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Food Chemistry 78 (2002) 89–93

Food Chemistry

www.elsevier.com/locate/foodchem

Metal ion uptake by mushrooms from natural and artificially enriched soils

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Received 10 October 2001; accepted 26 November 2001

Abstract

The metal bioaccumulation levels of three mushrooms were studied. Three different species of wild mushrooms growing in the East Black Sea region were analyzed spectrometrically for their trace element (Pb, Cd, Hg, Cu, Mn, and Zn) levels. Heavy metal (Hg, Pb, Cd and Cu) bioaccumulation levels of three mushrooms (*Armillaria mellea, Polyporus squamosus, Polyporus suiphureus*) samples obtained from the East Black Sea region were investigated. The Hg^{+2} level of *Armillaria mellea* samples increases sharply with increasing Hg^{+2} concentration in the fortified soil samples. The highest Hg^{+2} level was 2.65 mg/kg for *A. mellea,* whereas the lowest Hg^{+2} level was 1.45 mg/kg in *P. squamosus*. Cd^{+2} level increased with increasing Cd^{+2} concentration in the soil samples. The Hg content of *A. mellea* samples increased sharply with increasing Hg concentration in the fortified soil samples. The Cd content also increased with increasing Cd concentration in the soil samples, but the increase was less distinct than that of the Pb content. However, the Pb contents in mushrooms do not change significantly, despite increasing Pb content in the fortified soil.

Keywords: Metal ion; Bioaccumulation; Mushroom; Fortified soil

1. Introduction

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 with mild temperatures. The climate, especially, in spring and autumn, is ideal for flingal growth.

Numerous studies have carried out on the heavy metal contents of mushrooms in Turkey (Demirbaş, 2000a, 2001a, 2001b; Sesli & Tüzen, 1999; Tüzen, Özdemir, & Demirbaş, 1998a, 1998b; Tüzen, Sesli, & Demirbaş, 1999) 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, 1998; Liukkonen-Lilja, Kuusi, Laaksovirta, Lodenius, & Piepponen, 1983; Vetter, 1993). It is well known that all such cultivated mushrooms show bioaccumulation of metal ions (Falandyzs et al., 1994).

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). This would suggest that fungi possess a very effective mechanism that enables them to take up some trace elements from the substrate (Lepsova & Mejstrik, 1998).

In general, their fruiting bodies, on a dry weight basis, contain about 56.8% carbohydrate, 25.0% protein, 5.7% fats and 12.5% ash (Latiff, Daran, & Mohamed, 1996). There have been a few reports on the elemental (mainly metals) analysis of some species of edible mushrooms and, among them, is the study of heavy metal accumulator or/collectors in the species (Demirbaş, 2001a; Falandyzs et al., 1994; Lepsova & Mejstrik, 1998; Liukkonen-Lilja et al., 1983; Vetter, 1993).

Determinations of the heavy metal concentrations have been performed by atomic absorption spectrophotometry (AAS), using flame atomization (Gast et al., 1988). Hg content in mushroom samples has been determined by cold vapour atomic absorption spectrophotometer (CVAAS), using $NaBH_4$ as the reducing agent (Rincon-Leon & Zurera-Cosano, 1986). Al, Pb, and Cd contents have been determined using a carbon

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0308-8146/02/$ - see front matter
PII: S0308-8146(01)00389-2

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. Al, Cu, Mn, Fe, and Zn have been analyzed after dry ashing and digestion in HC1 by flame AAS (Kojo & Lodenius, 1988).

The present study relates to the determination of Hg, Pb, Cd, Fe, Cu, Mn, and Zn in the fruit bodies of three mushroom species of Turkish origin. The heavy metal (Hg, Pb, Cd and Cu) bioaccumulation levels of eight mushroom species were studied.

2. Materials and methods

In this study, three mushrooms and, in total, 12 samples of mushrooms were used. The mushroom specimens were collected from locations in the East Black Sea region of Turkey in 2000. Species include *Armillaria mellea, Polyporus squamosus,* and *Polyporus sulphureus*. These samples were washed with demineralized water. Each sample was dried at 50 °C overnight and crushed in a mortar and pestle.

