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Concentrations of 21 metals in 18 species of mushrooms growing in the East Black Sea region

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Abstract

Eighteen different species of wild mushrooms (*Agaricus bisporus, Agaricus silvicola, Amanita muscaria, Amanita rubescens, Amanita vaginata, Boletus* sp., *Hydnum repandum, Hypholoma fasciculare, Laccaria lacceta, Lactarius piperatus, Lactarius* sp., *Lactarius volemus, Pleurotus ostreatus, Russula cyanoxantha, Russula* sp., *Russula delica, Russula foetens* and*Tricholoma terreum*) growing in the East Black Sea region were analyzed spectrometrically for their metal element (Pb, Cd, Hg, Cu, Mn, Zn, Fe, Co, As, Ca, Na, K, Mg, Ba, Ni, Ti, Cr, Al, Bi, Sb, and Ag) levels. In the mushrooms, the highest metal concentrations were measured as 4.91, 3.48, 0.60, 92.5, 44.4, 176, 169, 0.72, 1.76, 106.4, 136, 51 000, 1320, 1.62, 145, 282, 1.68, 24.1, 1.84, 0.26, and 0.37 mg/kg (dry weight basis) for Pb, Cd, Hg, Cu, Mn, Zn, Fe, Co, As, Ca, Na, K, Mg, Ba, Ni, Ti, Cr, Al, Bi, Sb, and Ag in *Russula foetens, Agaricus bisporus, Hypholoma fasciculare, Hydnum repandum, Lactarius* sp., *Tricholoma terreum, Amanita vaginata, Laccaria lacceta, Pleurotus ostreatus, Hypholoma fasciculare, Pleurotus ostreatus, Hypholoma fasciculare, Agaricus bisporus, Pleurotus ostreatus, Lactarius piperatus, Hydnum repandum, Russula* sp., *Agaricus bisporus, Russula delica*, and *Lactarius* sp., respectively.

Keywords: Wild mushroom; Metal contents; Turkey

1. Introduction

It is already generally known that some living organisms possess the ability to take up and accumulate, in their structures, certain elements, especially metals, at high concentrations (Vetter, 1993). Recently, both international and Turkish studies have drawn attention to the occurrence of the metal contents of mushrooms (Demirbaş, 2000a, 2001; Falandaysz, Sicinska, Bona, & Kohnke, 1992; Lepsova & Mejstrik, 1998; Sesli & Tüzen, 1999; Tüzen, Özdemir, & Demirbaş, 1998a,b; Tüzen, Sesli, & Demirbaş, 1999; Vetter, 1993, 1994).

Metals occur naturally in the environment and are present in rocks, soil, plants, and animals. Metals occur in different forms: as ions dissolved in water, as vapours, or as salts or minerals in rock, sand, and soil. They can also be bound in organic or inorganic molecules, or attached to particles in the air. Both natural and anthropogenic processes emit metals into air and water.

Plants and animals depend on some metals as micronutrients. However, certain forms of some metals can also be toxic, even in relatively small amounts, and therefore pose a risk to the health of animals and people. While the effects of chronic exposure to trace amounts of some metals are not well understood, a legacy of incidents tells us about the seriousness of high levels of exposure to some metals, especially cadmium and methyl mercury.

The decomposition of mushroom samples is an important part of combined analytical methods. Determinations of the heavy metal concentrations have been performed with atomic absorption spectrophotometry (AAS) using flame atomization (Gast, Jansen, Bierling, & Haanstra, 1988). Hg content in mushroom samples has been determined by cold vapour atomic absorption spectrophotometry (CVAAS), using $NaBH_4$ as the reducing agent (Rincon-Leon & Zurera-Cosano, 1986). Contents of K, Na, Mg, and Ag were determined by standard procedures in a total of 46 stalks of *Aramillariella mellea* (Falandaysz et al., 1992). Concentrations of mineral elements (B, Ca, Cu, Na, Zn, K, Fe, Mg, Cd, Ni, P, Ti, Ba, Cs, Cr, and Li) of the caps and stipes of *Agarigus bisporus* and *Pleurotus ostreatus* were compared

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(Vetter, 1994). Al, Pb, and Cd contents have been determined using a carbon rod atomizer in AAS (Mandic, Grgic, & Seruga, 1992). The concentrations of four heavy metals (Pb, Cd, Hg, and Cu) in 149 samples of mushroom fruit bodies, representing 11 species, mainly edible ones, have been determined by AAS (Kalac, Burda, & Staskova, 1991). Al, Cu, Mn, Fe, and Zn have been analyzed after dry-ashing and digestion in HCl by flame AAS (Kojo & Lodenius, 1989).

