Uptake of arsenic by mushrooms from soil

Metka Slekovec¹ and Kurt J. Irgolic^{2*}

¹University of Maribor, Faculty of Agriculture, Vrbanska 30, 2000 Maribor, Slovenia

²Institut für Analytische Chemie, Karl-Franzens-Universität Graz, Universitätsplatz 1, A-8010 Graz, Austria

ABSTRACT

Graphite furnace atomic absorption spectrometry (standard addition method) was used to determine the total arsenic in wild-growing mushrooms after digestion with nitric acid, then with perchloric acid and in associated soils after digestion with mixtures of nitric and hydrofluoric acids in a microwave system. Among 83 species of mushrooms the highest concentrations of arsenic on a dry mass basis were found in *Laccaria amethystea* (26–125 mg kg⁻¹), *Laccaria laccata* (11–33 mg kg⁻¹), *Thelephora terrestris* (38 mg kg⁻¹), *Boletus cavipes* (11.6 mg kg⁻¹) and *Ramaria botrytis* (10 mg kg⁻¹). Mushroom caps of *L. laccata*, *L. amethystea*, and *B. cavipes* had approximately double the arsenic concentrations found in stems. The arsenic concentrations in caps of *L. amethystea* and *L. laccata* were directly proportional to the concentrations in the soils. The concentrations of arsenic in the soils were in the range 6.5–65 mg kg⁻¹. Among the 19 mushroom caps with arsenic concentrations above the method detection limit of 0.2 mg As/kg dry mass, only *L. amethystea* and *L. laccata* had arsenic concentration ratios 'cap/soil' higher than 1 (between 1.1 and 1.9). *Thelephora terrestris* had a ratio of 2.37.

Keywords: Arsenic, mushrooms, caps, stems, soil, concentration ratios caps/soils.

INTRODUCTION

Mushrooms in contact with soil, air, and rain may be used as biological monitors for trace elements. The aerial parts of mushrooms (caps and stems) grow within a few days to a few weeks to maturity and could be useful as short-term indicators of the deposition and bioavailability of trace elements. Some mushrooms are capable of accumulating certain trace elements.

Kalac *et al.* (1991) observed, that cadmium was accumulated by the edible *Amanita rubescens*, the toxic *Amanita muscaria*, and the edible *Boletus edulis*, and mercury, lead, and copper by *Lepista nuda* and *Lepiota rhacodes*. Many edible mushrooms including the most popular *Boletus edulis* accumulate selenium. Stijve (1977) found the average selenium concentration in nine samples of *Boletus edulis* to be 13 mg kg⁻¹.

Byrne et al. (1976) reported the average concentration of arsenic in 27 species of mushrooms as 1.3 mg kg⁻¹. High concentrations of arsenic were found in Lycoperdon perlatum (6.8 mg kg⁻¹, Byrne et al., 1976), in the edible Laccaria amethystea (up to 182 mg kg⁻¹, Byrne et al., 1983, Stiyve et al., 1990, 1991), in Laccaria laccata (average of 10 samples 10.9 mg kg⁻¹), in Laccaria fraterna (average of four samples 129 mg kg⁻¹, Stijve et al., 1990), in Agaricus haemorrhoidarius (1.1–7.3 mg kg⁻¹), in Agaricus macrosporus (1.5–17 mg kg⁻¹), in Agaricus perrarus (10.3 mg kg⁻¹, Stijve et al., 1991), in Coprinus atramentarius (11.8 mg kg⁻¹), in Langermannia gigantea (7.1 mg kg⁻¹), in Lepista nuda (5.4 mg kg⁻¹), and in Macrolepiota rhacodes

(26.6 mg kg⁻¹, Vetter, 1989, 1990). All of the concentrations are based on dry mass.

The literature data on arsenic in mushrooms cannot be used to calculate 'mushroom/soil' concentration ratios, because the concentrations of arsenic in the soils in which the mushrooms had grown were not reported. High concentrations of arsenic in mushrooms could be the result of biomagnification (preferential uptake of arsenic from a soil with low arsenic concentration) or the result of 'normal' uptake from a soil with high arsenic concentrations. To explore the mushroom/soil system, 83 edible and inedible, wild-growing mushroom species and samples of the soils associated with these mushrooms were collected in Slovenia. Total arsenic was determined in the mushroom caps and in the soil samples.

METHODOLOGY

Distilled water was deionised and then distilled twice in a quartz distillation unit. This NANOpure water was used for the preparation of all solutions. Nitric acid (p.a. Merck) was distilled twice in a sub-boiling quartz distillation apparatus. Perchloric acid (70%) and hydrofluoric acid (40%) were Merck p.a. grade. A nickel nitrate solution (1000 mg Ni/L) served as matrix modifier for the determination of arsenic by graphite-furnace atomic absorption spectrometry (GFAAS). Stock solutions containing 1000 mg As/L were prepared by dissolving 1.0410 g Na₂HAsO₄ heptahydrate to 250 mL, 186.8 mg methylarsonic acid to 100 mL, and

285.7 mg sodium dimethylarsinate trihydrate to 100 mL. These stock solutions were serially diluted as required immediately before use.

