

## Determination of trace elements on some wild edible mushroom samples from Kastamonu, Turkey

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### Abstract

Nine trace elements (Fe, Mn, Zn, Cu, Pb, Cd, Cr, Ni, Co) in eight mushroom species of Turkish origin were determined, using flame and graphite furnace atomic absorption spectrometry after microwave digestion. The mushrooms were collected from Kastamonu, Turkey. The ranges of element concentrations for Fe, Mn, Zn, Cu, Pb, Cd, Cr, Ni and Co were 180–407, 12.9–93.3, 40.3–64.4, 7.1–48.6, 6.9–14.1, 0.10–0.71, 1.2–4.2, 8.2–26.7 and 1.0–7.4 mg/kg, respectively.

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### 1. Introduction

Mushrooms are important in ecosystem because they are able to biodegrade the substrate and therefore use the wastes of agricultural production (Manzi, Aguzzi, Vivanti, Paci, & Pizzoferrato, 1999). Heavy metal concentrations in mushroom are considerable higher than those in agricultural crop plants, vegetables and fruit (Manzi, Aguzzi, & Pizzoferrato, 2001).

Mushrooms are valuable health foods, low in calories, high in vegetable proteins, iron, zinc, chitin, fibre, vitamins and minerals. Mushrooms also have a long history of use in traditional Chinese medicine (Demirbaş, 2001). In general, their fruiting bodies, on a dry weight basis, contain about 39.9% carbohydrate, 17.5% protein and 2.9% fats with the rest constituting the minerals (Demirbaş, 2001; Latiff, Daran, & Mohamed, 1996). Wild-growing macrofungi have been a favourite

delicacy in many countries. Some people collect macrofungi to make a substantial contribution to food intake. Therefore, it is necessary to know the levels of toxic and essential elements in edible mushrooms (İşiloğlu, Yılmaz, & Merdivan, 2001). Many wild-growing species accumulate elements at high concentrations, especially cadmium, mercury, lead and copper, considerably exceeding those in other foods. Edible mushrooms may contain higher amounts of heavy metals than plants, especially in the vicinity of highways subject to heavy traffic. Traffic density is very high in Kastamonu (1000 vehicle/h).

Turkey has a large edible mushroom potential and is becoming an important exporter of wild mushrooms. In the East Black sea region the climate is mild and rainy. The seasons are normally wet and mild. The climate, especially in spring and autumn, is ideal for fungal growth (Demirbaş, 2002). In recent years, there have been studies many of heavy metals in cultivated and uncultivated mushrooms of Turkish origin.

The purpose of this study is to determine toxic and essential elements (Fe, Mn, Zn, Cu, Pb, Cd, Cr, Ni, Co) in fruit bodies of several mushroom species from Kastamonu, Turkey.

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## 2. Materials and methods

The mushroom samples were collected from near the motorway in Kastamonu, Turkey. The collected samples were dried at 105 °C for 24 h. Dried samples were homogenized and stored in polyethylene bottles prior to analysis.

De-ionized water (18.2 MΩ cm) from a Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all aqueous solutions. All mineral acids and oxidants (HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) used were of the highest quality (Suprapure, 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.

Samples (0.5 g) were digested with 6 ml of HNO<sub>3</sub> (65%) and 2 ml of H<sub>2</sub>O<sub>2</sub> (30%) in a microwave digestion system for 31 min and diluted to 10 ml with deionized water. A blank digest was carried out in the same way (digestion conditions for microwave were: 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and vent for 8 min). This procedure was adopted because it was accurate with respect to both time and recovery values. The recovery values were nearly quantitative (>95%) for the above digestion method.

A Perkin Elmer AAnalyst 700 model atomic absorption spectrometer with deuterium background corrector was used in this study. Pb and Cd in samples were determined by an HGA graphite furnace, using argon as inert gas. Pyrolytic-coated graphite tubes with a platform were used and signals were measured as peak

height for Cd and peak area for Pb. Other measurements were carried out in an air/acetylene flame.

## 3. Results and discussion

The habitat, edibility and families of mushroom species are given in Table 1. The concentrations of trace elements in mushroom species analysed are shown in Table 2. Trace element concentrations were determined on dry weight as mg/kg and the relative standard deviations were less than 10% for all elements.

