REVIEW

Contents of cadmium and mercury in edible mushrooms

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Summary

Wild mushrooms are a popular delicacy in many countries and their consumption is rather high in some individuals. Some species, mainly from the genera *Agaricus, Macrolepiota, Lepista* and *Calocybe* accumulate a high content of cadmium and mercury even in unpolluted areas. Levels of these metals increase considerably in heavily polluted sites, such as in the vicinity of both working and abandoned metal smelters or inside cities. Current knowledge of the chemical forms of the metals bound in mushrooms is limited, as are data on their bioavailability in man. Consumption of the species which do accumulate these metals should thus be restricted. A low content of the metals in cultivated mushroom species is characteristic.

Keywords: heavy metals - cadmium - mercury - edible mushroom

INTRODUCTION

Mushrooms (higher fungi, macrofungi), both wild growing and cultivated, are a popular delicacy in many countries, with some people consuming several kilos per year, mainly in countries of Central and East Europe and the Far East. However, many mushroom species accumulate trace elements to a considerably higher extent than plants. About forty trace elements have been reported in the literature to date, with cadmium and mercury being the most important from the point of view of human health.

Existing research has had two main objectives. The first is to test the suitability of wild mushrooms as a bioindicator of environmental pollution by a number of heavy metals. Such an approach has been preferred in Western Europe, where the consumption of wild mushrooms has been very limited, culminated in the 1980's and attenuated after the observation that mushrooms cannot be used as a reliable indicator. The second objective is to search for edible species which accumulate high levels of harmful elements. This research has been carried out mainly in countries with a high consumption of wild mushrooms.

A number of reviews have been published of trace element content in mushrooms (Seeger 1982, Michelot et al. 1998, Kalač and Svoboda 2000). Moreover, many mushroom species accumulate high or very high levels of radioactive isotopes of caesium (reviewed by Kalač 2001). The literature dealing with potentially harmful cadmium and mercury content in edible mushrooms is reviewed in this article.

Several mycological terms are used within the article: *the fruiting body* is the visible, commonly aboveground part of a mushroom, *fructification* is the formation of the fruiting body. The fruiting body consists of a *cap* (pileus) with a spores-

forming part (*sporophore*), and a *stipe* (stem or stalk). A mushroom uptakes nutrients from a substrate via specious mycelium.

FACTORS AFFECTING THE METAL CONTENT IN FRUITING BODIES

Knowledge about the physiological roles of cadmium and mercury in mushrooms is very limited. The content of both metals is primarily species-dependent, while the importance of the genus or family, age and size of the fruiting body is limited. The nutritional strategy, mycorrhizal, parasitic or saprophytic, seems to be of significance. A higher content of both cadmium (Melgar et al. 1998) and mercury (Alonso et al. 2000) was reported for saprophytic species as compared to mycorrhizal ones, however, exceptions occurred. Great differences exist in the uptake of individual metals from substrate to fruiting bodies (Tyler 1982, Gast et al. 1988). The ability to accumulate a metal is characterised by the bioaccumulation factor, the ratio of content in the fruiting body dry matter to the substrate dry matter. Both cadmium and mercury are strongly accumulated in many mushroom species. Factors 50-300 and 30-500 were reported for cadmium and mercury, respectively, while, for instance, only 0.01-0.1 for lead (Seeger 1982).

The proportion of the metal content originating from atmospheric depositions seems to be also of less importance. The lifetime of a fruiting body is short, usually only 10-14 days. In our opinion, the metal content in fruiting bodies is considerably affected by the age of the mycelium and the interval between fructifications. However, scientific evidence for such opinion is lacking. Nevertheless, maximum metal content has been observed in the initial harvest wave of the cultivated white mushroom (Agaricus bisporus). Metal levels reported in wild growing A. bisporus are considerably higher than those in cultivated fruiting bodies. The probable explanation is that it is not only due to different substrate composition and contamination, but also to the very different age of the mycelium, which may exist for several years in nature, while only for several months in a cultivation plant. Thus, cadmium and mercury contents are considerably lower in the cultivated mushrooms than in the same or taxonomicallyrelated wild species (Haldimann et al. 1995).

The combination of all these factors causes a very wide variability of metal content within a species, commonly to one order of magnitude. Thus, ranges of the metal levels are remarkably broader than in plant materials. The metals are distributed unevenly within a fruiting body. The highest content has been observed in the sporeforming part, but not in the spores; lower content in the rest of the cap and the lowest level in the stipe (Thomet et al. 1999).

