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Contributed Paper

Content of Minerals and Trace Elements Determined by ICP-MS in Eleven Mushroom Species from Anatolia, Turkey

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ABSTRACT

The mineral and trace element content of 11 mushroom species; namely, *Fomes fomentarius*, *Funalia trogii*, *Ganoderma adspersum*, *Ganoderma applanatum*, *Ganoderma lucidum*, *Gyromitra esculenta*, *Lyophyllum decastes*, *Pleurotus ostreotus*, *Rhizopogon luteolus*, *Russula delica*, *Tricholoma fracticum* from Anatolia were analyzed by ICP–MS. 3 major minerals (Na, Mg, Ca) and 15 trace elements (V, Mn, Fe, Zn, Ga, Se, Al, Cr, Ni, As, Sr, Co, Cu, Tl, Pb) were studied comprehensively. The minerals and trace elements (mg/kg) were ranged as follows: Na 66.9-436., Mg 167.3-988, Ca 24.7-296.3, V 0.06-0.94, Mn1.89-76.5, Fe 19.2-383.1, Zn 6.6-49.6, Ga 0.24-3.36, Se 0.01-0.28, Al 18.08-2382, Cr 0.08-0.66, Ni 0.25-5.71, As 0.23-0.96, Sr 2.03-14.70, Co 0.02-1.49, Cu 0.14-8.46, Tl 0.01-0.17and Pb 0.10-1.80.

Keywords: mushroom species, mineral content, trace element content, ICP-MS

1. INTRODUCTION

Mushrooms are important due to their chemical and nutritional properties as well as their possessing various biological activities i.e. antimicrobial, antioxidant [1], antitumor, anti-inflammatory, anticancer, antiviral, anti-immunomodulatory and anticholesterol [2]. Mushrooms contains high amount of minerals e.g. Mg, Fe, P, K, Ca, Zn and Mn [3]. The essential metals such as Mn, Fe, Zn and Cu play important roles in biological systems. These essential metals can be toxic when taken in excess. Nonessential heavy metals of mushrooms particularly Pb and Cd are already known as toxic to our body [4]. There are numerous studies performed to investigate the presence metals in mushroom species [5-7]. In this study, we objected to analyze mineral and trace element contents of eleven wild mushrooms namely, *F. fomentarius*, *F. trogii, G. adspersum*, *G. applanatum*, *G. lucidum*, *G. esculenta*, *L. decastes*, *P. ostreotus*, *R. luteolus*, *R. delica*, *T. fracticum* collected from Anatolia by ICP-MS technique.

2. MATERIALS AND METHODS

2.1 Mushroom Materials

The species names, families, collection localities with dates and fungarium numbers of 11 mushroom species are given in Table 1.

Table 1. Collection localities and dates, family and numbers of the mushroom species studied.

No	Fungarium numbers	Family	Mushroom species	Collection localities and dates
1	AT-935	Polyporaceae	*Fomes fomentarius* (L.) Fr.	Uşak, November 2012
2	AT-678	Polyporaceae	*Funalia trogii* (Berk.) Bondartsev & Singer	Uşak, November 2012
3	AT-1403	Ganodermataceae	*Ganoderma adspersum* (Schulz.) Donk.	Muğla, November 2012
4	AT-2455	Ganodermataceae	*Ganoderma applanatum* (Pers.) Pat.	Muğla, January 2012
5	AT-1146	Ganodermataceae	*Ganoderma lucidum* (Curtis) P. Karst	Nevşehir, April 2012
6	AT-819	Discinaceae	*Gyromitra esculenta* (Pers. ex Pers.) Fr.	Uşak, April 2012
7	AT-760	Lyophyllaceae	*Lyophyllum decastes* (Fries: Fries) Singer	Uşak, November 2011
8	AT-1023	Pleurotaceae	*Pleurotus ostreotus* (Jacq. ex Fr.) P.Kumm.	Uşak, December 2011
9	AT-1831	Rhizopogonaceae	*Rhizopogon luteolus* Krombh.	Muğla, December 2012
10	AT-2456	Russulaceae	*Russula delica* Fr.	Muğla, December 2012
11	AT-4706	Tricholomataceae	*Tricholoma fracticum* (Britzelm.) Kreisel	Denizli, June 2012

Collected mushrooms were identified by Dr. Aziz Türkoğlu, Muğla Sıtkı Koçman University. Mushroom specimens were deposited at the Fungarium of Biology Department of Muğla Sıtkı Koçman University. Mushrooms were stored under −18 ºC before analyses.

