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# Accumulation of heavy metals in some edible mushrooms from Turkey

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**Abstract**

Four heavy metal (Hg, Pb, Cd, and Cu) contents bioaccumulated by six different species of edible mushrooms (*Laccaria laccata*, *Agaricus bitorquis*, *Tricholoma terreum*, *Agaricus silvicolla*, *Hydnum repandum* and *Russula delica*) of Turkish origin were analyzed by atomic absorption spectrometry. The natural levels of Hg (II), Pb (II), Cd (II), and Cu (II) were determined in concentrations of mg metal ion/kg dry, weight. The soils were fortified in situ with the four heavy inetals in concentrations of 0.35–11, 0.40–70, 0.21–8.45, and 0.55–32.5 ing metal ion/kg dry weight for Hg (II), Pb (II), Cd (II), and Cu (II), respectively. The highest metal levels were: 6.79 mg/kg Hg in *Hydnum repandum*, 6.87 mg/kg Pb in *Russula delica*, 16.8 mg/kg Cd in *Agaricus silvicolla*, and 66.4 mg/kg Cu in *Tricholoma terreum* on a dry-weight-basis. 

## 1. Introduction

Turkey has a large edible mushroom potential and is becoming an important exporter of wild mushrooms. However, the qualified studies have not been carried out dealing with this area in Turkey. In earlier work we have studied some heavy metals in cultivated and uncultivated mushrooms of Turkish origin (Tüzen, Özdemir & Demirbas, 1998a,b). In recent years, considerable attention has been focused on the bioaccumulation of heavy metals in fruit bodies of some cultivated mushrooms (Falandyzs, Bona & Danisievicz, 1994; Lepsova & Mejstrik, 1988; Liukkonen-Lilja, Kuusi, Laaksovirta, Lodenius & Piepponen, 1983). It is well-known that all such cultivated mushrooms have the ability of bioaccumulation of metal ions (Falandyzs et al., 1994). There have been reports of toxic elements, especially cadmium, mercury, selenium, lead, vanadium, copper and arsenic in different species of mushrooms (Lepsova & Mejstrik, 1988; Liukkonen-Lilja et al., 1983;, Mandic, Grgic & Seruga, 1992; Piepponen, Liukkonen-Lilja & Kussi, 1983; Vetter, 1993; Zurera-Cosano, Rincon-Leon, Arcos, & Pozo, 1986; Zurera-Cosano, Rincon-Leon, Moreno-Rojas, Salmeron-Egea & Pozo-Lora, 1988). As these metals are well-known for their toxicity at low concentrations, a great deal of effort has been made to evaluate the possible danger to human health from the ingestion of mushrooms (Gast, Jansen, Bierling & Haanstra, 1988).

The present study relates to the determination of mercury, lead, cadmium, and copper, by using AAS, accumulation by the fruit body of uncultivated edible mushrooms growing on soils containing the heavy metals at different concentrations.

## 2. Materials and methods

In this study, 24 samples of edible mushrooms corresponding to different species were used. In the experiments, mercury, lead, cadmium, and copper bioaccumulations of the fruit bodies of the edible mushrooms were determined. Samples of mushroom *Laccaria laccata*, *Agaricus bitorquis*, and *Tricholoma terreum* from Söğütlü and *Agaricus silvicolla* and *Hydmum repandum* from Yeşilyurt forestries and *Russula delica* from the Trabzon-Yomra highway, were collected. The water content of the materials was about 65%. The sods were fortified in situ with the four heavy metals in concentrations of 0.35–11, 0.40–70.2, 0.21–8.45, and 0.55–32.5 mg metal ionlkg dry weight for Hg (II), Pb (II), Cd (II), and Cu (II), respectively. The fruit bodies of mushrooms, which appeared in batches at several day intervals for up to 4 weeks, were collected separately within the consecutive crops. These samples were washed with demineralized water. Each sample was dried at 50°C overnight and crushed in a mortar.

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Digestion of mushroom samples was performed 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 heated on 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 was as follows. One half gram was taken from the dried homogenized sample and 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 at 60°C in a thermostatic bath, being completed in about 1.5 h. For oxidation of the sample, a solution of potassium permanganate at 6%, w/v, was used. The excess of permanganate was reduced with a solution of hydroxylamine sulfate (Tüzen et al., 1998a,b).

