

Determination of trace metals in mushroom samples from Kayseri, Turkey

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Abstract

Trace metal levels in seven different wild-growing mushroom species from Kayseri, Turkey were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The contents of trace metals in the mushroom samples were found in the ranges, 13.4–50.6, 0.14–0.95, 0.75–1.99, 33.5–89.5, 14.2–69.7, 102–1580, 0.34–1.10, 1.72–24.1 and 0.47–1.51 µg/g for Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni and Co, respectively. Results obtained are in agreement with data reported in the literature. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Mushrooms are valuable health foods, low in calories, high in vegetable proteins, vitamins, and minerals (Racz, Papp, Prokai, & Kovacz, 1996). Compared to green plants, mushrooms can build up large concentrations of some heavy metals, such as Pb, Cd and Hg, and a great effort has been made to evaluate the possible danger to human health from the ingestion of mushrooms (Gast, Jansen, Bierling, & Haanstra, 1988). The contents of trace metals are related to species of mushroom, collecting site of the sample, age of fruiting bodies and mycelium, and distance from the source of pollution (Kalac, Burda, & Staskova, 1991). Lead, cadmium, iron, copper, manganese, zinc, cobalt, chromium and nickel were chosen as representative trace metals whose levels in the environment represent a reliable index of environmental

pollution. Metals such as iron, copper, zinc and manganese are essential metals since they play an important role in biological systems, whereas lead and cadmium are non-essential metals as they are toxic, even in traces (Schroeder, 1973). The essential metals can also produce toxic effects when the metal intake is excessively elevated.

Kayseri is located in the middle Anatolia Region of Turkey (38.42°N, 35.28°E). Kayseri is an industrial-agricultural city in the central Anatolia-Turkey and has a population of one million. The climate in Kayseri dry, with hot summers and cold winters. Temperature ranges between –20 and 40 °C, average values being 30 °C during summer and –5 °C during winter. Various biological samples (spices, tea, tobacco) have been analyzed with respect to trace metals in this region (Narin, Tuzen, & Soylak, 2004; Soylak, Tuzen, Narin, & Sari, 2004). But, trace metal levels in mushroom samples in Kayseri have not yet been determined.

Decomposition of mushroom samples is an important consideration for combined analytical methods. In most cases, when using highly sensitive measuring methods, such as flame AAS, graphite furnace AAS,

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ICP-OES, ICP-MS, the sample is measured in an aqueous solution (Knapp, 1991).

In this study, the contents of trace metals in mushroom samples collected from Kayseri, Turkey were determined by flame and graphite furnace AAS after microwave digestion.

2. Materials and methods

Mushroom samples were collected in Kayseri, Turkey, in 2004 and dried at 105 °C for 24 h. Dried samples were homogenized using an agate homogenizer and stored in polyethylene bottles until analysis. All the plastic and glassware were cleaned by soaking, with contact, overnight in a 10% nitric acid solution and then rinsed with deionized water.

One gramme of sample was digested with 6 ml of HNO₃ (Suprapure, Merck), 2 ml of H₂O₂ (Suprapure, Merck) in a microwave digestion system and diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 MΩ cm⁻¹ resistivity). A blank digest was carried out in the same way (digestion conditions for the microwave system applied 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, then vent for 8 min). This procedure was preferred because it is more accurate with respect to both time and recovery values. The recovery values were nearly quantitative (>95%) for the above digestion method.

The concentrations of iron, copper, manganese and zinc were determined in an air-acetylene flame by the AAS (A Perkin–Elmer Analyst 700 model atomic absorption spectrometer) using a deuterium background correction. Lead, cadmium, cobalt, chromium and nickel contents in the mushroom samples were determined with an HGA graphite furnace, using argon as inert gas.

3. Results and discussion

Trace metal levels in the analysed samples are listed in Table 1. All metal concentrations were determined on a dry weight basis. The contents of trace metals in the samples were found to be in the ranges: 13.4–50.6, 0.14–0.95, 0.75–1.99, 33.5–89.5, 14.2–69.7, 102–1580, 0.34–1.10, 1.72–24.1 and 0.47–1.51 µg/g for Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni and Co, respectively.

