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Heavy metals in some edible mushrooms from the Central Anatolia, Turkey

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Abstract

Eight trace elements (Pb, Cd, Zn, Fe, Mn, Cu, Cr and Ni) in 15 different wild-growing edible mushroom species collected from Eskişehir, Turkey were determined. The highest Pb, Fe, Mn and Cu concentrations were 11.72, 11460, 480 and 144.2 mg/kg (dry weight basis), respectively. All of these highest metal concentrations were determined in *Lepista nuda*. Cadmium and chromium were determined at the highest concentrations in *Gymnopus dryophilus*, 3.24 and 73.8 mg/kg, respectively. The highest zinc and nickel content were observed in *Tricholoma equestre* and *Coprinus comatus* as 173.8 and 58.60 mg/kg dry matter, respectively. Mushrooms species determined as important metal accumulators were *L. nuda*, *G. dryophilus*, *T. equestre* and *C. comatus*, in this study. Heavy metal contents of all analysed mushrooms were generally higher than previously reported in the literature.

Keywords: Trace metals; Mushroom; Basidiomycetes; Eskişehir; Turkey

1. Introduction

Wild-growing and cultivated mushrooms (higher fungi, macrofungi), are considered as a popular delicacy in many countries, mainly in countries of Central and East Europe and the Far East (Kalač, Svoboda, & Havlíčková, 2004). Turkey has a very rich edible macrofungal flora because it possesses favorable environmental conditions for the growth of fungi. Therefore, Turkey is becoming an important exporter for wild edible mushrooms.

It is known that wild-growing mushrooms can accumulate great concentrations of toxic metallic elements and metalloids such as mercury, cadmium, lead, copper or arsenic and radionuclides (Falandysz, Kawano, Swieczkowski, Brzostowski, & Dadej, 2003; Gadd, 1993; Gaso et al., 1998; Kalač, 2001; Kirchner & Daillant, 1998; Svoboda, Zimmermannova, & Kalač, 2000; Vetter, 2004). There are a lot of international reports about the ability to take up and accumulate metals of wild-growing mushrooms from several countries such as France (Michelot, Siobud, Dore, Viel, & Poirier, 1998) Czech Republic (Svoboda, Kalač, Špička, & Janoušková, 2002), Poland (Falandysz et al., 2003; Malinowska, Szefer, & Falandaysz, 2004; Rudawska & Leski, 2005), Slovakia (Kalač, Niznanska, Bevilaqua, & Staskova, 1996; Svoboda et al., 2000), Spain (Garcia, Alonso, Fernandez, & Melgar, 1998), Turkey (Demirbaş, 2001a; Tüzen, Türkekul, Hasdemir, Mendil, & Sarı, 2003; Mendil, Uluözlü, Tüzen, Hasdemir, & Sarı, 2005) and USA (Aruguete, Aldstadt, & Mueller, 1998). The accumulation of heavy metals in macrofungi has been found to be affected by

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environmental and fungal factors (Garcia et al., 1998). Environmental factors such as organic matter amount, pH, metal concentrations in soil and fungal factors such as species of mushroom, morphological part of fruiting body, development stages, age of mycelium, biochemical composition, and interval between the fructifications affect metal accumulation in macrofungi (Garcia et al., 1998; Kalač & Svoboda, 2001).

The province of Eskişehir has a high production of wild mushrooms for commercialization and consumption. Some data exist on metal consist of mushrooms and/or soil from other sides of Turkey which is far from Eskişehir (Demirbaş, 2001a; Işıldak, Turkekul, Elmastaş, & Tüzen, 2004; Mendil, Uluözlü, Hasdemir, & Çağlar, 2004; Mendil et al., 2005; Soylak, Saracoğlu, Tüzen, & Mendil, 2005; Tüzen, Özdemir, & Demirbaş, 1998). However, no earlier study has reported metal concentrations in macrofungi from Central Anatolia region of Turkey. The aim of this study was to document metal concentrations in some edible fungi, saprotrophic and ectomycorrhizal, collected in Eskişehir, Turkey.