The present study relates to the determination of metal ions (Pb, Cd, Hg, Cu, Mn, Zn, Fe, Co, As, Ca, Na, K, Mg, Ba, Ni, Ti, Cr, Al, Bi, Sb, and Ag) concentrations of mushrooms growing in the East Black Sea region.

2. Materials and methods

In this study, 108 samples of wild-growing mushrooms, corresponding to 18 different species, were used. The samples of uncultivated mushroom were collected from the Eastern Black Sea region in Turkey. Species include *Agaricus bisporus, Agaricus silvicola, Amanita muscaria, Amanita rubescens, Amanita vaginata, Boletus* sp., *Hydnum repandum, Hypholoma fasciculare, Laccaria lacceta, Lactarius piperatus, Lactarius* sp., *Lactarius volemus, Pleurotus ostreatus, Russula cyanoxantha, Russula* sp., *Russula delica, Russula foetens* and *Tricholoma terreum*.

Before digestion, the samples were washed with demineralized water. Each sample was dried at 50 °C overnight and crushed in a mortar with achate beaker and pestle.

For recovery of Pb, Cd, Hg, Cu, Mn, Zn, Fe, Co, As, Ca, Na, K, Mg, Ba, Ni, Ti, Cr, Al, Bi, Sb, and Ag the mushroom samples were digested using an oxi-acidic mixture of HNO_3:H_2SO_4:H_2O_2 (4:1:1; 12 ml for 2–4 g sample) and heating at 75 °C for 3 h. After cooling, 20 ml demineralized water was added, the digest was again heated up to 150 °C for 4 h and brought to a volume of 25 ml with demineralized water.

For analysis of mercury, the technique described was as follows: 0.5 g was taken from the dried homogenized sample and its digestion was carried out using 7 ml of a HNO_3:H_2SO_4:H_2O_2 acid mixture at a ratio of 4:1:1; digestion was done at 60 °C in a thermostatic bath, being completed in about 1.5 h. For oxidation of the sample, a solution of potassium permanganate was reduced with a solution of hydroxylamine sulfate (Demirbaş, 2000b).

Metal ion concentrations were determined as three replicates by Pye Unicam SP-9 AAS. A flame photometer (Biotechnical Instruments, Model 8T 624D) was used for determinations of alkali and earth-alkali metals. To eliminate the errors derived from matrix effect, the standard addition method was used instead of plotting a calibration curve. To apply the standard addition technique, 25 g of mushroom sample were taken and 1 ml of heavy metal working solution was added, which contained a determined amount of the metal ion. Standard added sample was analyzed in the same way as the one without standard addition. The number of replicates were also three for standard added samples. Before applying the standard addition technique, a calibration curve was obtained to see the linear relationship between absorbance and lead concentration in the concentration range being worked.

Pb and Cd levels in the mushroom samples were determined using a GBC 3000 graphite furnace for AAS. For the determination of Pb and Cd contents,

Table 1
Average concentrations (mg/kg, dry weight basis) of heavy metals (Pb, Cd, Hg, Cu, Mn, Zn, and Fe) in mushroom samples

