ELSEVIER

Food Chemistry 79 (2002) 41–45

Food Chemistry

www.elsevier.com/locate/foodchem

Leaching of cadmium, lead and mercury from fresh and differently preserved edible mushroom, *Xerocomus badius*, during soaking and boiling

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Received 5 February 2002; accepted 7 March 2002

Abstract

Many mushroom species are known as cadmium, lead or mercury accumulators. A possibility to decrease the metal levels was therefore investigated. Leaching of the metals from fresh, freeze-dried, air-dried and frozen slices of widely consumed *Xerocomus badius* was tested in three experiments. Common culinary treatments, soaking in 0.3% table salt solution at ambient temperature for 5, 10 or 15 min or repeatedly for 3×5 min and boiling in the same solution for 15, 30 or 60 min, were investigated. Short-time boiling was observed as a more efficient operation than soaking. The metals were leached to the greatest extent from the most destroyed tissues of frozen mushroom slices, but less so from fresh or freeze-dried tissues. The most extensive leaching was observed for cadmium and the lowest for mercury.

Keywords: *Mushroom*; *Xerocomus badius*; Culinary treatments; Metal leaching; Cadmium; Lead; Mercury

1. Introduction

Many edible mushroom species are known to accumulate high levels of several heavy metals, and mainly cadmium, mercury and lead (for a review see Kalač & Svoboda, 2000). Consumption of wild-growing mushrooms, as a delicacy, has been high in many countries, exceeding 10 kg per year in some individuals. Thus, information on the metal losses during processing is necessary. While several original papers have reported factors affecting metal levels in fruiting bodies of different species, little has been published on changes of metal contents during mushroom preservation and culinary treatments.

Washing and hand-peeling of cultivated common white mushroom (*Agaricus bisporus*) caps and stalks decreased cadmium, lead, copper and zinc contents by about 30–40% of the initial levels (Źrodlowski, 1995). Blanching of the same species in a boiling diluted solution of citric acid, $NaHSO_3$ and NaCl for 15 min decreased manganese, iron, zinc and copper levels by 45, 35, 23 and 4%, respectively. No further significant changes in the metal contents were observed after 4-months' storage of canned blanched mushrooms (Coskuner & Özdemir, 1997). However, in a further report, blanching in solutions of 0.05 or 0.1% citric acid plus 0.1% NaCl did not cause significant changes of the metal levels (Coskuner & Özdemir, 2000).

Decrease of mercury levels, up to 70%, during mushroom preservation and cooking was mentioned in a book on mushrooms (Wennig, Wennig-Battin, & Jungblut, 1978). Mercury losses, of about one third of the initial contents, were observed in a thawed and mashed mixture of *Xerocomus badius* and *X. chrysenteron* during heating in an open vessel, simulating e.g. pan-frying (Cibulka, Čurdová, Miholová, & Stěhulová, 1999).

The objective of the present work was to investigate leaching of the most deleterious metals, i.e. cadmium, mercury and lead, during soaking and boiling of fresh and differently preserved *X. badius*. The results should indicate how to decrease the metal intake from mushroom meals.

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0308-8146/02/$ - see front matter
PII: S0308-8146(02)00175-9

2. Materials and methods

2.1. Mushrooms

Wild-growing *X.* (*Boletus*) *badius* (Fr.) Kühn. ex Gilb. (bay bolete) was used as a typical, widely consumed mushroom. Fruiting bodies in different growth stages, collected from a suburban forest north of České Budějovice, during November 1999, were cleaned from soil and substrate with a stainless knife. Three experiments (1–3) were carried out, using 480 g of mushrooms in each. The amount was divided into four variants (120 g each), fresh and prepared for preservation in three ways. Fruiting bodies were then cut along their vertical axes into eight pieces and the cuts were divided into eight groups of 15 ± 1 g within each variant, cut to slices 1–2 mm thick and treated in the following manner:

- fresh mushrooms, with dry matter contents of 56.5, 53.0 and 50.4 g kg^{-1} in experiments 1, 2 and 3, respectively, were used as the control variants,
- freeze-dried mushrooms, prepared in a freeze-drier Alpha 1–2 (Christ, Germany), were stored in polyethylene bags in a refrigerator. Dry matter contents were 926, 948 and 908 g kg^{-1} in experiments 1, 2 and 3, respectively,
- dried mushrooms were preserved by natural drying on a filter paper at ambient temperature, about 20 °C, for two weeks, and stored in paper sachets at laboratory temperature. Dry matter contents were 924, 954 and 919 g kg^{-1} in experiments 1, 2 and 3, respectively,
- frozen mushrooms were frozen and stored in a tight polyethylene bag at −18 °C in a freezer. A substantial proportion of water sublimating during storage was separated as ice. Dry matter contents were 867, 833 and 781g kg^{-1} in experiments 1, 2 and 3, respectively.

