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Mineral Contents of Some Wild Ascomycetous Mushrooms

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Minerals (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) contents of eight naturally growing ascomycetous mushrooms (*Geopora arenicola, Geopora sumneriana, Helvella acetabulum, Helvella leucomelaena, Helvella leucopus, Mitrophora semilibera, Morchella elata* and *Morchella rigida*) and the underlying soil samples, were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). In general, mineral contents of the fruit bodies are lower than the substrate soil, but Cd, Cu and Zn accumulation were found to be higher than the underlying soil in some mushrooms.

Key Words: Ascomycetes, Mushrooms, Mineral content, Adiyaman, Turkey.

INTRODUCTION

Collection and consumption of wild edible mushrooms has a long tradition in many countries of the world and has become increasingly popular in recent years. Though the knowledge of the nutritional value of wild growing mushrooms has been limited compared to other vegetables, they are usually considered as valuable nutrient sources and many of them are recommended against health problems such as headache, colds, asthma, diabetes, *etc.*[1].

Mineral accumulation in macrofungi has been found to be affected by environmental and fungal factors[2]. Amount of organic matter, pH and metal concentrations of underlying soil can be listed as environmental factors. Species of fungi, fruit body structure, development stage of mycelium, biochemical composition and fructification intervals are among the fungal factors influencing the mineral accumulation[2-5]. Because of such ecological and genetic factors, the fruiting bodies of mushrooms are often relatively rich in mineral contents[6,7]. Therefore, mushrooms can be used to evaluate the level of environmental pollution[8].

Above threshold concentration levels, trace elements may have hazardous effects on human such as morphological abnormalities, growth problems, or increase in mortality or mutagenicity[9]. Although some metals such as iron, copper, zinc and manganese are essential metals and play important roles in living systems, they may have toxic effects when taken in excess amounts[10].

Ascomycetous mushrooms constitute a small part of *Ascomycota*, including morels, false morels, saddles and cup fungi. Among them, morels comprise the most delicious and prized group as being an important non timber forest product. Almost 161 macrofungi taxa belonging to Ascomycota were reported to exist in Turkey[11] and 22 of them were also recorded from Adiyaman province[12].

This work aims to determine the mineral contents of the fruiting bodies of eight species of wild ascomycetous mushrooms (*Helvella acetabulum, Helvella leucomelaena, Helvella leucopus, Mitrophora semilibera, Morchella elata, Morchella rigida, Geopora arenicola, Geopora sumneriana*) and the soil samples, taken from the points where fruit bodies were collected.

EXPERIMENTAL

The macrofungi specimens and soil samples were collected from 5 localities within Adiyaman province (Turkey) in 2009. During field study, ecological and morphological properties of the samples were recorded and colour photographs were taken at their natural habitats. Soil samples were collected especially from the place where fruit bodies were pulled up. Carrying the macrofungi samples to the laboratory, they were dried. Macroscopic and microscopic investigations and the identification of the samples (Table-1) were carried out in the fungarium. The specimens are kept in Karamanoglu Mehmetbey University, Kamil Özdag Science Faculty, Karaman, Turkey.

TABLE-1
HABITAT AND LOCALITY OF THE MUSHROOM SPECIES

	Macrofungi taxa	Habitat & Locality
1	*Geopora arenicola* (Lév.) Kers.	Pine forest, Tepeönü, Samsat
2	*Geopora sumneriana* (Cooke) M. Torre	Pine-cedar forest; Around Çat Dam Lake, Çelikhan
3	*Helvella acetabulum* (L.) Quél.	Oak forest, Varlik village, central district
4	*Helvella leucomelaena* (Pers.) Nannf.	Pine forest, Yukariköy, Çelikhan
5	*Helvella leucopus* Pers.	Around arable field, Yukariköy, Çelikhan
6	*Mitrophora semilibera* (DC.) Lév.	Around arable field, Yukariköy, Çelikhan
7	*Morchella elata* Fr.	Under poplar, Yukariköy, Çelikhan
8	*Morchella rigida* (Krombh.) Boud.	Around arable field, Yukariköy, Çelikhan

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 and soils for element analysis: Wet digestion method[13] is used for preparation of the samples. The mushroom samples, washed with ultrapure deionized water, were dried at 60 ºC overnight and crushed in a mortar. Then, they were digested with the wet digestion method using a mixture of HNO_3 and $HClO_4$. In a 400 mL of borosilicate beaker, 2 g of accurately weighed mushroom samples were boiled gently in 25 mL of concentrated HNO_3 for 0.5 h. After cooling the mixture, 15 mL of concentrated $HClO_4$ was added and it was boiled gently for *ca.* 1 h untill a colourless solution was obtained. Then solution was cooled and filtered through cellulose acetate filter paper having 0.45 mm pore size. The mixture was transferred to 50 mL of volumetric flask and added ultrapure distilled water to make 50 mL of final volume.