2. Materials and methods

Fruiting bodies of mushrooms were collected in 2003 in Türkmenbaba Mountain, Eskişehir. The study area included especially forest areas (Fig. 1).

The collected samples were cleaned, cut, dried at 105 °C for 24 h. Dried samples were homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until the analysis started. Deionized water (18.2 MΩ cm^{-1}) from a Milli-Q system (Human Power I Plus, Korea) was used to prepare all aqueous solutions. All mineral acids and oxidants (HNO_3 and H_2O_2) used were of the highest quality (Merck, Darmstadt, Germany). All the plastic and glassware were cleaned by soaking, with contact, overnight in a 10% nitric acid solution and then rinsed with deionized water. For the elemental analysis, a Perkin–Elmer Optima 2000 ICP-OES was used in this study.

For digestion, CEM Mars 5 microwave closed system was used in this study. Sample (0.25 g) was digested with 9 ml of HNO_3 (65%) and 1 ml of H_2O_2 (30%) in microwave digestion system for 7 min and finally diluted to 50 ml with

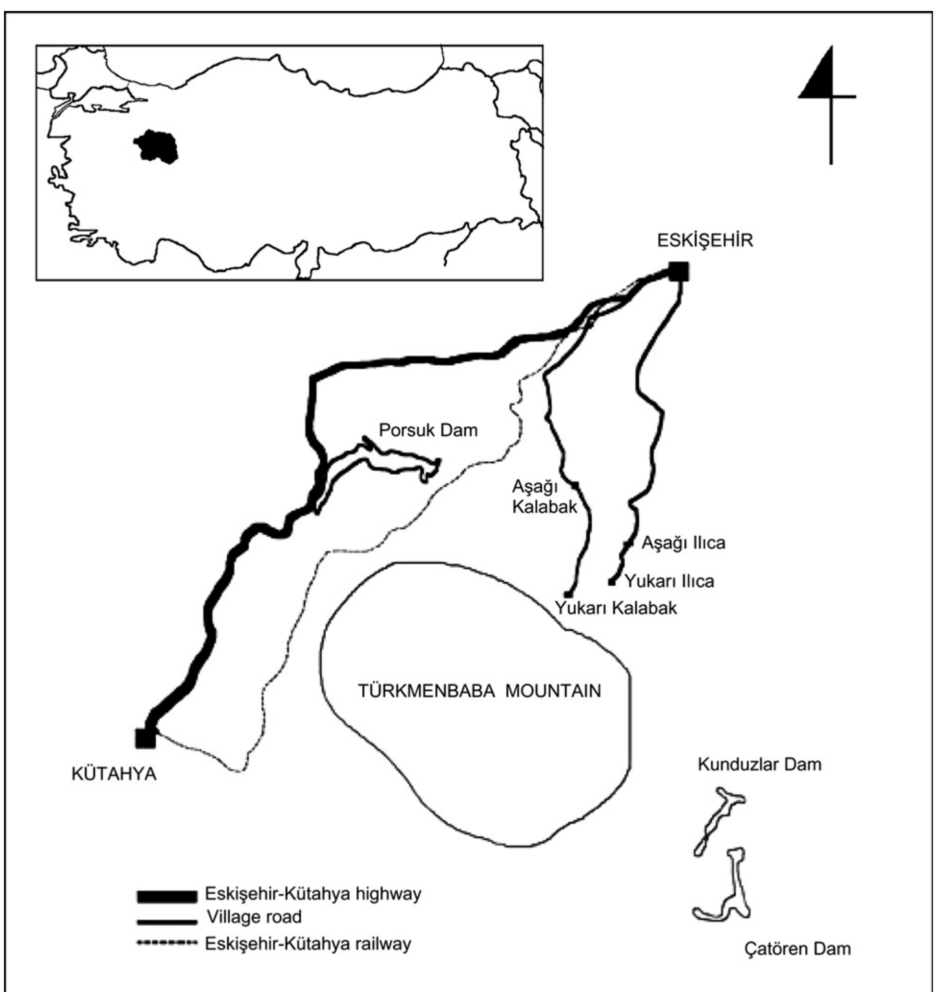

Fig. 1. Map of study area.

deionized water. A blank digest was carried out in the same way. Digestion conditions for the microwave system applied were: the heat was run up to 180 °C in 5 min, and kept constant for 2 min. This process was repeated once more. All sample solutions were clear.