Minimum and maximum values of copper were 13.4 and 50.6 µg/g. The highest and lowest levels of copper were found in *Marasmius oreades* and *Agrocybe dura*. Copper contents of mushroom samples in the literature have been reported to be in the ranges: 4.71–51.0 µg/g (Tüzen, Ozdemir, & Demirbaş, 1998), 12–181 µg/g (Tüzen, Turkecul, Hasdemir, Mendil, & Sari, 2003) and 10.3–145 µg/g (Sesli & Tüzen, 1999), respectively. Cop-

Table 1
Trace metal concentrations (as µg/g) in analyzed mushroom species

Mushroom species	Edibility	Cu	Cd	Pb	Zn	Mn	Fe	Cr	Ni	Co
<i>Stropharia coronilla</i>	Edible	16.9 ± 1.1	0.14 ± 0.01	0.75 ± 0.10	74.5 ± 5.2	65.7 ± 4.3	1580 ± 72	0.82 ± 0.10	24.1 ± 2.2	1.51 ± 0.11
<i>Agrocybe dura</i>	Edible	13.4 ± 1.2	0.45 ± 0.04	1.20 ± 0.11	33.9 ± 3.1	18.6 ± 1.4	102 ± 10	0.34 ± 0.03	1.72 ± 0.15	1.19 ± 0.10
<i>Pholiota ochrochlora</i>	Unknown	25.5 ± 2.4	0.71 ± 0.10	1.99 ± 0.16	54.1 ± 4.7	21.4 ± 1.8	246 ± 19	0.50 ± 0.04	6.10 ± 0.53	0.65 ± 0.07
<i>Panellus stipticus</i>	Not edible	18.8 ± 1.5	0.95 ± 0.10	1.24 ± 0.11	33.5 ± 2.1	14.2 ± 1.5	120 ± 11	1.05 ± 0.10	7.08 ± 0.50	0.86 ± 0.10
<i>Marasmius oreades</i>	Edible	50.6 ± 4.4	0.63 ± 0.05	1.05 ± 0.10	53.4 ± 3.2	25.1 ± 1.9	227 ± 16	1.10 ± 0.11	13.2 ± 1.2	0.70 ± 0.05
<i>Tricholoma argyraceum</i>	Edible	13.9 ± 1.3	0.91 ± 0.10	1.89 ± 0.15	89.5 ± 6.8	15.5 ± 1.4	216 ± 18	0.42 ± 0.04	5.74 ± 0.46	0.47 ± 0.04
<i>Psathyrella candolleana</i>	Unknown	23.4 ± 2.1	0.80 ± 0.07	0.82 ± 0.10	42.9 ± 2.6	69.7 ± 4.8	202 ± 15	0.61 ± 0.05	7.11 ± 0.50	0.95 ± 0.10

per values have been reported to be 34.5–83.0, 10.0–14.0 and 21.1–42.6 $\mu\text{g/g}$, respectively, in the literature (Demirbaş, 2002; Işıloğlu, Yılmaz, & Merdivan, 2001; Sivrikaya, Bacak, Saraçbaşı, Toroğlu, & Eroğlu, 2002). Copper contents found in this study are in agreement with those reported in the literature.

The lower and higher cadmium concentrations were 0.14 $\mu\text{g/g}$ in *Stropharia coronilla* and 0.95 $\mu\text{g/g}$ in *Panellus stipticus*, respectively. Cadmium contents of mushroom samples in the literature have been reported to be in the ranges: 0.81–7.50 $\mu\text{g/g}$ (Svoboda, Zimmermannova, & Kalac, 2000), 0.10–0.71 $\mu\text{g/g}$ (Mendil, Uluöz lü, Hasdemir, & Çağ lar, 2004a), 0.28–1.6 $\mu\text{g/g}$ (Mendil, Uluozlu, Tüzen, Hasdemir, & Sari, 2004) and 0.12–2.60 $\mu\text{g/g}$ (Malinowska, Szefer, & Falandaysz, 2004). Our cadmium levels were found to be lower than those reported in the literature.