The heavy metal concentrations in mushrooms are mainly affected by acidic and organic matter contents of the ecosystem and soil. The uptake of metal ions in mushrooms is in many respects different from plants; thus, the concentrations of metals depend on mushroom species and their ecosystems and soil (Gast, Jensen, Bierling, & Haonstran, 1988).

The contents of iron, manganese, zinc, copper, lead, cadmium, chromium, nickel and cobalt in mushroom species were found to be 180–407, 12.9–93.3, 40.3–64.4, 7.1–48.6, 6.9–14.1, 0.10–0.71, 1.2–4.2, 8.2–26.7 and 1.0–7.4 mg/kg, respectively.

Minimum and maximum values of iron were 180 and 407 mg/kg. The highest and lowest levels of iron were found in *Lepiota cristata* and *Lactarius deliciosus* (Fig. 1). The highest content of manganese was 93.3 mg/kg in *Lycoperdon perlatum*, whereas the lowest manganese content was 12.9 mg/kg in *Boletus luridus* (Fig. 2). Zinc levels were determined to be 40.3 mg/kg in *Polyporus* (sp.) and 64.4 mg/kg in *Boletus badius* (Fig. 3).

Table 1  
Families, habitat and edibility of mushroom species

No	Class, family and species of mushrooms	Habitat	Edibility
01	<i>B. badius</i> Fr.	In mixed woods	Edible
02	<i>L. deliciosus</i> L.: Fr. S. F. Gray	Under pines or spruce	Edible
03	<i>H. crustuliniforme</i> (Bull.:St.Amans)Quel	In open mixed woodland	Poisonous
04	<i>L. perlatum</i> Pers.: L.	Woodland	Edible
05	<i>B. luridus</i> Schaeff.: Fr.	Beech and on calcareous soils	Edible
06	<i>L. cristata</i> Kummer	In woods, garden refuse	Suspect
07	<i>Polyporus</i> (sp.)	–	–
08	<i>A. bisporus</i> (Lange) Pilat	On manure heaps, garden waste and roadsides, not in grass	Edible

Table 2  
Concentration of trace elements (as mg/kg) in mushroom species

Mushroom Species	Fe	Mn	Zn	Cu	Pb	Cd	Cr	Ni	Co
<i>B. badius</i>	377 ± 21.0	24.8 ± 1.3	64.4 ± 5.3	8.4 ± 0.5	8.9 ± 0.8	0.14 ± 0.01	1.2 ± 0.1	9.5 ± 0.8	1.8 ± 0.7
<i>L. deliciosus</i>	180 ± 10.8	15.4 ± 1.5	47.1 ± 3.2	13.4 ± 0.9	9.2 ± 0.7	0.10 ± 0.01	1.2 ± 0.1	9.2 ± 0.7	1.9 ± 0.1
<i>H. crustuliniforme</i>	228 ± 20.7	34.0 ± 1.2	51.9 ± 1.1	38.3 ± 2.3	10.1 ± 0.6	0.71 ± 0.04	1.3 ± 0.1	10.5 ± 1.0	6.8 ± 0.6
<i>L. perlatum</i>	382 ± 25.4	93.3 ± 8.1	56.9 ± 4.7	42.9 ± 3.9	11.2 ± 1.1	0.10 ± 0.01	3.7 ± 0.3	24.3 ± 2.1	7.4 ± 0.5
<i>B. luridus</i>	203 ± 11.2	12.9 ± 1.2	41.1 ± 3.3	25.3 ± 1.5	7.9 ± 0.4	0.21 ± 0.01	1.9 ± 0.1	11.0 ± 1.1	1.0 ± 0.1
<i>L. cristata</i>	407 ± 37.3	87.2 ± 6.5	60.2 ± 5.5	48.6 ± 4.7	14.1 ± 1.1	0.20 ± 0.01	2.5 ± 0.2	25.6 ± 1.8	4.0 ± 0.3
<i>Polyporus</i> (sp.)	398 ± 36.2	86.5 ± 7.4	40.3 ± 2.2	7.1 ± 0.6	8.0 ± 0.6	0.11 ± 0.01	4.2 ± 0.4	26.7 ± 2.3	6.2 ± 0.5
<i>A. bisporus</i>	332 ± 22.6	20.9 ± 1.3	51.8 ± 4.6	11.9 ± 1.0	6.9 ± 0.3	0.10 ± 0.01	3.1 ± 0.2	8.2 ± 0.6	1.3 ± 0.1

