelep, H., Demirel, K. (2017). Elemental Composition of Naturally Growing Wild Edible Mushroom. *Journal of Natural Product and Plant Resources,* 7 (4): 37-44.

Li, T., Wang, Y.Z., Zhang, J. (2011).Trace element content of Boletus tomentipes mushroom collected from Yunnan, China. *Food Chemistry*, 127: 1828-1830.

Liu, H., Zhang, J., Li, T. (2012). Mineral Element Levels in Wild Edible Mushrooms from Yunnan, China. *Biological Trace Element Research*, 147: 341-345.

Mendil, D., Uluozlu, O.D., Tuzen, M. (2005). Determination of trace metal levels in seven fish species in lakes in Tokat, Turkey. *Food Chemistry*, 90 (1-2): 175-179.

Mleczek, M., Rzymski P., Budka, A., Siwulski, M., Jasińska, A., Kalač, P., Poniedziałek, B., Gąsecka, M., Niedzielski, P. (2018). Elemental characteristics of mushroom species cultivated in China and Poland. *Journal of Food Composition and Analysis,* 66, 168–178.

Okoro, I.O., Achuba, F.I. (2012). Proximate and mineral analysis of some wild edible mushrooms. *African Journal of Biotechnology,* 11: 7720–7724.

Rzymskia, P., Mleczekb,M., Siwulskic, M., Jasinskac, A., Budkad, A., Niedzielskie, P., Kalaĉ, P., Gaseckab, M., Budzynska, S. (2017). Multielemental analysis of fruit bodies of three cultivated commercial Agaricus species. *Journal of Food Composition and Analysis,* 59: 170–178.

Sanmeea, R., Dellb, B., Lumyongc, P. (2003). Nutritive value of popular wild edible mushrooms from northern Thailand. *Food Chemistry,* 82: 527-532.

Sarikürkcü C., Tepe B., Solak M.H., Çetinkaya, S. (2012). Metal Concentrations of Wild Edible Mushrooms from Turkey. *Ecological Food Nutrition,* 51(4): 346-363.

Sesli, E., Tuzen, M. (1999). Levels of trace elements in the fruiting bodies of macrofungi growing in the East Black Sea region of Turkey. *Food Chemistry*, 65: 453-460.

Soylak, M., Karatepe, A. U., Elci, L., Dogan, M. (2003). Column preconcentration/ separation and atomic absorption spectrometric determinations of some heavy metals in table salt samples using amberlite XAD-1180. *Turkish Journal of Chemistry*, 27: 235–242.

Soylak, M., Saracaoğlu , S., Tüzen, M., Mendil, M. (2005). Determination of trace metals in mushroom samples from Kayseri, Turkey. *Food Chemistry*, 92: 649-652.

Tüzen, M., Ozdemir, M., Demirbaş, A. (1998). Study of heavy metals in some cultivated and uncultivated mushrooms of Turkish origin. *Food Chemistry*, 63: 247-251.

Tüzen, M., Sesli, E., Soylak, M. (2007). Trace element levels of mushroom species from East Black Sea region of Turkey. *Food Control,* 18: 806–810.

Versantvoort, C.H.M., Oomen, A.G., Van de Kamp, E., Rompelberg, C.J.M., Sips, A.J.A. M. (2005). Applicability of an in vitro digestion model in assessing the bioaccessibility of mycotoxins from food. *Food Chemical Toxicology,* 43: 31–40.

Wang, X.M., Zhang, J., Wu, L.H. (2014). A mini-review of chemical composition and nutritional value of edible wild-grown mushroom from China. *Food Chemistry,* 151: 279-285.

WHO, (1989). World Health Organization Health principles of housing. Geneva, Switzerland. p54.

WHO, (1996). World Health Organization. Safety evaluation of certain food dditives. Italy.

Zsigmond, A. R., Varga, K., Kántor, I., Urák, I., May, Z., Héberger, K. (2018). Elemental composition of wild growing Agaricus campestris mushroom in urban and peri-urban regions of Transylvania (Romania). *Journal of Food Composition and Analysis,* 72,15–21.