Species no.	Pb	Cd	Hg	Cu	Mn	Zn	Fe
1	2.41±0.83	3.48±0.58	0.60±0.32	5.22±0.72	22.3±4.7	17.8±5.8	126±14
2	0.92±0.37	1.04±0.18	0.15±0.04	6.24±2.81	3.0±1.24	25.6±7.6	59.3±6.1
3	1.43±0.56	1.60±0.59	0.18±0.04	23.5±5.1	36.4±6.5	28.1±8.4	148±20
4	0.71±0.30	0.79±0.43	0.23±0.07	51.2±9.6	11.1±2.0	17.2±6.3	68.4±8.8
5	0.12±0.04	0.56±0.22	0.32±0.18	5.11±0.67	10.5±2.1	19.6±5.5	58.1±12.6
6	6.88±2.85	1.36±0.41	0.48±0.26	11.5±3.5	12.6±2.4	19.6±7.2	68.4±6.8
7	0.38±0.22	0.76±0.24	0.10±0.03	6.84±2.55	3.12±1.60	14.1±6.32	33.5±3.6
8	1.42±0.45	1.28±0.51	0.48±0.06	72.6±14.7	44.8±15.1	65.4±22.3	423±87
9	1.95±0.92	2.14±0.32	0.39±0.18	92.5±14.1	56.2±12.4	70.0±9.8	596±46
10	0.92±0.27	1.08±0.16	0.42±0.08	16.8±4.5	7.6±1.8	29.4±6.1	145±11.3
11	1.62±0.54	2.05±0.41	0.58±0.16	54.0±10.2	36.7±7.0	176±31.6	242±25
12	3.52±1.15	0.88±0.33	0.54±0.12	18.1±4.8	7.92±2.33	25.4±6.9	141±28
13	3.24±1.28	1.18±0.36	0.42±0.14	13.6±2.9	6.27±2.12	29.8±7.4	86.1±10.5
14	1.40±0.42	1.26±0.18	0.13±0.04	18.9±5.6	5.42±1.98	21.7±5.8	63.2±7.4
15	2.05±0.76	3.16±0.72	0.14±0.05	19.1±5.2	12.6±2.5	26.1±7.1	56.8±8.7
16	3.15±1.32	1.14±0.28	0.24±0.06	13.6±4.0	6.62±1.81	32.6±8.5	74.8±6.5
17	4.91±1.83	2.04±0.37	0.22±0.08	11.0±3.7	12.3±2.3	19.6±5.3	62.0±7.8
18	2.43±0.78	1.67±0.61	0.06±0.02	35.8±6.9	24.8±5.2	48.0±9.3	169±22.6

Table 2
Average concentrations (mg/kg, dry weight basis) of metals (Co, As, Ca, Na, K, Mg and Ba) in mushroom samples

Species no.	Co	As	Ca	Na	K	Mg	Ba
1	0.32±0.09	0.76±0.19	74.5±22.6	96.3±52.7	35000±12000	1200±360	1.62±0.42
2	0.28±0.15	1.25±0.26	81.6±26.4	103±56.1	42000±14000	980±310	1.16±0.22
3	0.21±0.06	0.68±0.23	77.3±24.1	112±59.2	38000±13000	1100±340	0.86±0.19
4	0.35±0.09	0.96±0.26	55.9±18.5	85.7±42.3	32000±11000	1050±330	0.74±0.16
5	0.72±0.29	0.59±0.14	92.0±32.4	120.8±66.9	48000±20000	1300±400	1.44±0.32
6	0.17±0.06	1.41±0.30	76.3±20.0	108±60.1	41000±15000	1150±350	1.58±0.44
7	0.10±0.03	0.41±0.12	68.5±17.4	92.6±45.0	36000±12000	1030±370	1.23±0.26
8	0.18±0.05	0.77±0.28	102.7±35.5	136±71.0	50000±24000	1320±450	0.93±0.24
9	0.55±0.14	1.76±0.29	73.6±21.8	88.4±42.7	39000±16000	910±280	0.64±0.15
10	0.61±0.26	2.09±0.38	78.6±22.4	75.0±38.9	28000±10000	850±260	0.72±0.18
11	0.48±0.12	2.34±0.58	59.2±19.6	94.0±48.2	37000±12000	1140±380	1.24±0.36
12	0.36±0.13	0.88±0.22	75.8±19.0	95.6±46.1	40000±13000	960±320	0.78±0.16
13	0.42±0.11	1.39±0.40	106±36.0	133±68.0	51000±25000	1280±410	0.65±0.18
14	0.35±0.16	1.30±0.36	86.3±26.9	110±52.8	46000±16000	1160±390	0.93±0.21
15	0.23±0.06	1.15±0.32	88.6±28.0	90.5±46.2	43000±15000	940±290	1.48±0.41
16	0.25±0.12	0.61±0.16	72.8±23.5	82.9±44.0	34000±12000	1060±360	0.68±0.13
17	0.16±0.08	1.23±0.38	94.6±33.0	87.2±49.4	44000±16000	1120±390	0.96±0.21
18	0.27±0.13	0.90±0.30	82.7±24.6	98.4±51.0	45000±17000	1240±400	0.75±0.18