2.2. Treatments

Mushroom soaking and boiling, as common culinary treatments, were simulated. Fresh mushrooms were treated and analysed within 6 h after being collected. Preserved mushrooms were treated after storage for 3 months. Portions, 7×15 g, of fresh fruiting bodies or preserved mushrooms, in quantities corresponding to that weight, were used for each of seven treatments. Metals and dry matter contents were determined in the eighth portion as the initial levels within each of the variants.

Four variants of soaking were tested. Mushroom slices were mixed with distilled water of temperature 20 °C; 0.3 g of table salt was added (2% per fresh mushroom weight) and weight was adjusted with water to 90 g. The slices were then soaked for 5, 10 or 15 min or for 3×5 min. In the latter variant the mushrooms were separated using a plastic strainer and soaked repeatedly. Finally, mushrooms were separated from the liquid portion and both parts were analysed.

Similarly, three variants of boiling were tested. The same mixtures as prepared for soaking experiments were boiled under reflux for 15, 30 or 60 min and mushroom matter and liquid portion were then analysed separately.

2.3. Analytical methods

All metal concentrations were expressed in mg kg^{-1} dry matter to enable comparison of results between the variants. Dry matter contents were determined by drying in an oven at 105 °C for 6 h in each of preservation and treatment variants and used for calculations of metal concentrations.

Mushrooms (3, 3, 0.4 and 0.4 g of fresh, frozen, dried and freeze-dried, respectively) for cadmium and lead determinations were mineralised with 5 ml of concentrated HNO_3 in a micro-wave mineralisator (MDS 2000, CEM Corp., USA). A SpectrAA 640 apparatus (Varian Techtron, Australia) was used for atomic absorption spectrometry measurements of cadmium and lead contents using electrothermic atomisation. Mercury was determined in wet mushroom matter using a cold-vapour AAS analyser (AMA-254, Altec, Prague, Czech Republic). Cadmium and lead were determined in duplicates, mercury in triplicates and mean values are given below. Mean differences between parallel determinations were up to 10% for cadmium and lead and up to 6% for mercury. More details on analytical procedures are given in a previous paper (Svoboda, Zimmermannová, & Kalač, 2000).

Concentrations of the metals in the liquid portion after mushroom soaking or boiling were considerably lower than those in mushrooms and often below the detection limits. Thus, these data could not be used and only results dealing with mushroom matter are given below.

2.4. Statistical methods

Three main effects, three metals, fresh and differently preserved matter and nine levels of soaking and boiling, were tested by Duncan's multiple range test with alpha levels for critical ranges $P < 0.05$, using program Statistica for Windows, StatSoft, Inc., USA.

Table 1
Initial metal contents (mg kg^{-1} dry matter) in fruiting bodies used for experiments 1–3

Experiment	Cadmium	Lead	Mercury
1	13.5	9.7	1.3
2	9.2	8.6	0.9
3	9.7	4.7	1.0

Table 2
Cadmium levels after soaking or boiling (% of the initial content in fresh fruiting bodies; mean values of three experiments) and results of Duncan's test[a]

Treatment	Mushroom			
	Fresh	Freeze-dried	Dried	Frozen
Soaking (min)				
5	101±6.0 a	93.3±6.3 b	92.3±4.9 b	75.1±6.0 b
10	95.2±6.1 b	93.9±9.4 a,b	84.5±6.2 c	62.2±4.5 d
15	94.8±1.0 b	91.1±7.5 b	80.8±6.5 c	62.1±5.1 d
Repeatevmk soaking (min)				
1 × 5	95.7±2.6 a,b	89.7±6.2 b	80.4±3.7 c	68.5±6.8 c
2 × 5	97.4±3.8 a,b	89.1±8.9 b	72.8±4.7 d	69.4±5.7 c
3 × 5	97.9±4.1 a,b	90.5±7.8 b	71.7±4.9 d	69.0±7.9 c
Boiling (min)				
15	65.6±2.3 c	64.7±4.7 c	54.1±2.0 e	41.7±2.0 e
30	62.5±3.3 c,d	61.4±3.4 c	49.7±4.0 e,f	43.7±1.1 e
60	57.9±3.6 d	60.6±6.0 c	46.5±1.5 f	41.8±6.0 e

[a] Different letters in a column mean significant difference at $P<0.05$. The letters are given in alphabetical order with decreasing content of the metal. The initial metal content (100%) is designated by letter a.