The surprising ability of some mushroom species to accumulate promoted their testing as bioindicators for the metals. As reviewed by Wondratschek and Röder (1993), no mushroom species could be considered as a reliable indicator of environmental pollution with heavy metals. However, cadmium and mercury contents in fruiting bodies increase in polluted areas. High metal levels have been observed in mushrooms growing in heavily contaminated areas, such as those in the close vicinity of highways with heavy traffic (Cuny et al. 2001), emission areas (Lepšová and Meistřík 1988), and inner cities (Kuusi et al. 1981, Svoboda and Kalač 2003). Extremely high metal contents have been reported from the vicinity of metal smelters (Liukkonen-Lilja et al. 1986, Kalač et al. 1991, 1996, Svoboda et al. 2000, Collin-Hansen et al., 2002). A high metal content was reported also from areas contaminated historically by ore mining and processing (Bargagli and Baldi 1984, Fischer et al. 1995).

Metal content has usually been expressed in mg/kg dry matter. There is a consensus for recalculation to fresh matter that mushrooms have dry matter content 10 %. For intake calculations, usually 300 g of fresh mushrooms per meal is assumed.

HEALTH ASPECTS

Extensive information is available on the metal content in many mushroom species. Literature data for 25 species, commonly consumed from unpolluted areas in Central Europe, were tabulated in our previous review (Kalač and Svoboda 2000). However, a plausible assessment of the health risk from mushroom consumption has been difficult due to very limited knowledge on the chemical form of the metals (speciation) and their bioavailability in man.

Some countries have established statutory limits for the metals in edible mushrooms. For instance, current Czech regulations list 66 wild growing and 15 cultivated marketable species with limits of 2.0 and 5.0 mg/kg dry matter for cadmium and mercury, respectively in wild growing mushrooms, and 1.0 mg/kg dry matter for mercury in cultivated species. According to FAO/WHO recommendations, acceptable weekly intakes are 0.007 and 0.005 mg per kg body weight for cadmium and mercury, respectively.

Cadmium

Cadmium levels in most edible species growing in unpolluted (background) areas are below 2 mg/kg dry matter. However, the content in *Boletus aestivalis, Leccinum scabrum, Calocybe gambosa, Armillaria mellea* and *Russula cyanoxantha* can be up to 5 mg/kg dry matter (Kalač and Svoboda 2000) and in the genus *Agaricus* up to 50 mg/kg dry matter, mainly in species yellowing after tissue mechanical damage (Table 1). An extremely high content of up to 300 mg/kg dry matter has been reported (Schmitt and Meisch 1985). Such levels should be expected mainly in fruiting bodies of accumulating species growing in the close vicinity of metal smelters or within towns.

Information on the chemical forms of cadmium in mushrooms is very limited. Macrofungi have several tolerance mechanisms against toxicity of cadmium (Gadd 1993). Intracellular detoxification accomplished by cadmium and other metals binding to proteins probably has an important role. Such fungal proteins include metallothioneines containing cysteine, reported in *A. bisporus* with ability to bind copper (Münger and Lerch, 1985) and cadmium-mycophosphatin (Meisch and Schmitt 1986). The latter compound isolated from *A. macrosporus* is a phosphoglycoprotein of molecular weight 12 kDa lacking cysteine, with a high proportion of acidic amino acids, glucose and galactose. Moreover, four low-molecular glycoproteins containing sulphur and binding cadmium were isolated simultaneously. No metallothioneines were found in fruiting bodies of cultivated A. bisporus (Esser and Brunnert 1986) or in Boletus edulis (Collin-Hansen et al. 2003). Two other essential cadmium-detoxification mechanisms were observed in the inedible mycorrhizal mushroom Paxillus involutus - cadmium bound onto cell walls and accumulated in the vacuolar compartments (Blaudez et al., 2000).

The initial information (Schellmann et al. 1980, Diehl and Schlemmer, 1984) on cadmium bioavailability from mushrooms reported a low proportion, only up to 10 %. However, further work observed a comparable and higher absorption from mushrooms than from inorganic cadmium salts (Seeger et al. 1986, Lind et al. 1995, Mitra et al. 1995). Cadmium is accumulated mainly in the kidneys, spleen and liver and its level in blood serum increases considerably following mushroom consumption. Thus, cadmium seems to be the most deleterious among heavy metals in mushrooms. Its acceptable daily or weekly intake may be easily reached by consumption of an accumulating mushroom species.

