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Trace Element Contents of Edible Macrofungi Growing in Adiyaman, Turkey

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Trace elements (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) content were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in the samples of edible mushroom fruiting bodies of 24 species (*Agaricus campestris*, *Agrocybe aegerita*, *Agrocybe dura*, *Armillaria mellea*, *Boletus queletii*, *Coprinellus disseminatus*, *Coprinellus micaceus*, *Coprinus comatus*, *Gymnopus dryophilus*, *Lentinus tigrinus*, *Leucoagaricus leucothites*, *Lycoperdon molle*, *Macrocystidia cucumis*, *Macrolepiota excoriate*, *Macrolepiota mastoidea*, *Pleurotus ostreatus*, *Pluteus romellii*, *Psathyrella candolleana*, *Rhizopogon luteolus*, *Russula subterfurcata*, *Stropharia coronilla*, *Suillus luteus*, *Volvariella gloiocephala* and *Volvariella hypopithys*) collected from Adiyaman, Turkey. Trace element amouts in mushrooms varied widely depending on the site and mushroom species investigated.

Key Words: Macrofungi, Trace elements, Adiyaman, Turkey.

INTRODUCTION

It is known that the fruit bodies of mushrooms accumulate remarkably high concentrations of certain elements, especially heavy metals, in their structures[1]. Some of these elements are even hyperaccumaulated by different species of macrofungi[2]. Metals, whether essential or non-essential, are directly and/or indirectly involved in all aspects of fungal growth, metabolism and differentiation and all these elements can interact with fungal cells and be accumulated by physico-chemical mechanisms and transport systems of varying specificity[3,4]. Most of them exhibit toxicity above a certain concentration, which will vary depending on the organism, the physicochemical properties of the metal and environmental factors[5]. This may necessitate expression of a detoxification mechanism if the organism is to survive[6].

Starting from 1970s, hundreds of studies were presented on the metal contents of wild growing mushrooms[7] and usual content of 19 trace elements in fruiting bodies of mushrooms and accumulating genera were reviewed by Kalac[8]. Similar researches have also been conducted in Turkey. Sesli and Tuzen[9] determined 9

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trace elements in fruit bodies of 109 wild macrofungi, collected from the East Black Sea Region. Isiloglu *et al.*[10] carried out a comparative study to determine 8 metal contents in wild growing macrofungi of 179 samples of 16 species collected from background area and roadside in Balikesir and Akhisar. Soylak *et al.*[11] analyzed 9 trace metals in 7 mushrooms growing in Kayseri province. Similarly, Demirbas[12], Mendil *et al.*[13], Yesil *et al.*[14] and Genccelep *et al.*[15] also puplished studies on the metal contents of some mushrooms collected from different regions of Turkey.

In this study, 12 trace elements (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) were determined by using an ICP-OES method, in the fruit bodies of macrofungi species collected from Adiyaman, Turkey.

EXPERIMENTAL

Study area and sampling: Adiyaman is a vilayet of Turkey with a surface area of 7.606 km^2. The province takes place in Southeastern Anatolian region (Fig. 1) of Turkey and mainly in C7 square according to Davis' grid square system[16] and has a Mediterranean climate[17].