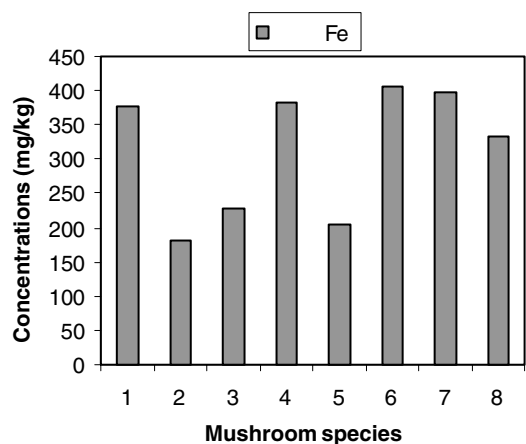


Fig. 1. Distribution of iron in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus* (sp.); 8, *A. bisporus*.

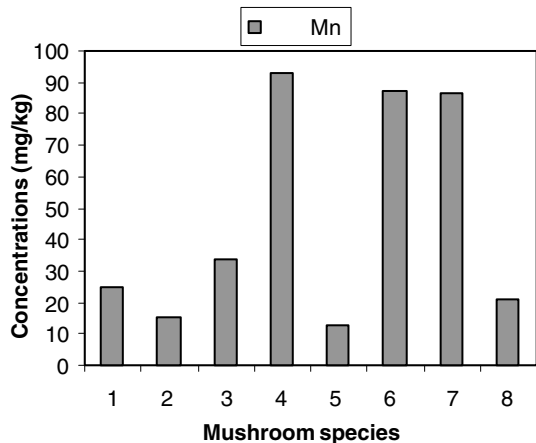


Fig. 2. Distribution of manganese in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus* (sp.); 8, *A. bisporus*.

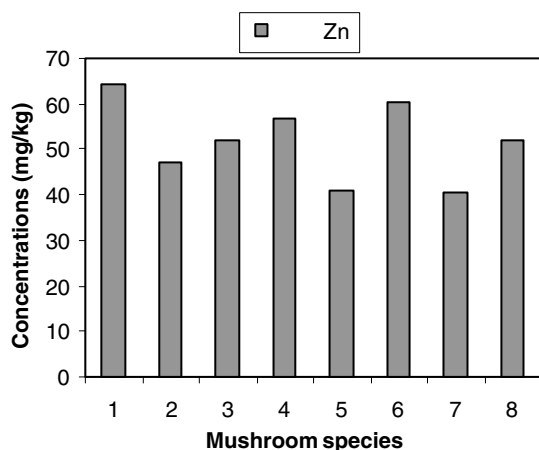


Fig. 3. Distribution of zinc in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus* (sp.); 8, *A. bisporus*.

Zinc is widespread among living organisms due to its biological significance. Mushrooms are known as zinc accumulators and the sporophore: substrate ratio for Zn ranges from 1 to 10 mg/kg (Bano, Nagaraja, Vibhakar, & Kapur, 1981; Işiloğlu et al., 2001). In this study, the highest copper content was 48.6 mg/kg in *L. cristata*; the lowest was 7.1 mg/kg in *Polyporus* (sp.) (Fig. 4). The lead concentrations were high in *L. cristata* (Fig. 5) and ranged from 6.9 to 14.1 mg/kg. Cadmium contents were between 0.10 and 0.71 mg/kg in the samples. The highest cadmium content was found in *Hebeloma crustuliniforme* (Fig. 6). The average chromium concentration was 1.2–4.2 mg/kg. The lowest and highest chromium values were observed in *B. badius*, *L. deliciosus* and *Polyporus* (sp.) (Fig. 7). Maximum nickel level was 26.7 mg/kg in *Polyporus* (sp.) and minimum nickel level was 8.2 mg/kg in *Agaricus bisporus* (Fig. 8). The range of