2.2 Determination of Metal Content with ICP-MS

The metal content of mushroom species was determined as reported earlier [23]. Agilent ICP-MS 7700x was used for the elemental analysis in this study. Limit of detection (LOD) is defined as the concentration corresponding to three times the standard deviation of 10 blanks. Detection limits of elements (µg/kg) in ICP-MS found as follows: Pb 0.0098, Zn 0.1151, Fe 0.0069, Mn0.0108, Cu 0.0029, Cr 0.0162, Ni 0.0311, Co 0.0006, Na 0.7630, Mg 0.1468, Al 0.7821, Ca 0.7393, V 0.0103, Ga 0.0175, As 0.0245, Se 0.4195, Sr0.0213 and Tl 0.0009. Multi-Element standard reference materials (AccuTrace MES-21-1 and AccuTrace MES-21-HG-1) were used to evaluate precision and accuracy. Standard material (NIST-CRM-1203) from VHG Labs, Inc. LGC Standards with 12.20.2012 date certificated (Teddington, UK) was diluted ten times with demineralized water by using 10.0 mL volumetric flask and 1 mL capacity Eppendorf pipette that was calibrated by Egemet Lmt. Sti. company an accredited laboratory from Izmir TURKEY. The uncertainty of 10 mL volume flask was 0.04 mL while the uncertainty of 1.0 mL capacity micropipette at 1 mL volume was 0.624 µL. Digested with microwave to check accuracy of the method.

2.3 Statistical Analysis

Data were recorded as mean ± S.E.M. Significant differences between means were determined by student's-*t* test, p values <0.05 were regarded as significant.

3. Results and Discussion

3 major minerals (Na, Mg, Ca) and 15 trace elements (V, Mn, Fe, Zn, Ga, Se, Al, Cr, Ni, As, Sr, Co, Cu, Tl, Pb) of the mushroom species are given in Table 2, expressed as mg/kg dry weight. At the same time, metals of studied mushrooms along with references are presented in Table 3. The relative standard deviations (RSD) for metal analysis were found below 5.0%.

Sodium (Na) is very essential element to both humans and animals due to its physiological role in cellular mechanisms and organs [24]. Na found in 11 species ranged from 66.9±3.2 to 436.3±7.3 mg/kg DW. The highest concentration of Na was found (436.3±7.3 mg/kg DW) in *R. delica* (Table 2).

Our body contains almost 25 g of magnesium (Mg) [25]. Thus it is considered as major

Table 2. Metal content (mg/kg mushroom of dry weight) of mushroom species[a].