Table 3
Average concentrations (mg/kg, dry weight basis) of metals (Ni, Ti, Cr, Al, Bi, Sb, and Ag) in mushroom samples

Species no.	Ni	Ti	Cr	Al	Bi	Sb	Ag
1	56.1±12.6	278±45	0.84±0.16	17.2±3.5	1.84±0.35	0.14±0.05	0.36±0.08
2	44.6±11.9	192±36	0.75±0.14	15.8±3.1	1.58±0.32	0.16±0.06	0.28±0.06
3	78.3±18.4	236±40	0.82±0.15	16.2±3.3	0.94±0.21	0.15±0.05	0.30±0.07
4	95.8±24.6	173±33	0.71±0.13	18.0±3.6	1.24±0.28	0.18±0.07	0.32±0.07
5	83.6±22.0	186±34	0.78±0.14	14.8±3.0	1.12±0.26	0.13±0.05	0.26±0.06
6	65.0±14.8	214±38	0.86±0.16	16.8±3.4	0.96±0.20	0.19±0.08	0.34±0.07
7	58.3±13.7	188±30	1.68±0.12	12.5±2.8	0.86±0.16	0.12±0.04	0.25±0.07
8	72.4±16.9	210±36	0.74±0.14	17.5±3.2	1.32±0.30	0.18±0.08	0.35±0.08
9	127±34.0	160±27	1.55±0.20	22.4±4.1	1.34±0.32	0.10±0.03	0.18±0.04
10	68.1±15.5	282±46	1.08±0.20	9.8±2.3	0.47±0.10	0.21±0.08	0.24±0.05
11	86.4±17.2	223±39	0.95±0.17	17.8±3.6	0.76±0.18	0.13±0.06	0.37±0.11
12	111±31.6	198±32	0.92±0.16	19.2±3.7	0.88±0.19	0.24±0.09	0.33±0.07
13	145±36.5	248±42	0.77±0.15	20.6±4.0	0.52±0.11	0.15±0.04	0.22±0.05
14	92.8±23.7	180±29	1.66±0.21	21.0±4.2	0.70±0.17	0.09±0.03	0.21±0.05
15	53.8±12.0	226±38	0.98±0.18	24.1±4.6	0.82±0.18	0.20±0.08	0.17±0.04
16	116±32.0	175±28	0.88±0.17	23.6±4.5	0.56±0.12	0.26±0.09	0.19±0.05
17	76.4±17.0	191±30	1.12±0.21	16.6±3.5	0.92±0.19	0.22±0.08	0.20±0.06
18	94.1±24.0	240±42	0.60±0.10	19.5±3.8	0.74±0.16	0.23±0.08	0.15±0.03

deuterium and Smith–Hieftje background correction have been used. The standard-addition procedure was used in all determinations.

3. Results and discussion

The average concentrations of the metals and heavy metals of the 18 selected species of uncultivated mushrooms are given in Tables 1, 2 and 3.

Toxic metals studied in the experiments are Cd, Pb, Hg, Cu, As, Al, Ag, Ni, Bi, and Sb. In aquatic systems, uptake of metal is influenced by various environmental factors such as temperature, salinity, pH, and the presence of organic matter (Gast et al., 1988).