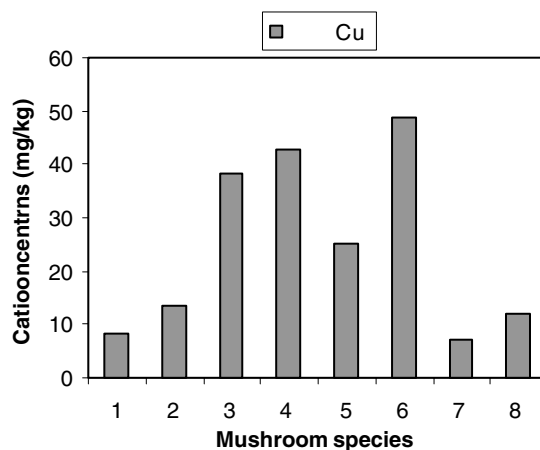


Fig. 4. Distribution of copper in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus* (sp.); 8, *A. bisporus*.

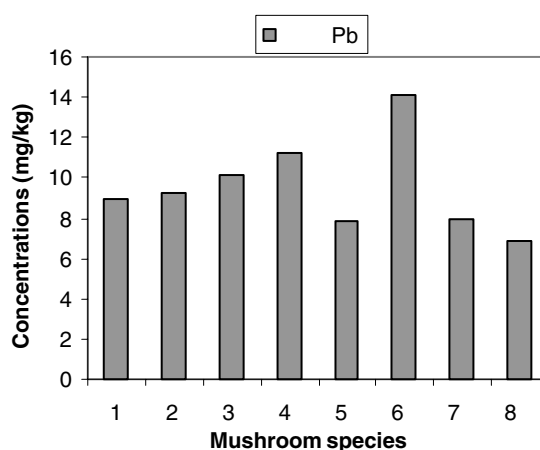


Fig. 5. Distribution of lead in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus* (sp.); 8, *A. bisporus*.

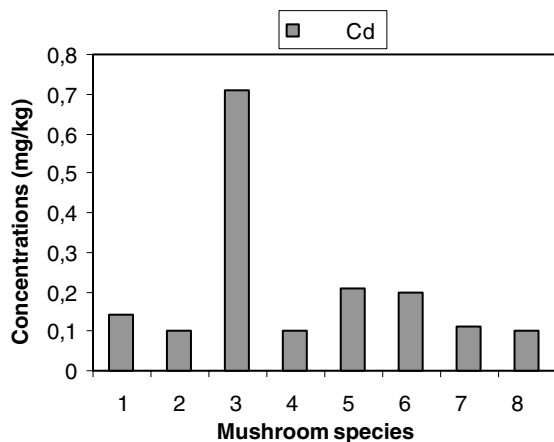


Fig. 6. Distribution of cadmium in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus (sp.)*; 8, *A. bisporus*.

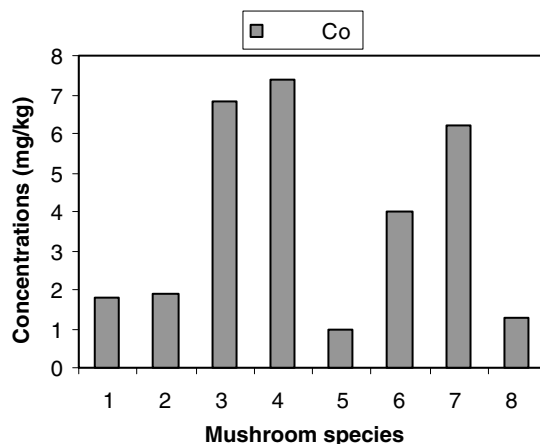


Fig. 9. Distribution of cobalt in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus (sp.)*; 8, *A. bisporus*.