Metals	1	2	3	4	5	6	7	8	9	10	11
Na	66.9±3.2	336.9±3.9	239.4±6.7	181.3±6.1	171.4±2.6	371.3±4.1	357.9±4.0	281.7±2.9	360.9±8.5	436.3±7.3	215.8±6.3
Mg	181.6±5.3	167.3±5.9	966.3±9.5	380.1±6.8	988.9±5.1	458.7±4.6	515.8±4.7	757.9±5.0	308.6±8.1	395.8±6.9	398.1±7.0
Ca	181.4±5.2	117.3±5.2	296.3±7.9	118.5±3.0	38.1±2.6	55.9±2.9	81.4±3.2	106.4±3.5	207.4±2.6	24.7±2.0	30.6±2.2
V	0.13±0.01	0.79±0.05	0.15±0.01	0.06±0.01	0.07±0.01	0.94±0.08	0.24±0.02	0.45±0.03	0.14±0.01	0.44±0.03	0.58±0.04
Mn	5.87±0.35	26.5±2.30	5.75±0.31	1.89±0.18	8.90±0.60	76.5±3.00	9.90±0.80	19.4±1.50	6.31±0.56	9.19±0.51	17.9±1.61
Fe	101.4±4.1	282.8±2.9	22.9±1.4	19.2±1.2	67.5±2.3	286.9±3.1	113.2±2.6	383.1±3.1	67.7±3.2	235.4±6.5	202.8±6.1
Zn	31.9±0.45	6.6±0.40	49.6±1.12	49.5±1.21	10.9±0.80	15.1±0.60	18.7±1.80	9.34±0.70	12.6±1.20	36.8±1.02	35.6±2.12
Ga	1.54±0.12	1.82±0.10	1.52±0.10	0.69±0.04	0.31±0.02	3.36±0.30	0.46±0.02	0.67±0.05	0.24±0.01	1.50±0.10	2.67±0.16
Se	0.06±0.01	0.18±0.02	0.06±0.01	0.01±0.00	0.04±0.00	0.18±0.03	0.10±0.01	0.09±0.01	0.08±0.01	0.28±0.02	0.17±0.01
Al	102.5±3.12	862.95±5.85	41.51±3.40	22.3±1.98	18.08±1.65	2382±7.25	527.29±4.32	950.40±6.78	25.1±1.80	25.96±2.20	31.04±2.98
Cr	0.58±0.05	0.66±0.04	0.20±0.01	0.23±0.02	0.08±0.01	0.65±0.06	0.33±0.02	0.63±0.06	0.50±0.04	0.15±0.01	0.33±0.02
Ni	1.91±0.12	2.45±0.17	1.90±0.06	0.27±0.02	1.18±0.10	1.97±0.16	0.28±0.02	5.71±0.52	0.26±0.01	0.25±0.02	1.47±0.12
As	0.53±0.13	0.96±0.08	0.67±0.12	0.45±0.02	0.69±0.05	0.74±0.03	0.30±0.02	0.35±0.03	0.58±0.04	0.23±0.01	0.37±0.03
Sr	13.96±0.73	14.70±1.25	3.60±0.28	7.35±0.69	2.03±0.08	8.60±0.32	8.76±0.27	13.05±0.45	2.10±0.16	9.02±0.87	11.91±0.52
Co	0.07±0.01	0.55±0.05	0.32±0.01	0.02±0.00	0.19±0.01	0.43±0.02	0.08±0.01	1.49±0.11	0.07±0.01	0.16±0.01	0.29±0.02
Cu	0.14±0.01	0.92±0.09	8.46±0.54	3.12±0.15	1.70±0.15	4.22±0.26	0.19±0.01	0.34±0.02	3.59±0.24	0.51±0.05	0.58±0.04
Tl	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.02±0.00	0.17±0.01
Pb	1.80±0.12	0.34±0.03	0.24±0.01	0.85±0.08	0.20±0.01	1.09±0.06	0.26±0.02	0.15±0.01	0.89±0.08	0.10±0.01	0.29±0.02

[a] Values expressed are means ± S.E.M. of three parallel measurements ($p<0.05$).

Table 3. Metals of studied mushrooms in reported literature.

Mushrooms	Metals	References
Funalia trogii	Mn, Fe, Zn, Cu, Pb	[7]
Ganoderma lucidum	Mg, Ca, Mn, Fe, Zn, Se, Cr, Ni, Co, Cu, Pb	[11]
Lyophyllum decastes	Ni, As, Cu, Pb	[13]
Pleurotus ostreotus	Mg, Ca, Mn, Fe, Zn, Ni, Cu, Pb	[16]
Rhizopogon luteolus	Fe, Zn, Cr, Ni, Co, Cu, Pb	[17]
Russula delica	Cu, Pb	[18]
Russula delica	Na, Mg, Ca, Mn, Fe, Zn, Al, Cr, Ni, As, Co, Cu, Pb	[19]
Russula delica	Mn, Fe, Zn, Cr, Ni, Co, Cu, Pb	[20]
Russula delica	Mg, Mn, Fe, Zn, Cr, Ni, Co, Cu	[21]
Russula delica	Ni, As, Cu, Pb	[13]
Russula delica	Zn, Cr, Cu, Pb	[5]
Tricholoma fracticum	Mn, Zn, Cr, Cu	[22]

mineral that plays an important part in bone growth and quality that will guarantee strong skeleton. Furthermore, the lack of Mg level in our body is also associated with a risk factor of osteoporosis [25]. The Mg concentrations in 11 mushrooms were found between 167.3±5.9 and 988.9±5.1 mg/kg DW. The highest and lowest of Mg concentration were found in *G. lucidum* and *F. trogii*, respectively (Table 2).