Mercury levels in the samples were determined by cold vapour AAS (Rincon-Leon & Zurera-Cosano, 1986). The determinations of mercury contents were carried out with a Pye Unicam SP9 series AAS, equipped with a cold vapour system and a mercury hollow cathode lamp, adjusted to 253.7 nm and fitted to the Pye Unicam mercury/hydride system, using 3%, w/v sodium borohydride in 1%, w/v, NaOH as a reducing solution. The analysis was done under the following conditions: wavelength 253.7 nm; slit 0.7 nm; carrier gas (purified $N_2$) pressure 2.5 kg/cm$^2$ and carrier gas flow rate 1100 ml/min.

Lead and cadmium levels in the mushroom samples were determined using a GBC 3000 graphite furnace on AAS. Determination of copper contents have been carried out with a GBC 905 model AAS using flame atomization. For the determination of lead and cadmium contents, deuterium and Smith-Hieftje background correction have been used. The standard-addition procedure was used in all determinations.

The wavelength and slit values (as nm) used for the determination of lead, cadmium, and copper were: 283.3 and 0.5, 228.8 and 0.5, 324.7 and 0.5, respectively.

## 3. Results and discussion

The heavy metal concentrations (as mg/kg) of the soil and the edible mushroom samples are given in Tables 1–3. From Table 1, in the mushrooms selected from Söğütlü forestries, the highest mercury content was 5.63 mg/kg for the species of *Agaricus bitorquis*. The highest values for mercury were 5.63 mg/kg for *Agaricus silvicolla*, obtained from Yeşilyurt (Table 2) and 7.0 mg/kg for *Russula delica* from the Trabzon-Yomra highway (Table 3).

From Table 1, the levels of lead in the samples obtained from Söğütlü forestries as a whole ranged from 0.462 to 0.996 mg/kg. In the mushrooms taken from the Yeşilyurt district, the highest lead was 1.38 for *Hydnum repandum* (Table 2). In the samples selected near the Trabzon-Yomra highway, the highest lead concentration was found to be 6.87 mg/kg for *Russula delica* (Table 3).

In the wild mushrooms from Söğütlü forestries the highest cadmium content was found as 16.9 mg/kg *Agaricus bitorquis* (Table 1). The highest values for

Table 1
Average concentrations (mg/kg, dry-weight basis) of heavy metal (Hg, Pb, Cd and Cu) of soil and mushroom (*L. laccata*, *A. bitorquis*, and *T. terreum*) samples obtained from Söğütlü forestry

| Mushroom sample | Metal concentration of soil | | | | Metal concentration of mushroom | | | |
|---|---|---|---|---|---|---|---|---|
| | Hg | Pb | Cd | Cu | Hg | Pb | Cd | Cu |
| *Laccaria laccata* | 0.513 | 0.820 | 0.268 | 0.546 | 0.084 | 0.686 | 1.07 | 12.9 |
| | 1.21 | 1.65 | 0.866 | 1.27 | 0.172 | 0.715 | 1.58 | 23.3 |
| | 1.84 | 2.83 | 1.86 | 3.03 | 0.243 | 0.954 | 3.44 | 47.9 |
| | 3.76 | 3.48 | 2.61 | 5.68 | 0.942 | 0.996 | 9.65 | 58.9 |
| | 6.10 | 6.37 | 3.51 | 14.6 | 0.864 | 0.762 | 6.48 | 60.6 |
| | 10.6 | 12.2 | 7.86 | 32.7 | 0.194 | 0.520 | 1.18 | 44.9 |
| *Agaricus bitorquis* | 0.547 | 0.864 | 0.214 | 0.604 | 0.034 | 0.490 | 0.750 | 10.3 |
| | 1.24 | 1.86 | 0.780 | 1.46 | 0.982 | 0.516 | 5.17 | 35.4 |
| | 2.04 | 2.92 | 1.65 | 3.25 | 2.5 | 0.886 | 9.15 | 47.3 |
| | 3.61 | 3.45 | 2.59 | 5.67 | 5.63 | 0.990 | 16.9 | 64.6 |
| | 6.11 | 6.33 | 3.9 | 13.9 | 4.65 | 0.810 | 12.6 | 66.2 |
| | 10.5 | 12.2 | 8.18 | 32.7 | 0.372 | 0.568 | 0.876 | 49.4 |
| *Tricholoma terreum* | 0.525 | 0.850 | 0.231 | 0.577 | 0.056 | 0.462 | 0.615 | 13.9 |
| | 1.23 | 1.78 | 0.812 | 1.39 | 0.217 | 0.586 | 0.785 | 38.7 |
| | 1.95 | 2.78 | 1.71 | 3.17 | 0.674 | 0.701 | 1.53 | 51.9 |
| | 3.65 | 3.46 | 2.60 | 5.66 | 1.66 | 0.950 | 4.56 | 71.1 |
| | 6.12 | 6.34 | 3.48 | 14.4 | 1.24 | 0.612 | 3.15 | 66.4 |
| | 10.5 | 12.2 | 7.98 | 32.7 | 0.128 | 0.540 | 0.546 | 45.8 |