0.25 g of soil sample was weighed and put into a 400 mL of a clean and dry borosilicate beaker. Then, 4 mL of concentrated HNO_3 and 1 mL of $HClO_4$ were added and heated at 150 ºC for 3 h. The mixture was cooled and 2 mL of HCl was added. After heating the mixture at 60 ºC for 1 h, 8 mL of water was added to the mixture. Then, the mixture was filtered through cellulose acetate filter paper having 0.45 mm pore size. Finally the volume was made 25 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 mineral concentrations in the mushroom species and the underlying soil substrates are shown in Table-3. The metal concentrations were determined on dry weight basis. Al, B, Cr, Cu, Fe, Mn, Ni, Sn and Zn were determined in all mushroom while Cd, Co and Pb were determined only in 2, 3 and 2 of the mushrooms respectively. The contents of trace elements in the mushroom samples ranged from 280.8-3018, 0.451-4.420, N.D.-0.328, N.D.-5.277, 0.905-22.93, 12.83-57.64, 498.5-6967, 22.31-779.0, 0.377-34.10, N.D.-2.937, 4.003-4.395 and 49.54-262.7 mg/kg dw for Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn, recpectively.

Mushroom samples contained Al in a range of 280.8 and 3018 mg/kg. The highest Al content was in *H. leucomelaena*, whereas the lowest Al content was in *M. rigida*. Any of the mushrooms are collected and consumed in the region. But the consumption of them may be hazardous according to the daily permissible aluminum dose of WHO[14]. Ascomycetous mushrooms seem to accumulate much more Al compared to basidiomycetous mushrooms growing in closer regions[15-17]. Aluminum contents of underlying soil samples were found to be in a range of 929.6 to 9392 mg/kg. Likewise, boron was also detected in all the samples and ranged from 0.451-4.420 mg/kg. According to Durkan *et al.*[18] boron contents of wild edible mushrooms ranged from 0.229 mg/kg to 46.93 mg/kg. Vetter[19] determined *Marasmius wynnei* to have a boron content between 5 and 15 mg/kg. The average boron content of the members of *Amanita* and *Agaricus* were determined as 5.99 and 3.35 mg/kg, respectively[20]. The content of boron for underlying soil samples ranged from 5.614 to 10.510 mg/kg.

Cadmium is detected only in *H. leucopus* and *M. elata* while it is not detected in any of the underlying soil. This may indicate that, these two mushrooms have a tendency to accumulate Cd much more than the other samples investigated. Mendil *et al.*[21] reported cadmium contents to be between 0.10 and 0.71 mg/kg for some wild edible mushrooms. Except *G. arenicola, G. sumneriana* and *H. leucomelaena*, Co was not detected in mushroom samples, while all the underlying soil samples contained remarkable amounts of this mineral. But the Co contents of the members of the genus *Geopora* are significantly higher than the literature values given for some ascomycetous and basidiomycetous mushrooms[15,22]. Konuk

TABLE-3
AVERAGE CONCENTRATIONS OF MINERALS IN MUSHROOM SAMPLES AND UNDERLYING SOILS

Mushroom / Soil samples		Amount of Elements (mg/kg dry weight)											
		Al	B	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
1	Fruit body	2255	0.748	N.D.	1.822	15.45	34.47	4365	127.2	20.57	0.315	4.164	49.63
	Soil	4137	5.614	N.D.	2.233	30.03	16.00	10010	248.6	38.37	10.05	18.82	35.38
2	Fruit body	1968	1.929	N.D.	5.277	22.93	57.64	6967	779.0	34.10	2.937	4.290	69.91
	Soil	5650	8.429	N.D.	20.78	85.74	93.19	29020	2698	115.3	14.43	19.70	81.82
3	Fruit body	1098	3.233	N.D.	N.D.	2.843	12,83	723.3	19.67	1.288	N.D.	4.328	78.72
	Soil	9392	10.51	N.D.	17.80	105.6	49.70	20740	665.2	67.60	N.D.	18.59	35.14
4	Fruit body	3018	1.192	N.D.	0.273	5.221	14.23	2761	106.2	5.102	N.D.	4.395	49.54
	Soil	6789	6.179	N.D.	9.830	42.95	31.12	23490	434.4	29.54	5.030	19.48	83.55
5	Fruit body	1647	3.043	0.014	N.D.	3.428	36.16	1571	34.99	1.345	N.D.	4.031	262.7
	Soil	6849	6.563	N.D.	13.71	55.98	42.69	26470	716.8	42.79	8.954	18.47	75.66
6	Fruit body	2031	2.317	N.D.	N.D.	4.053	31.67	1695	56.16	2.447	N.D.	4.003	102.3
	Soil	6517	6.551	N.D.	12.21	52.41	51.23	25340	649.5	38.24	8.001	18.29	78.92
7	Fruit body	929.6	4.420	0.328	N.D.	2.498	20.75	1125	44.99	1.574	N.D.	4.021	69.86
	Soil	4958	9.680	N.D.	7.931	52.36	32.65	21300	484.4	43.20	5.945	19.19	71.75
8	Fruit body	280.8	0.451	N.D.	N.D.	0.905	15.83	498.5	22.31	0.377	N.D.	4.141	73.49
	Soil	7510	7.536	N.D.	14.86	58.14	60.24	26640	675.0	39.84	10.75	25.65	86.11

N.D. = Not detected

et al.[23] reported *H. leucopus* and *M. rigida* to contain Co with the amounts of 0.024 and 0.018 mg/kg respectively while none of the two mushrooms contained Co according to our measurements.