For the identification of specimens, the colour, odour and other apparent properties of the mushrooms and vegetation were noted. The mushrooms were identified using the reference books of European Flora (Breitenbach & Kränzlin, 1984, 1986, 1991).

Digestion of mushroom samples was performed using an oxi-acidic mixture of $HINO_3$:H_2SO_4:H_2O_2 (4:1:1) (12 ml for 2–4 g sample) and heating at 75 °C for three h. After cooling, 20 ml-demineralized water were added; the digest was again heated up to 150 °C for four hours and brought to a volume of 25 ml with demineralized water (Tüzen et al., 1998a).

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, 2001a).

Pb and Cd levels in the mushroom samples were determined using a GBC 3000 graphite furnace for AAS. Determination of metal ion (Cu^{+2}, Mn^{+2}, Zn^{+2}) contents was carried out with a GBC 905 model AAS using flame atomization. For the determination of Pb and Cd contents, deuterium and Smith-Hieftje background correction have been used. The standard-addition procedure was used in all determinations.

The wavelength and slit values, in nm, used for the determination of Pb, Cd, Fe, Cu, Mn, and Zn were: 283.3 and 0.5, 228.8 and 0.5, 248.3 and 0.2, 324.7 and 0.5, 279.5 and 0.2, and 213.9 and 0.5, respectively.

For chemical analyses, moisture content was determined by drying a 3–5 g sample at 105 °C to constant weight (Demirbaş, 2000b). Ashing was carried out at 750 °C for 2 h (Perez & Andujar, 1980). The block digestion method and (for protein) ether-extractable intramuscular fat content method were used (Cunniff, 1995).

Table 1
Habitat, edibility and the families of mushroom species

Class, family and species of mushroom	Habitat	Edibility
Basidiomycetes Classe		
Polyporaceae Corda		
Polyporus squamosus (Huds.: Fr.) Fr.	Parasitic on deciduous trees	Edible
Polyporus sulphureus Bull.: Fr.	On deciduous trees	Edible
Trichlomataceae Roze		
Armillaria mellea (Vahl: Fr.) Kumm	On trunks or stumps of trees	Edible

3. Results and discussion

The habitat, edibility and the families of mushroom species (*A. mellea, P. squamosus* and *P. sulphureus*) are given in Table 1. The heavy metal ion levels of the mushrooms are given in Table 2. The chemical analysis results of the mushroom are given in Table 3. Table 4 shows the average concentrations (mg/kg, dry-weight basis) of heavy metal ions (Hg^{+2}, Pb^{+2}, Cd^{+2} and Cu^{+2}) of fortified soils and mushrooms samples. The metal contents of fortified soil samples and mushrooms are separately shown in Figs. 1–3.

Table 2
Average levels (mg/kg, dry-weight basis) of heavy metal ion (Pb^{+2}, Cd^{+2}, Hg^{+2}, Cu^{+2}, Mn^{+2}, and Zn^{+2}) in mushroom samples obtained from East Black Sea region

Species	Pb^{+2}	Cd^{+2}	Hg^{+2}	Cu^{+2}	Mn^{+2}	Zn^{+2}
Armillaria mellea	1.28±0.31	2.48±0.38	0.91±0.30	21.1±3.9	26.8±4.6	76.8±6.5
Polyporus squamosus	1.23±0.25	1.86±0.67	0.22±0.07	42.6±7.3	138±15.8	200±26.7
Polyporus sulphurous	0.81±0.24	1.48±0.32	0.30±0.12	33.8±5.3	85.0±11.6	150±23.6

The heavy metal levels in the mushrooms are hardly affected by pH and organic matter content of the soil (Gast et al., 1988).