Table 2
Average concentrations (mg/kg, dry-weight basis) of heavy metal (Hg, Pb, Cd and Cu) of soil and mushroom (*A. silvicolla* and *H. repandum*) samples obtained from Yeşilyurt forestry

| Mushroom sample | Metal concentration of soil | | | | Metal concentration of mushroom | | | |
|---|---|---|---|---|---|---|---|---|
| | Hg | Pb | Cd | Cu | Hg | Pb | Cd | Cu |
| *Agaricus silvicolla* | 0.346 | 0.378 | 0.212 | 0.576 | 0.028 | 0.410 | 0.671 | 10.3 |
| | 0.896 | 0.654 | 0.412 | 1.24 | 0.948 | 0.486 | 4.97 | 35.4 |
| | 1.24 | 1.08 | 0.724 | 3.27 | 2.38 | 0.880 | 9.14 | 47.4 |
| | 2.81 | 2.44 | 2.11 | 8.41 | 5.62 | 0.968 | 16.8 | 64.4 |
| | 6.08 | 5.85 | 4.37 | 18.0 | 4.87 | 0.811 | 12.3 | 66.2 |
| | 11.0 | 9.85 | 7.66 | 30.2 | 0.379 | 0.610 | 0.954 | 49.4 |
| *Hydnum repandum* | 0.418 | 0.463 | 0.233 | 0.675 | 0.076 | 0.453 | 0.124 | 5.15 |
| | 0.911 | 0.952 | 0.389 | 1.65 | 2.45 | 0.614 | 3.42 | 19.0 |
| | 1.41 | 1.28 | 0.750 | 4.8 | 4.82 | 0.912 | 7.45 | 33.4 |
| | 3.22 | 2.84 | 2.32 | 9.81 | 6.79 | 1.38 | 5.43 | 51.1 |
| | 5.67 | 6.01 | 5.78 | 20.2 | 3.46 | 0.781 | 3.12 | 55.1 |
| | 11.0 | 11.1 | 8.5 | 32.5 | 0.484 | 0.506 | 0.617 | 39.0 |

Table 3
Average concentrations (mg/kg, dry-weight basis) of heavy metal (Hg, Pb, Cd and Cu) of soil and mushroom (*R. delica*) samples obtained from Trabzon-Yomra highway

| Mushroom sample | Metal concentration of soil | | | | Metal concentration of mushroom | | | |
|---|---|---|---|---|---|---|---|---|
| | Hg | Pb | Cd | Cu | Hg | Pb | Cd | Cu |
| *Russula delica* | 0.422 | 2.42 | 0.189 | 0.514 | 0.121 | 0.865 | 0.654 | 10.8 |
| | 0.917 | 4.89 | 0.348 | 2.05 | 2.34 | 1.25 | 2.02 | 19.8 |
| | 1.57 | 6.37 | 0.760 | 4.21 | 4.27 | 2.35 | 4.31 | 30.9 |
| | 2.87 | 21.7 | 2.34 | 9.88 | 7.09 | 6.87 | 7.85 | 45.6 |
| | 6.04 | 35.7 | 4.88 | 17.5 | 36.2 | 5.56 | 4.02 | 52.1 |
| | 10.2 | 70.2 | 7.77 | 28.5 | 0.340 | 4.89 | 0.564 | 43.5 |

cadmium were in *Agaricus silvicolla* from Yeşilyurt (Table 2) and in *Russula delica* (Table 3) from the Trabzon-Yomra highway, 16.8 and 7.85 mg/kg, respectively.

In the wild mushroom samples, the highest copper content was 71.1 mg/kg for of *Tricholoma terreum*, whereas the lowest copper content was 5.15 mg/kg in *Hydnum repandum* (Table 2).