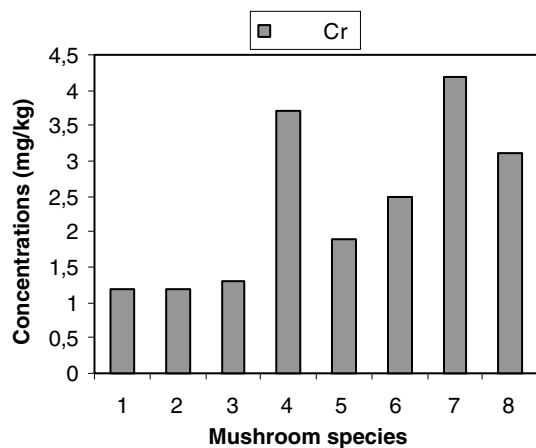


Fig. 7. Distribution of chrome in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus (sp.)*; 8, *A. bisporus*.

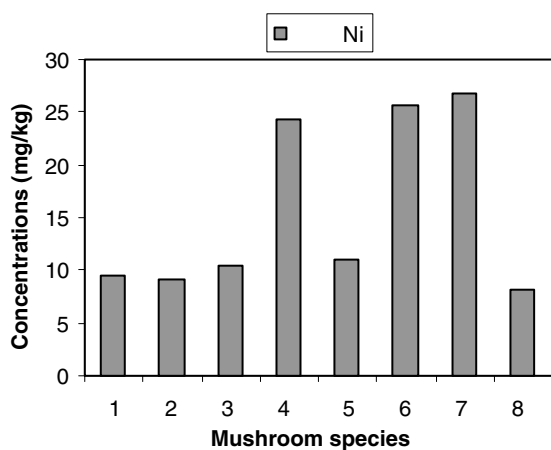


Fig. 8. Distribution of nickel in mushroom species: 1, *B. badius*; 2, *L. deliciosus*; 3, *H. crustuliniforme*; 4, *L. perlatum*; 5, *Boletus luridus*; 6, *L. cristata*; 7, *Polyporus (sp.)*; 8, *A. bisporus*.

cobalt concentrations was 1.0–7.4 mg/kg in *B. luridus* and *L. perlatum* (Fig. 9).

Iron contents of mushrooms were lower than our results in other studies (Sivrikaya, Bacak, Saraçbaşı, Toroğlu, & Eroğlu, 2002). The reported manganese values for mushrooms were 6.78–63.6 mg/kg, 7.6–56.2 mg/kg, and 15–19 µg/g, respectively (Demirbaş, 2001; Işıloğlu et al., 2001; Sivrikaya et al., 2002). Our zinc results are lower than those reported earlier (Işıloğlu et al., 2001; Sesli & Tüzen, 1999). Copper contents were very low in other studies (Demirbaş, 2000; Sesli & Tüzen, 1999). Copper values were reported as 34.5–83.0 mg/kg, 10.0–14.0 µg/g and 21.1–42.6 mg/kg, respectively (Demirbaş, 2002; Işıloğlu et al., 2001; Sivrikaya et al., 2002). Lead concentrations are very low compared to our results (Racz, Papp, Oldal, & Kovacs, 1998; Racz & Odal, 2000). Reported cadmium levels are very high compared to our results (Demirbaş, 2002; Sesli & Tüzen, 1999; Svoboda, Zimmermannova, & Kalac, 2000). Chromium contents were lower than literature values and nickel contents were higher than literature values. Cobalt values have been reported as 10.5–12.5 µg/g for different mushroom species (Sivrikaya et al., 2002).

A linear regression correlation test was performed to investigate correlations between metal concentrations. The values of correlation coefficients between metal concentrations are given in Table 3.

There are good correlations between iron and manganese ( $r = 0.75$ ), iron and nickel ( $r = 0.69$ ), manganese and lead ( $r = 0.60$ ), manganese and chromium ( $r = 0.73$ ), manganese and nickel ( $r = 0.97$ ), manganese and cobalt ( $r = 0.75$ ), zinc and lead ( $r = 0.55$ ), copper and lead ( $r = 0.83$ ), copper and cobalt ( $r = 0.49$ ), lead and nickel ( $r = 0.56$ ), chromium and nickel ( $r = 0.86$ ), chromium and nickel ( $r = 0.73$ ) and nickel and cobalt ( $r = 0.65$ ). The other correlations between metals were