From Table 2, in the mushrooms from the East Black Sea region, the highest Pb^{+2} content was 1.28 ± 0.31 mg/kg, for the species *A. mellea*. The lowest Pb^{+2} content was 0.81 ± 0.24 mg/kg in the species *P. sulphureus*. The highest Cd^{+2} content was determined as 2.48 ± 0.38 mg/kg for *A. mellea*. Among the wild mushrooms, the lowest Cd^{+2} content was 1.48 ± 0.32 mg/kg for the species *P. sulphureus*. The highest Hg^{+2} content was found as 0.91 ± 0.30 mg/kg for the species *A. mellea,* whereas the lowest Hg^{+2} content was 0.22 ± 0.07 mg/kg in *P. sulphureus*. The highest Cu^{+2} content was 42.6 ± 7.3 for species *P. sulphureus*. The lowest Cu^{+2} content was 2 1.1 ± 3.9 mg/kg for *Armillaria mellea*. The highest Mn^{+2} and Zn^{+2} contents were 138 ± 15.8 and 200 ± 26.7 mg/kg, respectively, for *P. squamosus*. The lowest Mn^{+2} and Zn^{+2} contents were 26.8 ± 4.6 and 76.8 ± 6.5 mg/kg, respectively, for *A. mellea*. The species *A. mellea* had the lowest heavy metal content.

Fig. 1, shows that the Hg^{+2} level of *A. mellea* sample increased sharply with increasing Hg concentration in the fortified soil samples. The Cd^{+2} level (Fig. 3) also increased with increasing Cd^{+2} concentration in the soil samples, but the increase was less distinct than that of the Pb^{+2} level (Fig. 2). However, the Pb^{+2} levels in mushrooms did not change significantly, despite increasing Pb^{+2} levels in the fortified soil. As can be seen in

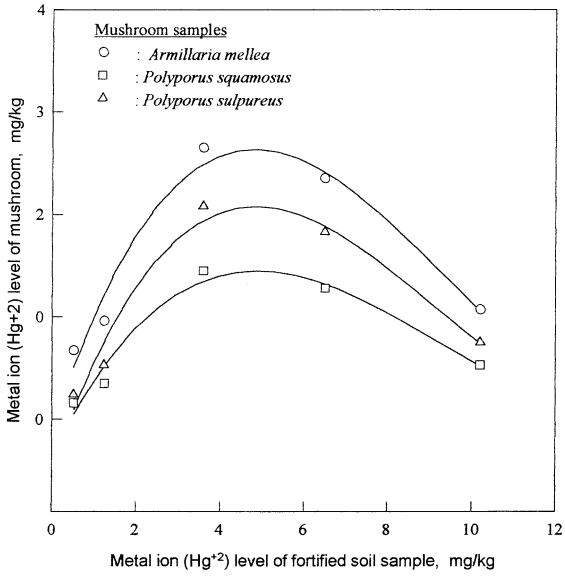

Fig. 1. Hg^{+2} contents of fortified soil samples and mushrooms.

Table 3
Chemical analysis results of selected mushroom species of *Armillaria mellea, Polyporus squamosus, Polyporus sulphureus* (dry-weight basis)

Species	Ash (%)	Fat (%)	Protein (%)	Carbohydrate (%)	Moisture (%)	Ca (mg/g)	P (mg/g)	Fe (mg/g)	Ph
Armillaria mellea	7.7	4.8	16.4	58.5	90.3	1.7	6.5	0.09	6.18
Polyporus squamosus	6.5	3.1	18.6	56.4	91.4	1.8	6.8	0.07	6.38
Polyporus sulphurous	11.8	6.0	26.8	55.8	92.7	1.6	6.7	0.08	6.50

Table 4
Average concentrations (mg/kg, dry-weight basis) of heavy metal (Hg, Pb, Cd and Cu) of fortified soils and mushrooms samples obtained from East Black Sea region

Sample	Metal concentration of soil				Metal concentration of mushroom			
	Hg^{+}	$^{+}1^{+}+^{2}$	Cd^{+2}	$^{+}+2$	Hg^{+2}	p^{++2}	Cd^{+2}	Cu^{+}
Armillaria mellea	0.51	0.82	0.24	0.58	0.67	0.96	1.14	16.8
	1.26	1.75	0.80	1.23	0.96	1.12	2.46	25.6
	6.51	*6.45*	3,74	14.9	2.38	1.34	4.39	81.5
	12.0	8.15	33.2	1.07	0.82	2.14	33.8	10.4
Polvporus squamosus	0.84	0.25	0.56	0.16	0.92	1.67	32.4	0.53
	1.25	1.72	0.78	1.22	0.35	1.08	3.73	44.3
	3.65	3.54	2.76	5.75	1.45	1.28	13.52	73.6
	6.44	6.35	3.51	14.5	1.28	1.13	9.21	92.0
	12.3	8.05	33.1	0.53	0.64	4.78	55.3	10.2
Polyporus sulphureus	0.46	0.23	0.55	0.24	0.67	*0.95*	25.7	0.52
	1.26	1.82	0.86	1.25	0.53	0.82	1.19	39.0
	3.48	3.38	2.80	5.72	2.08	0.99	5.25	67.8
	6.61	6.17	3.73	14.8	1.83	0.86	3.71	85.1
	12.4	8.05	33.4	0.75	0.58	1.65	47.0	10.2