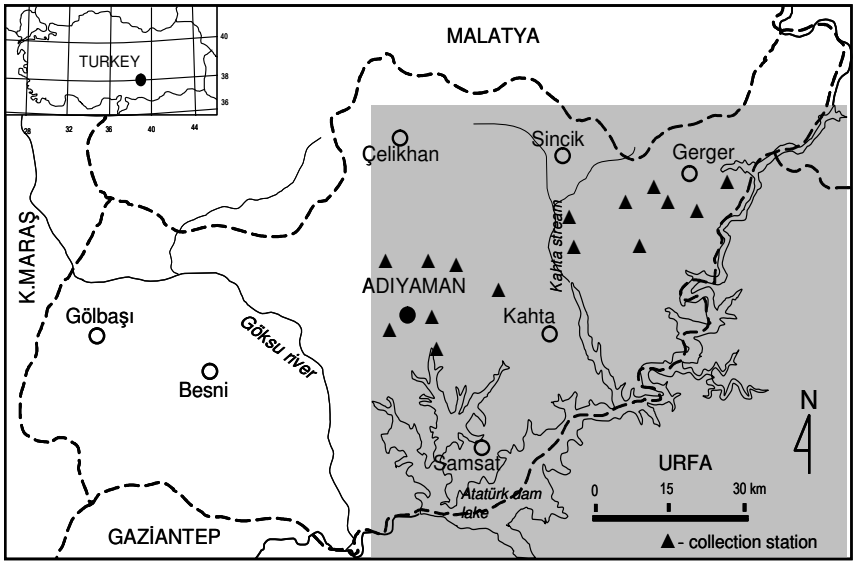

Fig. 1. Macrofungi collection stations

The macrofungi specimens were collected from 15 localities during field trips within Adiyaman province. Ecological and morphological properties of the samples were recorded during field work and macroscopic and microscopic measurement and micro chemical data were obtained by laboratory studies. Identification was performed with the help of relevant literature[18,19]. The specimens are kept in Adiyaman University, Education Faculty, Adiyaman, Turkey. The habitat and locality of the edible mushrooms used in this study are given in Table-1.

TABLE-1
HABITAT AND LOCALITIES OF EDIBLE MUSHROOM SPECIES

Macrofungi taxa	Habitat and locality
Agaricus campestris L.	In meadow, Cimen village, 37º43'N, 38º16'E, 600 m
Agrocybe aegerita (V. Brig.) Singer	On *Populus* sp. stump, Orenli village, 37º48'N, 38º18'E, 643 m
Agrocybe dura (Bolton) Singer	Among grass, Altinsehir quarter, 37º44'N, 38º14'E, 650 m
Armillaria mellea (Vahl) P. Kumm.	On *Salix* sp. stump, Gerger, Kutuklu village, 37º57'N, 38º48'E, 1085 m
Boletus queletii Schulzer	Among grass in *Quercus* sp. forest, Gerger, Gürgenli village, 37º58'N, 38º49'E, 1152 m
Coprinellus disseminatus (Pers.) J.E. Lange	On damp woody debris, Gerger, Kutuklu village, 37º57'N, 38º48'E, 1085 m
Coprinellus micaceus (Bull.) Vilgalys, Hopple & Jacq. Johnson	Around *Almond* sp. stump, Gerger, Sever village, 37º55'N, 38º48'E, 872 m
Coprinus comatus (O.F. Müll.) Pers.	Among grass, Indere village, 37º48'N, 38º15'E, 830 m
Gymnopus dryophilus (Bull.) Murrill	In *Pinus brutia* forest, Ziyaret village, 37º45'N, 38º20'E, 565 m
Lentinus tigrinus (Bull.) Fr.	On *Populus* sp. stump, Kahta, Damlacik village, 37º54'N, 38º39'E, 765 m
Leucoagaricus leucothites (Vittad.) M.M. Moser ex Bon	In meadow, Bogazozu village, 37º50'N, 38º25'E, 690 m
Lycoperdon molle Pers.	Among grass in *Quercus* sp. forest, Gerger, Dagdeviren village, 38º00'N, 38º58'E, 645 m
Macrocystidia cucumis (Pers.) Joss.	Among grass in *Pinus brutia* forest, Altinsehir quarter, 37º44'N, 38º14'E, 650 m
Macrolepiota excoriata (Schaeff.) M.M. Moser	Among grass in *Quercus* sp. forest, Gerger, Budakli village, 38º00'N, 39º00'E, 570 m
Macrolepiota mastoidea (Fr.) Singer	In *Pinus brutia* forest, Altinsehir quarter, 37º44'N, 38º14'E, 650 m
Pleurotus ostreatus (Jacq.) P. Kumm.	On *Populus* sp. stump, Kahta, Caltili village, 37º52'N, 38º30'E, 703 m
Pluteus romellii (Britzelm.) Lapl.	Around *Populus* sp. stump, Ziyaret village, 37º45'N, 38º20'E, 565 m
Psathyrella candolleana (Fr.) Maire	Around *Populus* sp. stump, Orenli village, 37º48'N, 38º18'E, 643 m
Rhizopogon luteolus Fr.	In *Pinus brutia* forest, Ziyaret village, 37º45'N, 38º20'E, 565 m
Russula subterfurcata Romagn.	Among grass in *Quercus* sp. forest, Gerger, Dagdeviren village, 38º00'N, 38º58'E, 645 m
Stropharia coronilla (Bull.) Quél.	Among grass, Gerger, Kesertas village, 37º58'N, 38º57'E, 560 m
Suillus luteus (L.) Roussel	In *Pinus brutia* forest, Kahta, Cingil village, 37º53'N, 38º38'E, 909 m
Volvariella gloiocephala (DC.) Boekhout & Enderle	Among grass on floodplain, Ziyaret village, 37º45'N, 38º20'E, 565 m
Volvariella hypopithys (Fr.) M.M. Moser	In *Pinus brutia* forest, Altinsehir quarter, 37º44'N, 38º14'E, 650 m

A Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Optima 2100 DV model was used for the determination of elements in this study. The instrumental parameters and operating conditions are given in Table-2.

TABLE-2
INSTRUMENTAL ANALYTICAL CONDITIONS OF ELEMENT ANALYSES

Element	Wavelength (nm)	Element	Wavelength (nm)
Al	396.153	Fe	238.204
B	249.677	Mn	257.610
Cu	327.393	Ni	231.604
Co	228.616	Sn	189.927
Cd	228.802	Zn	206.200
Cr	267.716	Pb	220.353

Preparation of mushrooms for element analysis: In this study, 24 species of naturally growing edible macrofungi, were used. At the beginning, the mushroom samples were washed with ultrapure deionized water. Then the samples were dried at 60 ºC overnight and crushed in a mortar. The mushroom samples were digested using a mixture of HNO_3 and $HClO_4$. The wet digestion procedure was applied as follows. 2 g of accurately weighed samples were put in to a 400 mL of borosilicate beaker. Then, 25 mL of concentrated HNO_3 added and boiled gently for 0.5 h. The mixture was cooled and 15 mL of concentrated $HClO_4$ was added. After boiling the mixture gently for *ca.* 1 h, a colourless solution was obtained. The solution was cooled and transferred to 50 mL of volumetric flask. Finally the volume was made 50 mL by adding ultrapure distilled water.

Metal ion concentrations were determined as three replicates by ICP-OES. The absorption measurements of the elements were performed under the conditions recommended by the manufacturer. The samples were spiked with the analytes to test the accuracy of the analysis.

All chemicals used were of analytical reagent grade unless otherwise specified. Ultrapure distilled water was used throughout the experiments. Working metal standard solutions were prepared just before use by diluting the stock standard solution with water. After calibration of the instrument using standards, several standards were repeated throughout each set of analyses (*ca.* 5 samples).

RESULTS AND DISCUSSION

The results of heavy metal concentrations in the mushroom species are shown in Table-3. The metal concentrations were determined on dry weight basis.

All the metal concentrations were determined on a dry weight basis and given in Table-3. The contents of trace elements in the mushroom samples ranged from 18.71-1486, N.D.-2.630, N.D.-6.128, 0.202-1.180, N.D.-7.422, 4.592-62.89, 31.66-1482, 2.697-180.8, 0.319-6, 883, 1.445-3.371 and 22.1-250.2 mg/kg dw for Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively. Al and Fe were found to be most abundant element among the mushroom studied while Sn was not detected in any of them.