Hg and Cd contents of the mushrooms generally increased sharply with increasing Hg and Cd concentrations in the soils. In general, the mushrooms bioaccumulated low amounts of Hg, Pb and Cd; any higher concentrations of those metals showed a phytotoxical effect, causing a lower yield. It appears that the mushrooms take up the heavy metals readily. This might cause a threat to health of consumers and demand soil remediation programs.

The results obtained show that the content of mercury differs according to species analyzed and anatomical groups. In a previous study (Zurera-Cosano et al., 1986), there were found to be significant differences between species although not between anatomical groups. The significance of the species factor in the capacity for concentration of heavy metals has been pointed out by other authors (Bowen, 1966; Crowley, 1978; Hopwood, 1975). According to Stijve and Besson (1976), the mechanism by which some heavy metals are accumulated is somewhat obscure although it seems to be associated with a chelation reaction with the sulfhydryl groups of protein and especially with methionine. However, these same authors found very low levels of lead, cadmium and mercury in samples of *Psalliota bispora* cultivated with a high content of methionine in relation to other species.

The fact that toxic metals are present in high concentrations in the fruiting bodies of both edible and inedible fungi from an area greatly favoured by mushroom pickers is of particular importance in relation to the FAO/WHO Standards (1976) for lead and cadmium as toxic metals. The maximum permissible dose for an adult is 3 mg lead and 0.5 mg cadmium per week, but the recommended doses are only one-fiftieth of those quantities.

Gast et al. (1988) investigated the uptake of cadmium, copper, lead, and zinc in mushrooms and their relationship with soil characteristics. In Tables 1–3, the content of mercury increased with increasing mercury concentration in the soil, but the increase is less distinct than that of the cadmium content. The cadmium contents of the mushrooms increase sharply with increasing

Table 4
Average natural concentrations (mg/kg, dry-weight basis) of Hg, Pb, Cd, and Cu of soil samples obtained from the zones given in Tables 1–3

| Soil sample | Hg | Pb | Cd | Cu |
|---|---|---|---|---|
| Söğütlü forestry | 0.084 ± 0.035[a] | 0.513 ± 0.126 | 0.153 ± 0.041 | 0.412 ± 0.056 |
| Yeşilyurt forestry | 0.072 ± 0.024 | 0.261 ± 0.078 | 0.138 ± 0.029 | 0.467 ± 0.070 |
| Trabzon-Yomra highway | 0.091 ± 0.018 | 2.382 ± 0.678 | 0.112 ± 0.024 | 0.376 ± 0.064 |

[a] Standard deviation for three separate determinations.

Table 5
Average natural concentrations (mg/kg, dry-weight basis) of Hg, Pb, Cd, and Cu of mushrooms obtained from the zones given in Tables 1–3

| Mushroom sample | Hg | Pb | Cd | Cu |
|---|---|---|---|---|
| *Laccaria laccata* | 0.072 ± 0.030[a] | 0.865 ± 0.214 | 0.655 ± 0.162 | 12.9 ± 4.534 |
| *Agaricus bitorquis* | 0.142 ± 0.048 | 1.34 ± 0.352 | 2.17 ± 0.446 | 26.4 ± 7.163 |
| *Tricholoma terreum* | 0.096 ± 0.039 | 0.008 ± 0.002 | 0.756 ± 0.182 | 42.5 ± 9.606 |
| *Agaricus silvicolla* | 0.106 ± 0.041 | 0.418 ± 0.132 | 4.15 ± 0.891 | 4.86 ± 1.692 |
| *Hydnum repandum* | 0.285 ± 0.087 | 2.36 ± 0.585 | 3.08 ± 1.368 | 18.9 ± 5.620 |
| *Russula delica* | 0.164 ± 0.056 | 3.89 ± 0.946 | 1.68 ± 0.362 | 8.47 ± 3.427 |

[a] Standard deviation for three separate determinations.

cadmium concentration in the soil. However, the lead contents in the mushrooms do not differ significantly in the same way. In general, lead, cadmium, and mercury concentrations accumulated by the mushrooms were low; any higher concentrations of those metals show a pyhtotoxical effect and consequently lower the yield. Lower concentrations of copper were accumulated to some extent by the mushrooms; on the other hand, higher concentrations of copper reached an equilibrium and remained constant.