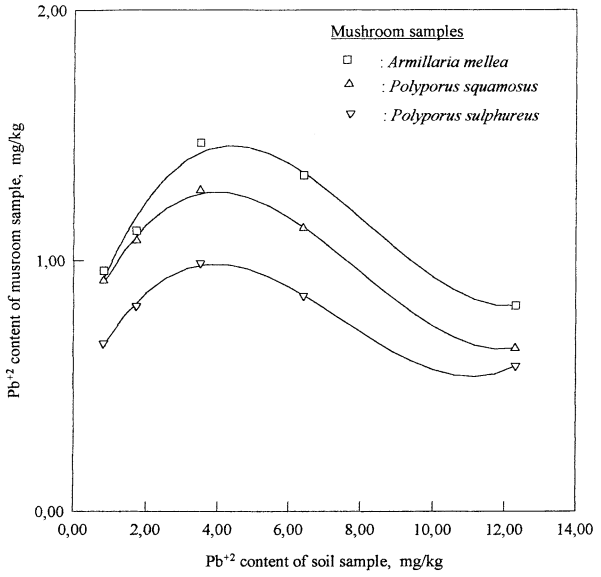

Fig. 2. Pb^{+2} contents of fortified soil samples and mushrooms.

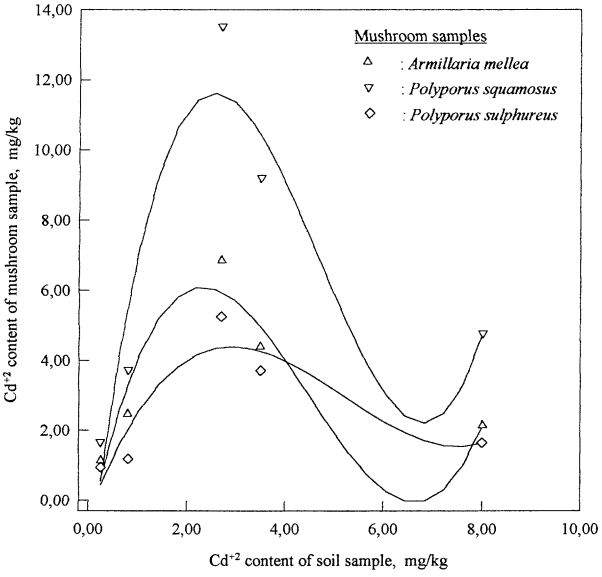

Fig. 3. Cd^{+2} contents of fortified soil samples and mushrooms.

Table 4, the highest concentration of Pb^{+2} found was 1.47 mg/kg in *Armillaria mellea* samples.

In the wild mushroom samples, the highest copper content was 251 mg/kg for *Amanita muscaria,* whereas the lowest copper content was 56.8 mg/kg in *Amanita rubescens* (Table 4).

There has been a previous report on the uptakes of cadmium, copper, lead, and zinc in mushrooms and their relationship with soil characteristics (Gast et al., 1988). 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. Maximum permissible doses for an adult are 3 mg lead and 0.5 mg cadmium per week. Hg^{+2} and Cd^{+2} levels of the mushrooms generally increased sharply with increasing Hg^{+2} and Cd^{+2} concentrations in the soil samples (Figs. 1 and 3). In general, the mushrooms bioaccumulated low amounts of Hg^{+2}, Pb^{+2} and Cd^{+2} 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 redemption programs.