3. Results and discussion

The habitat, trophic status and the taxonomic categories of mushrooms used in presented study and average metal concentrations in fruiting bodies samples are given in Tables 1 and 2, respectively. All of the analysed mushrooms were identified as edible fungi, belonging to the class Basidiomycetes.

In the presented study Pb concentrations of mushroom samples were low, generally. But, Pb levels of *Lepista nuda* and *Melanoleuca stridula* were very high at 11.72 and 9.04 mg/kg dry matter, respectively. *L. nuda* was also reported as a highly Pb accumulating species in the literature. The reported Pb values for mushrooms were 0.5–20 mg/kg (Kalač & Svoboda, 2001).

Minimum and maximum levels of Cd were measured as 0.26 and 3.24 mg/kg dry matter in *Hydnum repandum* and *Gymnopus dryophilus*, respectively. The Cd content of *H. repandum* was higher than the most of literature values (Işıldak et al., 2004; Mendil et al., 2004; Mendil et al., 2005; Türkekul, Elmastaş, & Tüzen, 2004). A higher content of cadmium was reported for saprotrophic species compared to mycorrhizal ones; however, exceptions occurred (Melgar, Alonso, Pérez-López, & Garcia, 1998). It was reported that cadmium is accumulated mainly in kidneys, spleen and liver and its blood serum level increases considerably following mushroom consumption (Kalač & Svoboda, 2001). Thus, cadmium seems to be the most deleterious among heavy metals in mushrooms. Its acceptable daily or weekly intake may be easily reached by consumption of an accumulating mushroom species (Kalač et al., 2004).

Zinc has a biological significance for living organisms and mushrooms are known as good zinc accumulators (Işıloğlu, Yılmaz, & Merdivan, 2001). The Zn concentrations of previous studies were between 30 and 150 mg/kg (Kalač & Svoboda, 2001). Among wild-grown edible mushroom species, the greatest levels of Zn were obtained in the *Tricholoma equestre* (173.8 mg/kg) and *L. nuda* (121 mg/kg). Our values for these species are higher than those reported earlier (Işıldak et al., 2004; Kalač & Svoboda, 2001; Mendil et al., 2005).

The range of Fe concentrations were between 110 and 3640 mg/kg in mushroom species except *L. nuda*. In this species, the highest Fe concentration was determined as 11460 mg/kg. Iron content of this mushroom was much higher than literature values (Demirbaş, 2001a; Işıldak et al., 2004; Işıloğlu et al., 2001; Mendil et al., 2004; Mendil et al., 2005; Soylak et al., 2005; Türkekul et al., 2004).

The highest value of Mn was 480 mg/kg in *L. nuda,* whereas the lowest level was 6.2 mg/kg in *Suillus collitinus*. The reported manganese contents in previous studies for wild-growing mushrooms were 7.6–56.2, 21.7–74.3, 14.5–63.6, 5.0–60.0, 12.9–93.3, 7.1–81.3 (Demirbaş, 2001b; Işıldak et al., 2004; Işıloğlu et al., 2001; Kalač & Svoboda, 2001; Mendil et al., 2004; Tüzen, 2003), respectively. There-