TABLE-3
AVERAGE CONCENTRATIONS (mg/kg, DRY WEIGHT BASIS) OF HEAVY METALS IN EDIBLE MUSHROOM SAMPLES

No.	Amount of elements (mg/kg dry weight											
	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
1	84.70	2.630	0.329	0.559	1.609	31.24	131.1	6.696	2.647	2.820	N.D.	163.0
2	27.83	0.566	0.412	0.234	0.029	10.33	57.16	7.109	0.319	2.387	N.D.	28.12
3	1222	N.D.	N.D.	1.180	2.099	28.01	775.9	92.33	5.577	2.364	N.D.	35.38
4	773.9	0.243	N.D.	0.925	3.416	22.49	936.1	34.37	4.712	1.803	N.D.	38.58
5	497.5	N.D.	N.D.	0.501	0.844	33.60	502.6	43.03	1.266	2.204	N.D.	68.80
6	20.92	1.134	0.267	0.330	0.062	4.592	76.10	6.646	0.658	2.026	N.D.	22.10
7	59.66	0.731	1.377	0.402	0.630	32.79	117.3	4.434	1.155	1.919	N.D.	53.42
8	264.5	0.757	6.128	0.687	7.422	41.05	449.7	12.10	6.883	2.133	N.D.	250.2
9	62.33	1.525	0.075	0.244	0.416	5.637	82.23	3.526	0.540	1.989	N.D.	27.28
10	638.2	1.132	N.D.	0.724	1.244	62.89	478.5	48.89	1.644	3.371	N.D.	44.74
11	260.9	0.945	N.D.	0.662	2.134	27.29	449.6	180.8	4.927	1.445	N.D.	29.61
12	217.0	0.595	2.624	0.761	1.579	29.17	286.1	21.52	3.371	2.641	N.D.	85.78
13	103.5	0.094	0.447	0.513	0.473	10.19	135.2	8.409	1.129	1.551	N.D.	45.18
14	210.6	N.D.	N.D.	0.380	1.328	13.84	333.4	13.00	3.528	1.655	N.D.	33.17
15	204.1	0.089	N.D.	0.486	1.127	45.59	194.7	16.49	2.982	2.000	N.D.	31.38
16	353.1	N.D.	0.297	0.649	2.381	31.40	290.4	27.26	6.147	1.666	N.D.	49.53
17	20.87	0.417	2.114	0.906	0.218	39.36	40.57	4.228	1.232	2.141	N.D.	86.83
18	1486	0.482	N.D.	1.030	4.696	22.24	1482	100.8	6.521	1.787	N.D.	80.61
19	1389	0.129	0.284	1.090	2.330	22.53	1265	90.41	3.126	2.827	N.D.	59.19
20	1382	2.571	N.D.	0.811	1.769	16.14	962.9	51.87	1.871	2.323	N.D.	62.91
21	24.99	0.616	0.039	0.260	N.D.	14.12	31.66	2.697	0.866	2.294	N.D.	36.90
22	69.31	2.219	N.D.	0.202	0.349	15.34	92.26	4.174	0.722	1.796	N.D.	32.07
23	28.28	1.431	2.131	0.347	0.459	26.75	52.53	7.365	0.725	1.903	N.D.	56.11
24	18.71	2.459	1.443	0.446	0.128	10.40	65.97	5.104	0.536	2.928	N.D.	48.57

ND: Not detected

Al content was found in a range of 18.71 and 1486 mg/kg. The highest Al content was in *Psathyrella candolleana*, whereas the lowest Al content was in *Volvariella hypopithys*. Compared to the reported values, ranged 8.5-365 mg/kg[20], 68-420 µg/g[21] and 4.8-42.7 mg/kg[22], the aluminium contents of *Agrocybe dura*, *Lentinus tigrinus*, *Rhizopogon luteolus* and *Russula subterfurcata* are also rather high and the consumption of them may be hazardous according to the daily permissible aluminum dose (60 mg per day)[23]. During field study, it has been found that none of the above species have been collected and consumed in the region.

Similarly, the highest Fe content was 1482 mg/kg in *Psathyrella candolleana* whereas the lowest Fe content was 31.66 mg/kg in *Stropharia coronilla*. The determined iron values are in agreement with the reported Fe contents which were 31.3-1190[9], 568-3904[24], 56.1-7162[25], 102-1580[12], 30-150[7] and 50.1-842[15] mg/kg.