Agreement of the results were verified by UV vis spectrophotometric methods of AOAC (Horwitz, 1970). The results obtained from AA and UV vis spectrophotometric methods were compared, and agreement was found as average ±6%.

Table 4 shows the average natural concentrations (mg/kg, dry-weight basis) of Hg, Pb, Cd, and Cu of soil samples obtained from the zones given in Tables 1–3. Table 5 shows the average natural concentrations (mg/kg, dry-weight basis) of Hg, Pb, Cd, and Cu of mushroom samples obtained from the zones given in Tables 1–3. In the samples selected near the Trabzon-Yomra highway, the highest lead concentration was found 3.89 mg/kg for the species of *Russula delica* (Table 5). The results of sampling in polluted and relatively unpolluted zones are reflected in a wide range of concentrations found in mushrooms and accessory soil samples. Cd and Pb concentrations heavily depend on the type of species. For example, *Agaricus silvicolla* has a consistently high level of Cd (4.15 mg/kg) and *Laccaria laccata* on the other hand, has a low value of 0.655 mg/kg. *Russula delica* has a high level of Pb (3.89 mg/kg) and *Tricholoma terreum* has a low value of 0.008 mg/kg.

## References


Bowen, H. J. M. (1966). *Trace elements in biochemistry*. New York: Academic Press.

Crowley, M. K. (1978). *Atomic absorption spectrometry in food analysis*. New York: Academic Press.

Falandyzs, L., Bona, H., & Danisievicz, D. (1994). Silver uptake by *Agaricus bisporus* from an artifically enriched substrate. *Z. Lebensm Unters Forsch., 199*, 225–228.

FAO/WHO Standards (1976). List of maximum levels recommended for contaminants by the Joint FAO/WHO Codex Alimentarius Commission. Second Series. CACIFAL, Rome, 3, 1–8.

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.

Hopwood, R. (1975). *Advanced food science*. London: G.Bell and Sons Ltd.

Horwitz, W. (Ed.) (1970). *Official methods of analysis of the association of official analytical chemist's*. Washington, DC.

Lepsova, A., & Mejestrik, V. (1988). Accumulation of trace elements in fruiting bodies of macrofungi in the Krusne Hory Mountains. Czecholovakia. *Science of the Total Environment, 76*, 117–128.

Liukkonen-Uja, H., Kuusi, T., Laaksovirta, K., Lodenius, M., & Piepponen, S. (1983). The effect of lead processing works on the lead, cadmium and mercury contents of fungi. *Z. Lebensm. Unters. Forsch., 176*, 120–123.

Mandic, M. L., Grgic, J. Z., & Seruga, M. (1992). The natural levels of aluminum, cadmium and lead in wildlife mushrooms in Eastern Croatia. *Deutsche Lebensmittel-Rundschau, 88*(3), 76–77.

Piepponen, S., Liukkonen-Lilja, H., & Kuusi, T. (1983). The selenium content of edible mushrooms in Finland. *Z. Lebensm Unters Forsh, 177*, 257–260.

Rincon-Leon, F., & Zurera-Cosano, G. (1986). Flameless atomic absorption spectrophotometric determination of mercury in mushroom samples, using a mercury/hydride system. *Atomic Spectroscopy, 7*, 789–799.

Stijve, T., & Besson, R. (1976). Mercury, cadmium lead and selenium content of mushroom species belonging to the genus. *Agaricus Chemosphere, 2*, 151–158.

Tüzen, M., Özdemir, M., & Demirbas, A. (1998a). Study of heavy metals in some cultivated and uncultivated mushrooms of Turkish origin. *Food Chemistry, 63*, 247–251.

Tüzen, M., Özdemir, M., & Demirbas, A. (1998b). Heavy metal simulation by cultivated *Agarcus bisporus* from artificially enriched substrates. *Z. Lebensm Unters Forsh., 206*, 417–419.

Veter, J. (1993). Toxic elements in certain higher fungi. *Food Chemistry, 48*, 207–208.

Zurera-Cosano, G., Rincon-Leon, F., Arcos, F., & Pozo, R. (1986). Mercury content in mushroom species in the Cordava area. *Bull. Environ. Contam. Toxicol., 36*, 662–667.

Zurera-Cosano, G., Rincon-Leon, F., Moreno-Rojas, R., Salmeron-Egea, J., & Pozo-Lora, R. (1988). Mercury content in different species of mushroom grown in Spain. *Journal of Food Protection, 51*(3), 205–207.