Table 1
Species, trophic status and habitats of analysed mushroom

Family and species	Trophic status	Habitat
Rhizopogonaceae		
Rhizopogon roseolus (Corda) Th. Fr.	Mycorrhizal	In mixed woodlands
Boletaceae		
Boletus chrysenteron Bull	Mycorrhizal	In mixed woodlands
Suillaceae		
Suillus bovinus (Pers.) Kuntze	Mycorrhizal	In pine forest
Suillus collitinus (Fr.) Kuntze	Mycorrhizal	In pine forest
Hydnaceae		
Hydnum repandum L.	Mycorrhizal	In pine forest
Russulaceae		
Lactarius deliciosus (L.) Gray	Mycorrhizal	In pine forest
Coprinaceae		
Coprinus comatus (O.F.Müll.) Gray	Saprotrophic	In meadows
Pluteaceae		
Amanita caesarea (Scop.) Pers.	Mycorrhizal	In pine forest
Agaricaceae		
Macrolepiota procera var. procera (Scop.) Singer	Saprotrophic	In pine forest
Macrolepiota excoriata (Schaeff.) M.M. Moser	Saprotrophic	In pine forest
Tricholomataceae		
Melanoleuca stridula (Fr.) Singer	Saprotrophic	In meadows
Lepista nuda (Bull.) Cooke	Saprotrophic	In pine forest
Clitocybe geotropa (Bull.) Quél.	Saprotrophic	In pine forest
Gymnopus dryophilus (Bull.) Murrill	Saprotrophic	In mixed woodlands
Tricholoma equestre (L.) P. Kumm.	Mycorrhizal	In pine forest

Table 2
Trace metal concentrations (mg/kg, dry weight basis) in mushroom samples (mean ± standard deviation)

Fungal species	Pb	Cd	Zn	Fe	Mn	Cu	Cr	Ni
Rhizopogon roseolus	0.54 ± 0.13	0.47 ± 0.00	62.40 ± 0.22	824 ± 0	18.20 ± 0.07	33.80 ± 0.20	9.44 ± 0.07	17.44 ± 0.06
Boletus chrysenteron	0.98 ± 0.15	0.34 ± 0.00	59.80 ± 0.10	143 ± 2	45.40 ± 0.64	15.70 ± 0.18	1.95 ± 0.06	5.96 ± 0.21
Suillus bovinus	1.47 ± 0.01	0.37 ± 0.01	57.00 ± 0.28	562 ± 6	32.60 ± 0.10	20.40 ± 0.30	5.72 ± 0.05	4.92 ± 0.04
Suillus collitinus	0.69 ± 0.32	0.28 ± 0.01	45.20 ± 0.08	228 ± 2	6.20 ± 0.06	26.60 ± 0.36	10.88 ± 0.04	5.00 ± 0.12
Hydnum repandum	2.34 ± 0.03	0.26 ± 0.01	48.80 ± 0.16	502 ± 2	56.80 ± 0.32	23.80 ± 0.04	5.24 ± 0.33	5.68 ± 0.01
Lactarius deliciosus	0.42 ± 0.23	0.47 ± 0.03	69.80 ± 0.04	146 ± 0	16.80 ± 0.22	10.60 ± 0.01	4.24 ± 0.01	2.46 ± 0.07
Coprinus comatus	2.04 ± 0.44	0.70 ± 0.00	63.40 ± 0.06	3640 ± 2	81.40 ± 2.76	60.60 ± 0.20	38.60 ± 0.38	58.60 ± 0.86
Amanita caesarea	0.30 ± 0.05	2.46 ± 0.03	68.00 ± 0.24	132 ± 1	37.00 ± 0.30	50.80 ± 0.30	0.54 ± 0.02	1.22 ± 0.03
Macrolepiota procera	0.79 ± 0.15	1.08 ± 0.05	83.80 ± 0.20	110 ± 1	11.80 ± 0.04	88.80 ± 1.88	ND[a]	1.77 ± 0.03
Macrolepiota excoriata	1.43 ± 0.07	0.64 ± 0.02	87.00 ± 0.28	542 ± 2	52.20 ± 0.56	80.60 ± 0.02	5.22 ± 0.00	4.42 ± 0.01
Melanoleuca stridula	9.04 ± 0.03	1.30 ± 0.03	90.60 ± 0.54	524 ± 0	197.40 ± 1.88	75.40 ± 0.28	3.30 ± 0.05	4.54 ± 0.03
Lepista nuda	11.72 ± 0.08	0.73 ± 0.01	121.00 ± 0.50	11,460 ± 6	480.00 ± 5.36	144.20 ± 2.22	15.84 ± 0.11	7.16 ± 0.09
Clitocybe geotropa	1.22 ± 0.36	0.58 ± 0.04	86.60 ± 0.40	516 ± 7	54.20 ± 0.88	82.40 ± 0.20	8.32 ± 0.16	14.00 ± 0.07
Gymnopus dryophilus	1.30 ± 0.15	3.24 ± 0.03	58.20 ± 0.36	778 ± 5	78.60 ± 1.32	26.40 ± 0.62	73.80 ± 0.02	12.48 ± 0.28
Tricholoma equestre	1.59 ± 0.16	1.99 ± 0.03	173.80 ± 0.44	632 ± 1	100.40 ± 3.70	25.20 ± 0.34	5.12 ± 0.04	5.68 ± 0.19