Table 3
Lead levels after soaking or boiling (% of the initial content in fresh fruiting bodies; mean values of three experiments) and results of Duncan's test[a]

Treatment	Mushroom			
	Fresh	Freeze-dried	Dried	Frozen
Soaking (min)				
5	87.5±6.1 b	85.6±5.4 b	87.9±7.2 b	86.4±6.7 b
10	86.9±6.4 b	84.3±2.5 b	88.6±8.9 b	77.3±8.4 b
15	84.1±7.8 b	83.7±3.4 b	84.9±5.5 b	76.7±6.5 b
Repeated soaking (min)				
1 × 5	84.3±9.9 b	83.6±8.3 b	86.2±8.6 b	76.9±8.1 b
2 × 5	83.8±8.9 b	86.6±5.4 b	81.7±8.9 b	79.1±1.8 b
3 × 5	84.9±7.9 b	84.5±6.7 b	84.0±9.8 b	78.4±7.4 b
Boiling (min)				
15	74.1±4.0 c	71.0±2.0 c	59.2±3.7 c	43.3±6.3 c
30	73.7±6.1 c	65.6±0.8 c	61.2±4.7 c	44.1±4.9 c
60	72.2±4.1 c	67.8±3.9 c	57.4±3.1 c	44.8±3.5 c

[a] Different letters in a column mean significant difference at $P<0.05$. The letters are given in alphabetical order with decreasing content of the metal. The initial metal content (100%) is designated by letter a.

3. Results and discussion

Cadmium, lead and mercury contents in fruiting bodies used for the experiments 1–3 are given in Table 1. Mercury levels are common, lead contents elevated and cadmium levels considerably increased as compared with data typical for *X. badius* from unpolluted areas (Kalač & Svoboda, 2000). The fruiting bodies were collected from a site adjacent to an area where historical mining activities were recorded and mainly silver was exploited from polymetallic ores. However, these elevated levels helped to decrease experimental errors.

Remaining levels of the individual metals in fresh and differently preserved fruiting bodies after soaking and boiling are given in Tables 2–4. Results of the statistical tests for two characteristic treatments, soaking for 15 min as a mild operation and boiling for 60 min as a hard operation, are given in Tables 5 and 6 and residual levels of the metals after both treatments are given in Figs. 1 and 2.

Boiling proved to be a more efficient operation for decreasing the metal levels in mushroom than soaking. High efficiency was observed, even after boiling for 15 min; increasing time of boiling had only a limited effect. Increasing the time of single or repeated soaking affected cadmium levels to a limited extent; contents of the other metals did not decrease markedly. The highest proportions of the metals were leached from frozen

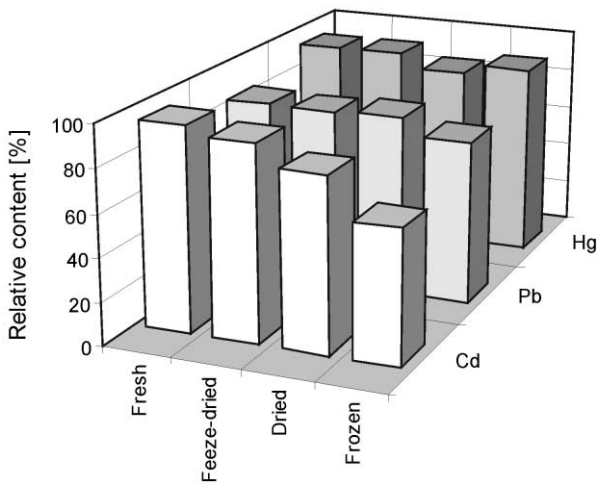

Fig. 1. Relative contents (% of the initial content in fresh fruiting bodies) of the metals after soaking for 15 min.

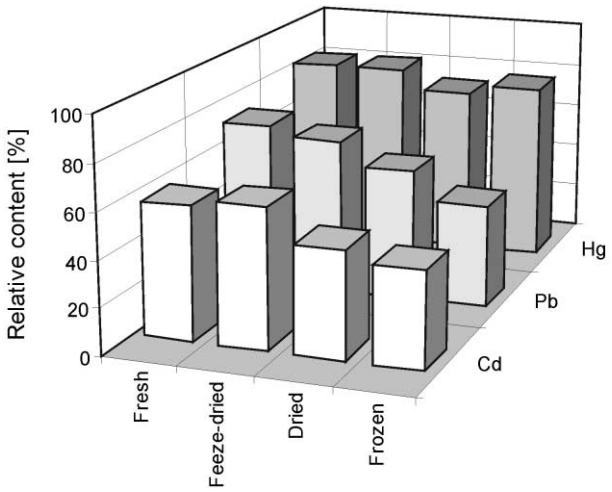

Fig. 2. Relative contents (% of the initial content in fresh fruiting bodies of the metals after boiling for 60 min.