The lower lead content was 0.75 $\mu\text{g/g}$ in *Stropharia coronilla*. The higher lead content was 1.99 $\mu\text{g/g}$ in *Pholiota ochrochlora*. Lead contents of mushroom samples in the literature have been reported to be in the ranges: 0.40–2.80 $\mu\text{g/g}$ (Svoboda et al., 2000), 0.75–7.77 $\mu\text{g/g}$ (Tüzen et al., 2003) and 1.43–4.17 $\mu\text{g/g}$ (Tüzen, 2003). The fact that toxic metals are present in high concentrations in mushrooms is of particular importance in relation to the FAO/WHO (1976) standards for Pb and Cd as toxic metals. The maximum permissible doses for an adult are 3 mg Pb and 0.5 mg Cd per week, but the recommended doses are only one-fifth of those quantities.

Minimum zinc concentration was 33.5 $\mu\text{g/g}$ in *Panellus stipticus*. Maximum zinc concentration was 89.5 $\mu\text{g/g}$ in *Tricholoma argyraceum*. Zinc concentrations of mushroom samples in the literature have been reported to be in the ranges: 40.3–64.4 $\mu\text{g/g}$ (Mendil et al., 2004) and 29.3–158 $\mu\text{g/g}$ (Işıloğlu et al., 2001). Zinc is widespread among living organisms due to its biological significance. Mushrooms are known as zinc accumulators and sporophore: substrate ratio for Zn ranges from 1 to 10 (Bano, Nagaraja, Vibhakar, & Kapur, 1981; Işıloğlu et al., 2001).

The lower manganese level was 14.2 $\mu\text{g/g}$ in *Panellus stipticus*. The higher manganese level was 69.7 $\mu\text{g/g}$ in *Psathyrella candolleana*. The reported manganese values in the literature for mushrooms were 7.6–56.2, 21.7–74.3 and 7.1–81.3 $\mu\text{g/g}$ (Demirbaş, 2001; Isıldak, Turkekul, Elmastas, & Tuzen, 2004; Tüzen, 2003), respectively. Our manganese values are in agreement with those reported in the literature.

The lower and higher iron concentrations were 102 $\mu\text{g/g}$ in *Agrocybe dura* and 1580 $\mu\text{g/g}$ in *Stropharia coronilla*, respectively. Iron values in mushroom samples have been reported to be in the ranges: 31.3–1190 $\mu\text{g/g}$ (Sesli & Tüzen, 1999), 568–3904 $\mu\text{g/g}$ (Turkekul, Elmastas, & Tüzen, 2004) and 56.1–7162 $\mu\text{g/g}$ (Işıloğlu et al., 2001), respectively. Our iron values are in agreement with those reported in the literature.

Chromium values in mushroom samples have been reported to be in the ranges: 0.16–4.86 $\mu\text{g/g}$ (Malinowska et al., 2004), 0.87–2.66 $\mu\text{g/g}$ (Tüzen, 2003) and 7.0–11.0 $\mu\text{g/g}$ (Sivrikaya et al., 2002), respectively. The lower chromium content found was 0.34 $\mu\text{g/g}$ in *Agrocybe dura*. The higher chromium content found was 1.10 $\mu\text{g/g}$ in *Marasmius oreades*. Our chromium levels were found to be lower than those reported in the literature.

The lower and higher nickel concentrations were 1.72 $\mu\text{g/g}$ in *Agrocybe dura* and 24.1 $\mu\text{g/g}$ in *Stropharia coronilla*, respectively. Nickel values have been reported in the ranges: 1.18–5.14 $\mu\text{g/g}$ (Tüzen, 2003), 8.2–21.6 $\mu\text{g/g}$ (Mendil et al., 2004) and 0.4–15.9 $\mu\text{g/g}$ (Isıldak et al., 2004), respectively. Our nickel values are in agreement with those reported in the literature.