Table 1. Ranges of cadmium content in mushroom species accumulating above 5 mg/kg dry matter in unpolluted sites(adapted from Kalač and Svoboda 2000)

Species	Content (mg/kg dry matter)
Agaricus campestris	5-50
Agaricus arvensis	5-20
Agaricus silvaticus	5-50
Agaricus silvicola	10->50

Mercury

Heavily accumulating species with up to 20 mg/kg dry matter of mercury in unpolluted areas are *Calocybe gambosa*, *Lepista nuda* and *Agaricus arvensis*. High contents up to 10 mg/kg dry matter are typical for the genera *Agaricus* and *Macrolepiota* (Table 2) and levels up to 5 mg/kg dry matter for the genus *Boletus* (Kalač and Svoboda 2000). An extremely high content, one order of magnitude higher than the levels from unpolluted areas, was observed in sites polluted from both historical and/or present mercury smelters

(Fischer et al. 1995, Kalač et al. 1996, Svoboda et al. 2000). A similar situation was reported in the vicinity of a chemical plant using mercury as an electrode in the production of sodium hydroxide from common salt (Lodenius and Herranen 1981). Thus, a content up to 200 mg/kg dry matter was determined.

Interesting information on the distribution of mercury in cap and stipe and on the values of the bioaccumulation factor between mercury content and underlying substrate from depth 0–10 cm for numerous species was reported by Falandysz et al. (2003 a,b,c). Surprisingly high bioaccumulation

factor levels of 960 and 310 were found for cap and stipe, respectively, of *Calvatia excipuliformis* (Falandysz et al. 2003a).

Unfortunately, information on the chemical forms of mercury in mushrooms has been very scarce. Lasota and Florczak (1991) observed in cultivated *A. bisporus* most mercury bound in high-molecular weight proteins, while in cultivated *Pleurotus ostreatus* in protein fraction 17–45 kDa.

Limited data are also available on the proportion of highly toxic methylmercury CH_3Hg^+ . This was reported to be usually only a few per cent, rarely up to 16 % of total mercury (Stijve and Besson 1976, Bargagli and Baldi 1984, Kojo and Lodenius 1989, Fischer et al. 1995). Mushrooms accumulate methylmercury from a substrate with a bioaccumulation factor of about 20. Moreover, they are likely able to methylate inorganic mercuric salts (Fischer et al. 1995).

Table 2. Ranges of mercury content in mushroom species accumulating above 5 mg/kg dry matter in unpolluted sites (adapted from Kalač and Svoboda 2000)

Species	Content (mg/kg dry matter)
Agaricus campestris Agaricus arvensis Macrolepiota rhacodes Macrolepiota procera Lepista nuda Calocybe gambosa	$ \begin{array}{r} 1 - 10 \\ 2 - 20 \\ 2 - 10 \\ 1 - 10 \\ 2 - 20 \\ 5 - 20 \\ \end{array} $

EFFECTS OF MUSHROOM PRESERVATION AND COOKING

Only a few data are available on the decrease of cadmium and mercury content during different mushroom preservation and culinary treatments. Washing and peeling of A. bisporus lowered cadmium content by about 30-40% (Źródlowski 1995). Mercury loss of about one third was observed during mushroom thermal treatment under high temperature, simulating e.g. pan-frying (Cibulka et al. 1999). Svoboda et al. 2002 investigated the leaching of cadmium and mercury from fresh, freeze-dried, air-dried and frozen slices of the widely consumed Xerocomus badius. Treatments were tested: soaking in 0.3% table salt solution at ambient temperature for 5, 10 or 15 min or repeatedly for 3x15 min, or boiling in the same solution for 15, 30 or 60 min. Short-time boiling was observed to be a more efficient treatment than soaking. The metals were leached to the greatest extent from the most destroyed tissues of frozen slices. The lowest decrease was in fresh or freezedried mushrooms. Cadmium was leached to a higher extent than mercury.

CONCLUSION

While comprehensive literature has been available on the content of cadmium and mercury in many mushroom species from both unpolluted and differentially polluted areas, only very limited data deal with factors affecting their potential risk in human nutrition. Knowledge of chemical forms of the bound metals and their bioavailability in man has been scrappy. Thus, a critical, plausible assessment of the health risk from mushroom consumption has not been as yet possible and the consumption of both the accumulating species even from unpolluted areas and non-accumulating species from polluted sites should be restricted.

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