From Tables 1, 2, and 3, in the mushrooms supplied from the East Black Sea region, the highest metal concentrations were measured as 4.91, 3.48, 0.60, 92.5, 44.4, 176, 169, 0.72, 1.76, 106, 136, 51 000, 1320, 1.62, 145, 282, 1.68, 24.1, 1.84, 0.26, and 0.37 mg/kg (dry weight basis) for Pb, Cd, Hg, Cu, Mn, Zn, Fe, Co, As, Ca, Na, K, Mg, Ba, Ni, Ti, Cr, Al, Bi, Sb, and Ag in *Russula foetens, Agaricus bisporus, Agaricus bisporus, Hypholoma fasciculare, Hydnum repandum, Lactarius* sp., *Tricholoma terreum, Amanita vaginata, Laccaria lacceta, Pleurotus ostreatus, Hypholoma fasciculare, Pleurotus*

ostreatus, Hypholoma fasciculare, Agaricus bisporus, Pleurotus ostreatus, Lactarius piperatus, Hydnum repandum, Russula sp., *Agaricus bisporus, Russula delica*, and*Lactarius* sp., respectively.

Cadmium is known as a principal toxic element, since it inhibits many life processes (Vetter, 1987, 1989, 1993). It can be taken up directly from water, and to some extent from air and via food, and it has a tendency to accumulate in both plants and animals. Mushrooms, in particular, can be very rich in cadmium. Cadmium is a byproduct in the production of zinc and lead, and the pyrometallurgical production of zinc is the most important anthropogenic source into the environment. Other major sources are fossil fuel combustion and waste incineration. Cadmium accumulation has been demonstrated by Schmitt and Meisch (1985). From the fruit bodies of *Agaricus macrosporus*, a cadmium-binding phospho-glycoprotein, cadmium mycophosphatin, was isolated (Schmitt & Meisch, 1985). This protein has a molecular weight of 12 000 daltons, contains phosphorus, but not sulfur, and contains glucose and galactose. Another group of mycologists has analyzed taxonomic groups/species with a higher cadmium content and, in general, the phenomenon of its accumulation (Kojo & Lodenius, 1989; Santoprete & Innocenti, 1984; Stijve & Besson, 1976; Vetter, 1987).

Lead is especially toxic to the growing brain and can affect the behavioural development of the young, even at low concentrations. For example, in polluted cities, fumes from cars burning leaded gasoline have probably caused air concentrations high enough to affect children's development. Lead can pass through the placenta and thus affect a growing foetus. Organic lead compounds are fat-soluble and are more toxic than other forms. Lead contamination varies and manifests itself in other ways than in the green plants. Lead-accumulating species of fungi are not known; the lead concentration of the analyzed mushroom species and the samples was 0.1–40 ppm (Laaksovirta & Alakuijala, 1978; Seeger, Meyer, & Schönut, 1976). Imported lead contaminants were registered in some urban fungi samples from England (Thomas, 1992). Beside busy streets the concentrations were so high that the fungi could not be recommended for food use (Laaksorvirta & Alakuijala, 1978).

Many studies support a connection between mercury levels and the concentration of humic matter. The mean mercury level in macrofungi surpasses, by two orders of magnitude, that in green plants (green plants: 0.015 ppm; macrofungi: 1–1.5 ppm) and varies according to the type of fungi, since litter-decomposing species (*Agaricus, Marasmius*) have higher mercury concentrations (0.1–72 ppm) than the wood-destroying species and genera (1.5–2.0 ppm) (Laaksovirta & Lodenius, 1979).

The copper content in macrofungi is significantly higher than that of the green plants (the average of Hungarian fungi samples amounts to 44–48 ppm; Vetter, 1987). This toxic metal is accumulated by the genera *Macrolepiota* and *Agaricus*.

The average arsenic content was 1.6 ppm (Vetter, 1987) on the basis of 80 mushroom samples, but in certain taxonomic groups (e.g. the genus *Agaricus* and the family *Tricholomataceae*), a significant bioaccumulation was shown (*Agarigus augustus*: 11.9 ppm; *Macrolepiota rhacodes*: 26.6 ppm; Vetter, 1990). The extremely high arsenic concentrations of *Laccaria* species (mainly *L. Amethystina* and *L. Fraterna*) has been measured as 260 ppm (Stijve, Vellinga, & Herrmann, 1990). An extreme arsenic level (360–2130 ppm) was reported in *Sacosphaera* coronaria (*Ascomycetes*), but nothing is known of the mode of action for accumulation.

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