$n = 5$.
[a] ND: Not determined.

fore, our Mn results for especially *L. nuda* and *M. stridula* can be regarded as high concentrations.

Kalač and Svoboda (2001) reported that Cu levels in the accumulating species are usually 100–300 mg/kg dry matter, which is not considered a health risk. In the present study, the highest concentrations of Cu were 144.2 and 88.8 mg/kg in *L. nuda* and *Macrolepiota procera*, respectively. These two species were determined as metal accumulators in the vicinity of a copper smelter (Kalač et al., 1996). The copper results of all mushroom species were in agreement with those found in the literature (Demirbaş, 2001a; Işıldak et al., 2004; Kalač et al., 1996; Svoboda et al., 2000).

The highest Cr concentration determined was 73.80 mg/kg dry matter in *G. dryophilus*. However, the Cr levels in other mushrooms were between 1.95–38.60 mg/kg dry matter. Cr content was not determined in *M. procera*. Our chromium results, especially for *G. dryophilus* and *Coprinus comatus* are higher than those reported earlier (Demirbaş, 2001a; Işıldak et al., 2004; Kalač & Svoboda, 2001; Mendil et al., 2004; Mendil et al., 2005; Soylak et al., 2005).

The highest nickel content was observed in *C. comatus* as 58.60 mg/kg dry matter. For the other mushrooms species in this study, Ni levels were between 1.22–17.44 mg/kg. The reported Ni values for wild-growing mushrooms were 44.6–127, 0.4–15.9, 2.73–19.4, 0.4–2, 8.2–26.7, 1.72–24.1, 44.6–127 mg/kg (Demirbaş, 2001a; Işıldak et al., 2004; Işıloğlu et al., 2001; Kalač & Svoboda, 2001; Mendil et al., 2004; Soylak et al., 2005), respectively. Hence, in this study, Ni levels are in agreement with previous studies except in *C. comatus*.

Results from over 150 original papers, dealing with heavy metals in edible mushrooms show that cadmium, mercury and lead are the toxic metals for man (Kalač & Svoboda, 2001). According to FAO/WHO (1989, 1993) standards, acceptable intakes of cadmium and lead for an adult are 0.42–0.49 and 1.5–1.75 mg per week, respectively. The trace element concentrations in mushrooms are generally species-dependent (Kalač & Svoboda, 2001) and hardly affected by pH or organic matter content of the soil (Mendil et al., 2005). In many case metal concentrations of fruiting bodies can be higher than soil (Falandysz, Gucia, Skwarzec, Frankowska, & Klawikowska, 2002) and plants (Işıldak et al., 2004).

In conclusion, heavy metal (Pb, Cd, Zn, Fe, Mn, Cu, Cr and Ni) contents of analysed wild-growing mushrooms collected from Eskişehir, were generally higher than those reported from Turkey and other countries. The highest metal concentrations were measured in *L. nuda* for Pb, Fe, Mn and Cu as 11.72, 11460, 480 and 144.2 mg/kg (dry weight basis), respectively. Cadmium and chromium were determined at the highest concentrations in *G. dryophilus*, 3.24 and 73.8 mg/kg, respectively. The other mushrooms species determined as important metal accumulator were *T. equestre* and *C. comatus*, in this study.

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