The chromium levels ranged from 0.905 to 22.93 mg/kg for the fruit bodies of *M. rigida* and *G. sumneriana* and 30.03 to 105.6 mg/kg for the underlying soils of *G. arenicola* and *H. acetabulum*, respectively. Similar data were presented by Durkan *et al.*[24] for *Funalia trogii* (22.43 mg/kg) and by Ouzouni *et al.*[25] for *Agaricus cupreobruneus* (13.1 μg/g d.w.). Present Cr contents are remarkably high compared to values presented for some ascomycetous mushrooms in literature[23,26]. All the mushroom samples and the underlying soil contained cupper in a range of 12.83 to 57.64 and 16.00 to 93.19 mg/kg, respectively. The determined copper values of mushrooms are in agreement with literature values which ranged from 12-181 mg/kg[26], 10.3-145 mg/kg[27] and 4.59-62.89 mg/kg[15].

The iron content of the mushroom samples ranged from 498.5 to 6967 mg/kg while it ranged from 10010 to 29020 mg/kg for underlying soil samples. Iron contents of mushrooms samples in the literature have been reported in the range of 56.1-7162 mg/kg[28], 568-3904 mg/kg[29] and 110-3640 mg/kg[30]. Our iron values for mushroom samples are in agreement with literature values. Manganese was also determined in all mushrooms. Mn concentrations of mushrooms ranged from 22.31 to 779 mg/kg while it ranged from 248.6 to 2698 mg/kg for underlying soil samples. The reported manganese values in the literature for mushrooms are 21.7-74.3 mg/kg[27] and 5.54-135 mg/kg[31] dw respectively. Though the manganese values related to seven mushrooms are in agreement with results in the literature, it is remarkably high for *G. sumneriana*. *G. arenicola* also seems to have a special tendency to accumulate Mn.

The nickel content was varied in the range of 0.38 mg/kg to 34.10 mg/kg for mushrooms and 29.54 mg/kg to 115.30 mg/kg for underlying soils. 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[3,28,30]. Nickel has been linked to lung cancer[32] and the tolerable upper intake level for this toxic element is reported as 1 mg/day[33]. Though the Ni levels are generally in agreement with previous studies, obtained Ni levels are higher than the allowed amount (0.05-5 mg/kg) of National Academy of Sciences[34] for plants and foods. Quantifiable lead contents were determined only in two species, while it was detected in all the underlying soils except the one for *H. acetabulum*. Pb concentrations of mushroom samples were generally under detection limits, except *G. sumneriana* and *G. arenicola* with the amounts of 2.94 and 0.32 mg/kg dw, respectively. These values are in agreement with literature values[17,18].

Tin was also detected in all mushroom species and the underlying soil samples. Sn concentrations of mushrooms ranged from 4.003 to 4.395 mg/kg. These concentrations ranged from 18.290 to 25.650 mg/kg for underlying soil samples. Durkan *et al.*[18] reported tin values for 34 wild edible mushroom in the ranges 2.809 to 4.711 mg/kg. The zinc content ranged from 49.54 mg/kg for *H. leucopus* and 262.7 mg/kg for *G. sumneriana*. Zinc concentrations of mushrooms samples are in agreement with literature. The literature values for zinc have been reported in the range of 45-188 mg/kg[26], 33.5-89.5 mg/kg[3], 43.5-205 mg/kg[35] and 15.00-447 mg/kg[17]. Our data presents that zinc content of *G. arenicola, H. acetabulum, H. leucopus* and *M. semilibera* are 1.3 to 3.47 times greater than the underlying soil samples. These results show that mushrooms are good zinc accumulators as stated by Isiloglu *et al.*[28].

Conclusion

This comparative study between the accumulated mineral content of ascomycetous mushrooms and the present mineral content of the underlying soil may reveal a perspective about the mineral accumulating potential of mushrooms. Though the measured data for *G. sumneriana* indicates a positive correlation between the mineral contents of the soil and the accumulation of them in fruit body, it seems that the mineral accumulation capacity of mushrooms is not directly related with the amount of the soil mineral content. The mineral bioaccumulation tendency of edible morels seems to be lower than that of the members of the genus *Geopora*.

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