According to Campos, Calcium (Ca) can discriminate phylogenetic position and lifestyle significantly [26]. Minimum and maximum calcium levels were found in *R. delica* (24.7±2.0 mg/kg DW) and *G. adspersum* (296.3±7.9 mg/kg DW), respectively (Table 2). Demirbas [19] found Ca amount 72.8±23.5 mg/kg DW that is 3 fold higher than our amount.

Nearly all living cells general contain very low concentrations of vanadium. Vanadium (V) have been reported as anti-diabetic both *in vitro* and *in vivo* [27]. In the current study, V concentrations ranged from 0.06±0.01 to 0.94±0.08 mg/kg DW in the 11 mushroom species (Table 2).

Manganese (Mn) is essential constituent of many enzymes or activating various enzymes [28]. Mn concentration was detected in 11 mushrooms between 1.89±0.18 and 76.5±3.0 mg/kg DW. The lowest and highest manganese values were observed in *G. applanatum* and *G. esculenta,* respectively (Table 2).

Iron (Fe) is the backbone of red blood cells that captures oxygen and transport to each cell. Iron-deficiency can cause anemia. Iron intake becomes more important during puberty, menses and pregnancy. In these cases, more iron intake is even prescribed [29]. *P. ostreotus* (383.1±3.1 mg/kg DW) had the highest amount of Fe, whereas the lowest iron concentration was found in *G. applanatum* (19.2±1.2 mg/kg DW) (Table 2).

Zinc (Zn) is also a necessary component to some living organisms. Roots of some mushrooms collect Zn around it, for which, they are as zinc accumulators. The ratio of mushroom/underlying soil of zinc ranges from 1 to 10 mg/kg [5]. The zinc concentration ranged from 6.6±0.4 to 49.6±1.12 mg/kg DW, where *F. trogii* had the lowest, while *G. adspersum* had the highest Zn amount (Table 2).

The gallium (Ga) concentration, however, ranged from 0.24±0.01 to 3.36±0.30 mg/kg DW, where *R. luteolus* and *G. esculenta* had the minimum and maximum Ga concentrations, respectively (Table 2).

Selenium (Se) is an essential mineral that is also reported as antioxidant. Lack of Se in biological systems can cause damage to immune system. In addition, it is a useful element to prevent carcinogenesis and some other chronic diseases. There are reports that selenium can play an antioxidant role even in human [4]. The minimum and maximum concentrations of Se were found 0.01±0.00 mg/kg DW in *G. applanatum* and 0.28±0.02 mg/kg DW in *R. delica*, respectively (Table 2).

Aluminum (Al) is not an essential element for human beings. Exposure of aluminum has been associated with a number of human pathologies including Alzheimer's disease and Parkinson disease as well as dementia. Al can be found in foods via contact of food during cooking in aluminum utensils [30]. As shown in Table 2, the aluminum concentration of the mushroom species ranged from 18.08±1.65 mg/kg DW in *G. lucidum* to 2381.53±7.25 mg/kg DW in *G. esculenta* (Table 2).

Although chromium (Cr) is a heavy metal, it becomes essential mineral to humans when taken 50–200 μg daily. It has been related to protein, lipid and carbohydrate metabolisms [4]. Concentration of Cr, Co and Tl were found averaged between 0.01 and 1.49 mg/kg DW (Table 2).

Trace amounts of nickel (Ni) can activate certain enzymes. However, it is suspected to be toxic at higher levels. Accumulating of Ni in the lungs may cause some diseases such as bronchial haemorrhage or collapse [4]. The highest (5.71±0.52 mg/kg DW) and the lowest (0.25±0.02 mg/kg DW) concentrations of nickel were found in *P. ostreotus* and *R. delica,* respectively (Table 2).

Arsenic (As) raises chemical and toxicological questions at higher concentrations. In general, as is found at low concentrations (0–20 μg/kg) in the earth surface. In rice, it is found between 25 and 150μg/kg while in some edible mushrooms it can be found in few milligrams per kilogram. The minimum and maximum concentrations of As in the 11 mushroom species were found as 0.23±0.01 and 0.96±0.08 mg/kg DW. The highest value was found in *F. trogii* and the lowest in *R. delica* (Table 2).