Table 3  
Correlations between metal concentrations

	Fe	Mn	Zn	Cu	Pb	Cd	Cr	Ni	Co
Fe	1.00								
Mn	0.75	1.00							
Zn	0.48	0.16	1.00						
Cu	0.09	0.47	0.34	1.00					
Pb	0.33	0.60	0.55	0.83	1.00				
Cd	-0.38	-0.16	0.02	0.42	0.18	1.00			
Cr	0.64	0.73	-0.24	0.02	-0.03	-0.43	1.00		
Ni	0.69	0.97	0.01	0.41	0.56	-0.23	0.73	1.00	
Co	0.34	0.75	0.04	0.49	0.42	0.39	0.46	0.65	1.00

not significant. There are positive correlations of iron-zinc, iron-copper, iron and lead, iron and cobalt, manganese and zinc, manganese and copper, zinc and copper, zinc and cadmium, zinc and nickel, zinc and cobalt, copper and cadmium, copper and chromium, copper and nickel, lead and cadmium, lead and cobalt, cadmium and cobalt and chromium and cobalt. Negative correlations were found between iron and cadmium, manganese and cadmium, zinc and chromium, lead and chromium, cadmium and chromium, and cadmium and nickel.

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### References

- Bano, Z., Nagaraja, K., Vibhakar, S., & Kapur, O. P. (1981). Mineral and the heavy metal contents in the sporophores of pleurotus species. *Mushroom Newsletter Tropics*, 2, 3–7.
- Demirbaş, A. (2000). Accumulation of heavy metals in some edible mushrooms from Turkey. *Food Chemistry*, 68, 415–419.
- Demirbaş, A. (2001). Heavy metal bioaccumulation by mushrooms from artificially fortified soils. *Food Chemistry*, 74, 293–301.
- Demirbaş, A. (2002). Metal ion uptake by mushrooms from natural and artificially enriched soils. *Food Chemistry*, 78, 89–93.
- Gast, C. H., Jensen, E., Bierling, J., & Haonstran, L. (1988). Heavy metals in mushrooms and their relationship with soil characteristics. *Chemosphere*, 75, 417–422.
- İşiloğlu, M., Yılmaz, f., & Merdivan, M. (2001). Concentrations of trace elements in wild edible mushrooms. *Food Chemistry*, 73, 163–175.
- Latiff, L. A., Daran, A. B. M., & Mohomed, A. B. (1996). Relative distribution of minerals in the pileus and stalk of some selected edible mushrooms. *Food Chemistry*, 56, 115–121.
- Manzi, P., Aguzzi, A., Vivanti, V., Paci, M., & Pizzoferrato, L. (1999). Mushrooms as a source of functional ingredients. In Euro. Food Chem X European conference on: Functional foods. A new challenge for the food chemist. 22–24 September, Budapest, Hungary, (Vol. 1, pp. 86–93).
- Manzi, P., Aguzzi, & Pizzoferrato, L. (2001). Nutritional value of mushrooms widely consumed in Italy. *Food Chemistry*, 73, 321–325.
- Racz, L., Papp, L., Oldal, V., & Kovacs, Zs. (1998). Determination of essential and toxic metals in cultivated champignons by inductively coupled plasma atomic emission spectrometry. *Microchemical Journal*, 59, 181–186.
- Racz, L., & Odal, V. (2000). Investigation of uptake processes in a soil/mushroom system by AES and AAS methods. *Microchemical Journal*, 67, 115–118.
- Sesli, E., & Tüzen, 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.
- Sivrikaya, H., Bacak, L., Saraçbaşı, A., Toroğlu, I., & Eroğlu, H. (2002). Trace elements in *pleurotus sajor-caju* cultivated on chemithermomechanical pulp for bio-bleaching. *Food Chemistry*, 79, 173–176.
- Svoboda, L., Zimmermannova, K., & Kalac, P. (2000). Concentrations of mercury, cadmium, lead, and copper in fruiting bodies of edible mushrooms in an emission area of a copper smelter and a mercury smelter. *The Science of the Total Environment*, 246, 61–67.