Boron was not detected in the species of *Agrocybe dura*, *Boletus queletii*, *Pleurotus ostreatus*, *Macrolepiota excoriata*. Among the determined samples the content of B ranged from N.D. to 2.630 mg/kg. The highest B content was in *Agaricus*

campestris. Like Boron, Cd was not detected in 10 of the determined mushroom species either and *Coprinus comatus* (6.128 mg/kg) had the highest contents of Cd.

Minimum and maximum values of cobalt in the present study were 0.202 and 1.180 mg/kg. The highest and lowest levels were found in *Agrocybe dura* and *Suillus luteus*, respectively. The Cr content of the mushrooms studied in the present work ranged from N.D. to 7.422 mg/kg. The highest Cr content was in *Coprinus comatus* whereas it was not detected in *Stropharia coronilla*.

The highest copper content was 62.89 mg/kg in *Lentinus tigrinus* whereas the lowest cupper content was 4.592 mg/kg in *Coprinellus disseminatus*. The reported literature cupper contents are 4.71-51.0[26], 10.3-145[9], 12-181[27] and 9.23 µg/g and 107[15] mg/kg dw. The manganese was measured in all of the mushroom samples and ranged from 2.697-180.8 mg/kg in *Stropharia coronilla* and *Leucoagaricus leucothites*, respectively. The reported values of manganese in the literature for mushrooms collected from various regions of Turkey are 7.1-81.3,[27] 14.2-69.7[28] and 21.7-74.3 µg/g[12]. Genccelep *et al*. measured the the manganese content of *Stropharia coronilla* as 135 mg/kg dw[15] whereas it was measured as 2.697 mg/kg dw in the current study. This must be a typical example for the environmental factors affecting the heavy metal accumulation in fruit bodies together with the fungal factors such as developmental stage, mycelium age and fructification interval[29]. The nickel content ranged from 0.319 mg/kg in *Agrocybe aegerita* to 6.883 mg/kg in *Coprinus comatus*. The nickel levels are in agreement with the reported nickel values for previously studied mushrooms which were 0.4-15.9, 0.4-2, 1.72-24.1, 1.22-58.60 mg/kg, respectively[12,25,30]. The average lead content of the mushrooms in this study was 2.166 mg/kg. The lowest lead content was in *Leucoagaricus leucothites* (1.445 mg/kg) and the highest content was in *Lentinus tigrinus* (3.371 mg/kg). Lead contents of the mushrooms in this study are remarkably high compared to the reported ranges which were 0.4-2.80,[31] 0.75-1.99[12] and 0.9-2.6 mg/kg[22]. The zinc content was varied in the range of 22.10 and 250.2 mg/kg in the present study. The highest value was found in *Coprinus comatus* whereas the lowest value was found in *Coprinellus disseminatus*. From Table-3, it can be seen that the zinc content is considerably high in all mushroom species. The reason of this is that zinc is wide-spread among living organisms due to its biological significance[13]. Zinc concentrations of mushrooms samples in literature have been reported in the range of 45-188,[27] 33.5-89.5[12] and 43.5-205 mg/kg[22].

Conclusion

Twelve trace elements (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) were determined by using an ICP-OES method, in the fruit bodies of macrofungi species collected from Adiyaman, Turkey. Though most of the mushrooms studied contained considerably high amounts of minerals, all the contents are in the range reported from Turkey and other countries and in acceptable limits for human consumption except aluminum. The aluminum contents of *Agrocybe dura*, *Lentinus tigrinus*, *Psathyrella candolleana*, *Rhizopogon luteolus* and Russula subterfurcata are

remarkably high. Containing the highest Cd, Cr, Ni and Zn contents, *Coprinus comatus* is of particular interest as well since this mushroom has heavily been collected and consumed in the region. In this study, tin was not detected in any of mushroom samples.

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