Table 4
Mercury levels after soaking or boiling (% of the initial content in fresh fruiting bodies; mean values of three experiments) and results of Duncan's test[a]

Treatment	Mushroom			
	Fresh	Freeze-dried	Dried	Frozen
Soaking (min)				
5	94.7±3.8 a,b	89.5±5.3 a,b	89.5±5.9 b	92.5±4.9 b
10	90.0±2.9 b,c	87.6±7.8 b	85.0±9.5 b	87.8±5.0 b
15	90.5±3.3 b,c	89.2±10.0 b	83.2±7.2 b,c	88.1±4.6 b
Repeated soaking (min)				
1 × 5	88.7±1.2 c	89.9±4.5 b	84.2±5.1 b	88.2±4.0 b
2 × 5	88.8±5.5 c	87.0±6.3 b	80.8±5.9 b,c	87.6±4.4 b
3 × 5	90.3±4.5 b,c	86.9±8.5 b	81.8±3.6 b,c	87.3±2.7 b
Boiling (min)				
15	85.1±2.0 c,d	80.9±5.9 b,c	76.5±7.8 c,d	78.5±5.7 c
30	79.3±0.4 e	78.5±1.0 c	71.9±8.4 d,e	71.5±2.6 d
60	75.4±3.5 e	75.9±0.4 c	67.9±5.0 e	73.5±3.9 c,d

[a] Different letters in a column mean significant difference at $P<0.05$. The letters are given in alphabetical order with decreasing content of the metal. The initial metal content (100%) is designated by letter a.

Table 5
Results of Duncan's test of different preservation treatment effects on metal levels after mushroom soaking or boiling[a]

Mushroom	Soaking for 15 min			Boiling for 60 min		
	Cadmium	Lead	Mercury	Cadmium	Lead	Mercury
Fresh	a	a	a	a	a	a
Freeze-dried	a	a	a	a	a	a
Dried	b	a	a	b	b	b
Frozen	c	a	a	b	c	a,b

[a] Different letters in a column mean significant difference at $P<0.05$. The letters are given in alphabetical order with decreasing content of the metal. The initial metal content (100%) is designated by letter a.

Table 6
Results of Duncan's test on differences between the individual metals on their leaching from differently preserved mushroom after its soaking or boiling[a]

Metal	Soaking for 15 min				Boiling for 60 min			
	Fresh	Freeze-dried	Dried	Frozen	Fresh	Freeze-dried	Dried	Frozen
Cadmium	a	a,b	a	b	c	b	c	b
Lead	b	b	a	a,b	b	b	b	b
Mercury	a	a	a	a	a	a	a	a

[a] Different letters in a line mean significant difference at $P < 0.05$. The letters are given in alphabetical order with decreasing content of the metal. The initial metal content (100%) is designated by letter a.

mushrooms, and the lowest from fresh and freeze-dried mushrooms. Both boiling and freezing are treatments that destroy tissues and cells to the greatest extent, thus enabling release of metal-binding compounds. Comparable decrease of the mercury level was observed by heating of mushrooms in an open vessel (Cibulka et al., 1999). Similar results were reported for leaching of radiocesium from several mushroom species (for review see Kalač, 2001).

Cadmium was leached to the greatest extent, by both boiling and soaking, while mercury was relatively fixed in the mushroom tissue. The differences are probably due to characteristics of compounds binding the metals. Unfortunately, information about chemical forms of the metals in mushrooms has been very limited. Cadmium-mycophosphatin, a phosphoglycoprotein of molecular weight 12,000 Da, lacking sulphur, with a high proportion of acidic amino acids, glucose and galactose, was isolated from *Agaricus macrosporus*. Moreover, four low-molecular glycoproteins containing sulphur and binding cadmium were isolated (Meisch & Schmitt, 1986). No metallothioneines were found in fruiting bodies of cultivated *Agaricus bisporus* (Esser & Brunnert, 1986). Usually only a few per cent of highly toxic methylmercury (of the total mercury level) has been reported for different mushroom species from several countries, as reviewed by Kalač and Svoboda (2000). Fischer, Rapsomanikis, Andreae, and Baldi (1995) found, in *X. badius*, methylmercury proportions of 0.7–1.1% of the total mercury.

Thus, levels of cadmium, lead and mercury in *X. badius* can be lowered in decreasing order by short-time boiling or the considerably less-efficient short-time soaking in table salt solution. The metals are leached most efficiently from frozen mushrooms, moderately so from air-dried mushrooms and least well from fresh and freeze-dried fruiting bodies. However, many of the attractive aroma compounds are lost with the decanted solution.

Acknowledgements

The authors wish to thank Mrs. Hedvika Štolcpartová and Mr. Jan Bastl for their technical assistance.

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