The Hg^{+2} content of *A. mellea* sample increased sharply with increasing Hg^{+2} concentration in the fortified soil samples (Fig. 1). The highest Hg^{+2} level was 2.65 mg/kg for of *A. mellea,* whereas the lowest Hg^{+2} content was 1.45 mg/kg in *P. squamosus* (Table 4). The Cd^{+2} content also increased with increasing Cd^{+2} concentration in the soil samples (Fig. 3), but the increase was less distinct than that of the Pb^{+2} content (Fig. 2). However, the Pb^{+2} contents in mushrooms do not change significantly despite increasing Pb^{+2} content in the fortified soil. The highest concentration of Pb^{+2} found was 1.47 mg/kg in *A. mellea* samples.

4. Conclusion

The heavy metal (Hg, Pb, Cd and Cu) bioaccumulation levels of three mushrooms (*Armillaria mellea, P. squamosus, P. sulphureus*) samples obtained from the East Black Sea region were investigated. The Hg^{+2} level of *Amanita vaginate* samples increased sharply with increasing Hg^{+2} concentration in the fortified soil samples. The highest Hg^{+2} level was 2.65 mg/kg for of *A. mellea,* whereas the lowest Hg^{+2} level was 1.45 mg/kg in *P. squamosus*. Cd^{+2} level also increased with increasing Cd^{+2} concentration in the soil samples.

Results obtained were verified by UV Vis spectrophotometric methods of the AOAC (Horwitz, 1970). The results obtained from AA and UV Vis spectrophotometry methods were compared, and agreement was found on average $\pm 5.3\%$.

References

Breitenbach, J., & Kranzlin, F. (1984). *Fungi of Switzerland.* Lucerna: Verlag Mykologia.

Breitenbach, J., & Kränzlin, F. (1986). *Fungi of Switzerland.* Lucerna: Verlag Mykologia.

Breitenbach, J., & Kränzlin, F. (1991). *Fungi of Switzerland.* Lucerna: Verlag Mykologia.

Cunniff, P. (Ed.). (1995). *Official methods of analysis of AOAC International* (16th ed.). Arlington, Virginia: AOAC International.

Demirbaş, A. (2000a). Accumulation of heavy metals in some edible mushrooms from Turkey. *Food Chemistry*, *68*, 415–419.

Demirbaş, A. (2000b). Proximate analyses and mineral contents of goose and turkey tissues. *Energy Education Science Technology*, *5*, 85–92.

Demirbaş, A. (2001a). Heavy metal bioaccumulation by mushrooms from artificially fortified soils. *Food Chemistry*, *74*, 293–301.

Demirbaş, A. (2001b). Levels of trace elements in the fruiting bodies of mushrooms growing in the East Black Sea region. *Energy Education Science & Technology*, *7*, 67–81.

Falandyzs, L., Bona, H., & Danisievicz, D. (1994). Silver uptake by Agarigus bisporus from an artifically enrichedsubstrate. *Zeitschrift für Lebensmittel-Untersuchung und Forschung A*, *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*, 789–799.

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

Kojo, M. R., & Lodenius, M. (1988). Cadmium and mercury in macrofungi-mechanisms of transport and accumulation. *Angew. Bot.*, *63*, 279–292.

Latiff, L. A., Daran, A. B. M., & Mohamed, A. B. (1996). Relative distribution of minerals in the pileus and stalk of some selected edible mushrooms. *Food Chemistry*, *56*, 115–121.

Lepsova, A., & Mejstrik, 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-Lilja, 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. *Zeitschrift für Lebensmittel-Untersuchung und Forschung A*, *177*, 257–260.

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

Perez, D., & Andujar, G. (1980). Determination of ash content in meat products. *Meat Science*, *5*, 165–170.

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.

Sesli, E., & Tüzen, M. (1999). Levels of trace elements in the fruiting bodies of macroflingi growing in the East Black Sea region of Turkey. *Food Chemistry*, *65*, 453–460.

Tüzen, M., Özdemir, M., & Demirbaş, A. (1998a). Heavy metal bioaccumulation by cultivated *Aganicus bisporus* from artifically enriched substrates. *Zeitschrift für Lebensmittel-Untersuchung und Forschung A*, *206*, 417–419.

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

Tüzen, M., Sesli, E., & Demirbaş, A. (1999). Levels of heavy metals in the alga of *Ulva lactuca* growing in the Aegean Sea. *Energy Education Science & Technology*, *4*, 21–23.

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