Strontium (Sr) concentrations were found in between 2.03±0.08 and 14.70±1.25 mg/kg DW, where the highest amount was found in *F. trogii* while the lowest amount was found in *G. lucidum* (Table 2).

In the low concentrations, copper (Cu) is an essential element. For example, some of the enzymes contain copper. Cu centered enzymes of the body transport iron [5]. The highest concentration of Cu was found in *G. adspersum* (8.46±0.54 mg/kg DW) while the lowest was found in *F. fomentarius* (0.14±0.01 mg/kg DW) (Table 2).

Lead (Pb) is a heavy metal that is considered as toxic because it affects the kidneys, nervous system and blood. Anemia can occur when Pb concentration in the blood goes high; it inhibits the formation of red blood cells. Pb is used in some industrial, domesticand rural purposes. However, we engulf it mostly via diet. The minimum and maximum lead concentrations in the 11 mushroom species were found to be in the range of 0.10±0.01−1.80±0.12 mg/kg DW. These values were determined in *R. delica* and *F. fomentarius*, respectively (Table 2).

The metal contents of *Ganoderma* species studied ranged from 171.4 to 239.4, 380.1-988.9, 38.1-296.3, 0.06-0.15, 1.89-8.90, 19.2-67.5, 10.9-49.6, 0.31-1.52, 0.01-0.06, 18.08-41.51, 0.08-0.23, 0.27-1.90, 0.45-0.69, 2.03-7.35, 0.02-0.32, 1.70-8.46, 0.01-0.01 and 0.20-0.85 mg/kg DW for Na, Mg, Ca, V, Mn, Fe, Zn, Ga, Se, Al, Cr, Ni, As, Sr, Co, Cu, Tl and Pb, respectively. There are some differences with respect to the each other. The observed differences in the metal content may be different origin, collection localitiesand different environmental conditions of mushroom.

The heavy metal concentrations of Al, Cd, Cu, Pb and Zn in *G. applanatum* collected in polluted and unpolluted areas were reported by Gabriel *et al.* [9]. These concentrations were found 228.1-71.7, 1.88-1.03, 24.48-20.45, 2.19-0.50, 55.0-66.6 mg/kg in polluted and unpolluted areas, respectively.

The concentrations of Fe, Cu, Mn, Zn, Pb and Cd of *F. trogii* have been reported by Turkekul *et al.* [7]. The Fe, Cu, Mn, Zn and Pb concentrations were found as 1665, 32, 33, 25 and 0.8 mg/kg, respectively, that are less than our values. The metal contents of *G. lucidum* and twenty five mushroom species were reported by Michelot *et al.* [11]. The Mg, Fe, Mn, Cr concentrations were between 335-8990, 10.4-4900, 5.1-400 and 0-56 ppm, respectively, which are comparable with those found in this study. The Co, Cu, Ni, Se and Zn values ranged between 0.21-148, 6-148, 5.1-400, 4.7-155 and 23.9-369 ppm, respectively. These values are also more than our values. The metal contents such as Cu, Ni, Pb, Cd, As, Hg of *L. decastes* and nine mushroom samples have been reported by Chen *et al.* [13]. The Cu and Pb contents of these mushroom species ranged between 39-181.5 and 1.9-10.8 mg/kg, more than the metal content in this study. The Ni concentration ranged from 0.11 to 1.35 mg/kg that is in agreement with this study. The metal contents in *P. ostreotus* collected from two different locations were reported by Uzun *et al.* [16]. The Ca, Fe, Mg, Zn, Cu, Mn and Ni contents were 295-340, 65-125, 1130-1540, 250-265, 0.51-1.25, 54-62, 0.20-9.3 and 2.51-2.64 mg/kg, respectively. The Fe, Mn and Ni contents are more than those found in this study while Ca, Mg, Zn and Cu contents are less.