The minimum and maximum cobalt levels were 0.47 $\mu\text{g/g}$ in *Tricholoma argyraceum* and 1.51 $\mu\text{g/g}$ in *Stropharia coronilla*, respectively. Cobalt values in the literature have been reported in the ranges: 0.28–1.32 $\mu\text{g/g}$ (Tüzen, 2003), 0.12–0.62 $\mu\text{g/g}$ (Sesli & Tüzen, 1999) and 0.15–6.03 $\mu\text{g/g}$ (Işıloğlu et al., 2001), respectively. Our cobalt values are in agreement with those reported in the literature.

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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. (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.
- FAO/WHO. (1976). List of maximum levels recommended for contaminants by the Joint FAO/WHO Codex Alimentarius Commission. (Vol. 3, pp. 1–8). Second Series. CAC/ FAL, Rome.
- Gast, C. H., Jansen, E., Bierling, J., & Haanstra, L. (1988). Heavy metals in mushrooms and their relationship with soil characteristics. *Chemosphere*, 17(4), 789–799.
- Isıldak, O., Turkekul, I., Elmastas, M., & Tuzen, M. (2004). Analysis of heavy metals in some wild grown edible mushrooms from the middle black sea region, Turkey. *Food Chemistry*, 86, 547–552.
- Işıloğlu, M., Yılmaz, F., & Merdivan, M. (2001). Concentrations of trace elements in wild edible mushrooms. *Food Chemistry*, 73, 163–175.
- Kalac, P., Burda, J., & Staskova, I. (1991). Concentrations of lead, cadmium, mercury and copper in mushrooms in the vicinity of a lead smelter. *The Science of the Total Environment*, 105, 109–119.
- Knapp, G. (1991). Mechanized techniques for sample decomposition and element preconcentration. *Microchemica Acta*, 2, 445–455.

- Malinowska, E., Szefer, P., & Falandaysz, J. (2004). Metals bioaccumulation by bay bolete, *Xerocomus badius*, from selected sites in Poland. *Food Chemistry*, 84, 405–416.
- Mendil, D., Uluözlu, O. D., Hasdemir, E., & Çağlar, A. (2004). Determination of trace elements on some wild edible mushroom samples from Kastamonu, Turkey. *Food Chemistry*, 88, 281–285.
- Mendil, D., Uluozlu, O. D., Tüzen, M., Hasdemir, E., & Sari, H. (2004). Trace metal levels in mushroom samples from Ordu, Turkey. *Food Chemistry* (in press).
- Narin, I., Tuzen, M., & Soylak, M. (2004). Comparison of sample preparation procedures for the determination of trace metals in house dust, tobacco and tea samples by atomic absorption spectrometry. *Annali di Chimica*, 94, 867–873.
- Racz, L., Papp, L., Prokai, B., & Kovacz, Zs. (1996). Trace element determination in cultivated mushrooms: an investigation of manganese, nickel, and cadmium intake in cultivated mushrooms using ICP atomic emission. *Microchemical Journal*, 54, 444–451.
- Schroeder, H. A. (1973). *The trace elements and nutrition*. London: Faber and Faber.
- 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.
- Soylak, M., Tuzen, M., Narin, I., & Sari, H. (2004). Comparison of microwave and wet digestion procedures for the determination of trace metal contents in spice samples produced in Turkey. *Journal of Food and Drug Analysis*, 12, 254–258.
- 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.
- Turkecul, I., Elmastas, M., & Tüzen, M. (2004). Determination of iron, copper, manganese, zinc, lead, and cadmium in mushroom samples from Tokat, Turkey. *Food Chemistry*, 84, 389–392.
- Tüzen, M. (2003). Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry. *Microchemical Journal*, 74, 289–297.
- Tüzen, M., Ozdemir, M., & Demirbaş, A. (1998). Study of heavy metals in some cultivated and uncultivated mushrooms of Turkish origin. *Food Chemistry*, 63(2), 247–251.
- Tüzen, M., Turkecul, I., Hasdemir, E., Mendil, D., & Sari, H. (2003). Atomic absorption spectrometric determination of trace metal contents of mushroom samples from Tokat, Turkey. *Analytical Letters*, 36, 1401–1410.