The metal concentration such as Fe, Zn, Cr, Ni, Co, Cu and Pb of *R. luteolus* has been reported recently [17]. In that study, Fe and Zn concentrations as minerals were found as 67.7±3.2 and 12.6±1.80 mg/kg, respectively. However, Severoglu *et al.* [17] found that both minerals in less concentration than the current study (26.9±0.31 and 2.49±0.02 mg/kg, respectively). On the other hand, data of metal contents of current study showed that except Cu concentration, other metals tested previously were found to be in low concentrations when compared with the study of Severoglu *et al.* [17].

The metal concentration of *R. delica* has been reported by some studies [5,18-21]. In a study by Demirbas [19] the concentration of Na was found 82.9±44.0 mg/kg that is 5-fold less than the concentration found in this study. The collection date as well as the collection localities may cause the difference of Na concentrations.

The concentration of Mg of *R. delica* was studied by Ouzouni *et al.* [21] and Demirbas [19] previously. In these studies Mg concentrations were found to be 1060±36.0and 688.7±5.3 mg/kg, respectively. Both Ouzouni *et al.* [21] and Demirbaş [19] results are higher than the Mg concentration of *R. delica* in this study. Demirbas [19] also found the concentration of Ca 72.8±23.5 mg/kg that is 3-fold higher than our results. Mn concentration in *R. delica* has been found in range 6.62±1.81 and 35.08±2.4 mg/kg [19-21] that is somewhat in agreement with our results.

Iron (Fe) concentration of *R. delica* ranged between 74.8±6.5–203.3±13.3 mg/kg [19-21]. In this study, it was found 235.4±6.5 mg/kg that is higher than the previous results. In some previous studies, Zn concentration of *R. delica* was found in range 32.6±8.51–56.9±0.54 mg/kg [5, 19-21]. We found Zn as 36.8±1.02 mg/kg that is accordance with the previous results.

The metal concentration of *R. delica* has also been reported by some studies [5, 13, 18-21]. In a study by Demirbas [19] the concentration of Al of *R. delica* was found 23.6±4.5 mg/kg which is very close to that of concentration (25.96±2.2 mg/kg) in this study. The concentration of Cr of *R. delica* was studied by Çayır *et al.* [5], Ouzouni *et al.* [21], Işıldak *et al.* [20] and Demirbaş [19] previously. In these studies Cr concentrations ranged between 0.12±0.04 and 7.23±0.6 mg/kg. In this study it was found 0.15±0.04 mg/kg which is accordance with the previous results. The concentration of Ni of *R. delica* was studied previously [13, 19-21]. In these studies Ni concentrations ranged between 0.24±0.05 and 116.0±32.0 mg/kg. In this study it was found 0.25±0.06 mg/kg which is very close to that of data by Chen et al. [13]. The concentration of As of *R. delica* was studied by Demirbaş [19] and Chen *et al.* [13] previously. In these studies As concentrations were found to be 0.61±0.16and 0.66±0.06 mg/kg, respectively. Both results by Ouzouni *et al.* [21] and Demirbaş [19] are higher than the As concentration of *R. delica* in this study. In the previous studies, Co concentration of *R. delica* ranged between 0.05±0.02–3.14±0.3 mg/kg [19-21]. In this study it was found 0.16±0.03 mg/kg which is accordance with the previous results. In the previous studies, Cu concentration of *R. delica* ranged between 13.6±4.0–61.9±4.7 mg/kg [5, 13, 18-21]. In this study, it was found 0.51±0.09 mg/kg which is very lesser than the previous results. In the previous studies, Pb concentration of *R. delica* ranged between 0.59±0.03–3.63±2.48 mg/kg [5, 13, 18-21]. In this study Pb was found 0.10±0.02 mg/kg which is lesser than previous results.

The metal content such as Cd, Cr, Cu, Mn and Zn of *T. fracticum* has been reported in a recent study [22]. Unlikely, in this study Cr, Cu and Zn contents were found to be higher while the Mn content was lesser than that of *T. fracticum* in this study.

4. Conclusions

The contents of essential elements in studied mushrooms were higher than toxic elements such as Pb and As. Their low content of toxic metals exhibited that the mushroom collection areas was not polluted. All studied mushroom species appear to be good sources of many minerals which are essential for biological systems. The biological importance of minerals and trace elements were also discussed and compared with the previous studies. Also the results showed that many factors such as season, temperature, altitude, growing conditions can lead to quantitative differences in the concentration of metals.

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