Instrumentation

Mushroom tissues and soil samples were digested in 120-mL Teflon vessels with screw caps in a CEM Corporation MDS 2000 microwave system. Total arsenic in the digests was determined with a Hitachi Zeeman Z-9000 Simultaneous Multi-Element Graphite Furnace Atomic Absorption Spectrometer at a wavelength of 193.7 nm. The Cathodeon arsenic hollow cathode lamp was operated at 10 mA. The argon carrier gas flow at 200 mL min⁻¹ was stopped during the atomisation. The temperature program for the determination of arsenic by GFAAS consisted of drying at 50–80°C and 80–120°C for 10 s each, ashing at 200°C and 400° C for 10 s each, atomization at 2,600°C for 5 s, and cleaning at 3,000°C for 3 s.

Collection and preparation of the mushroom and soil samples

Mushroom and soil samples were collected from six sites in Slovenia and stored in plastic bags in a freezer at -25°C. Soil was collected to a depth of 15 cm at each place at which mushrooms were taken. The samples were freeze dried at 20°C under a vacuum of 1.33 kPa (10 torr) for 48 h to constant mass. The mushroom caps were separated from the stems and pulverised in a steel mill. After removal of stones and plant materials, the dried soil samples were ground in an agate mill with agate balls until the entire sample had passed through a 1-mm sieve.

Mineralisation of mushrooms

Pieces of dried caps or aliquots of the powdered caps (0.3-0.5 g) were weighed to 0.1 mg into 120-mL Teflon digestion vessels. Concentrated nitric acid (2.0 mL) and 200 μL of an aqueous nickel nitrate solution (1,000 mg Ni/L) were added to each vessel. The vessels were closed. Six of these loaded vessels were placed symmetrically onto the turntable in the microvawe oven. One of the vessels was connected to the pressure monitor. The microwave oven was programmed to give 50% power for 15 min. The vessels were allowed to cool to room temperature, carefully vented in a well ventilated hood by loosening the vent nut, and then opened. Concentrated perchloric acid (200 μ L) was added to each digest. The vessels were closed and the digestion continued at 50% power for 25 min. The vessels were left to cool to room temperature, again vented, and opened. Digests that were not colourless and clear were mixed with 200 μL concentrated perchloric acid and heated again at 50% power for 25 min. The colourless solutions were quantitatively transferred into 10-mL volumetric flasks. The flasks were filled to the mark with NANOpure water.

Mineralisation of soils

Aliquots (0.4-0.5 g) of the dry, sieved soils were weighed to 0.1 mg and placed into the digestion

vessels. To each vessel were added concentrated nitric acid (2.0 mL), concentrated hydrofluoric acid (500 μL), and nickel solution (200 μL). After digestion at 50 % power for 15 min, additional hydrofluoric acid (500 μL) was added and heating continued at 50 % power for 35 min. The colourless solutions were quantitatively transferred into 25-mL volumetric flasks. The flasks were filled to the mark with NANOpure water.

Determination of total arsenic in the digests by standard addition

Aliquots (2.00 mL) of the diluted digests were transferred with Eppendorf pipettes into three 10-mL volumetric flasks. The first flask was filled with NANOpure water to the mark. To the second and third flasks appropriate volumes of the arsenate standard solution were added. The flasks were filled to the mark with NANOpure water. Aliquots (20 $\mu L)$ of these solutions were analysed by GFAAS.

The NIST Reference Standard Material 1566a 'Oyster Tissue' was put through the same procedure as the mushroom caps. Three replicates produced an average arsenic concentration of 13.6 ± 0.7 mg As/kg (90% confidence interval). The certified value is 14.0 ± 1.2 mg As/kg.

RESULTS AND DISCUSSION

All mushroom samples were collected during the autumn of 1991 at six sites in the northeast of Slovenia (Figure 1). Industrial activities that could release arsenic into the environment are generally a long way from the collection sites. Only near sites 1 and 2 (in the vicinty of Maribor) are factories that produce ferro-alloys (FeSi, FeCr, FeSiMg, FeSiCa), calcium carbide, and textiles. As well as the mushrooms, soil samples were also taken.

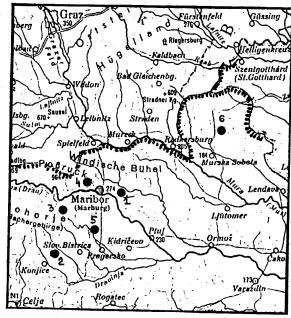


Figure 1 Sites in Slovenia for the collection of mushrooms: 1, Lenart; 2, Vrhole; 3, Areh; 4, Kam. Graba; 5, Fram; 6, Goricko.

The mushrooms cleaned from adhering soil and the soil samples, from which stones and easily recognisable organic material had been removed, were freeze-dried to constant mass and then ground to a powder. Generally, the caps and the stems of the dry mushrooms were separated. Such a separation was not possible with the coral-like *Ramaria botrytris* and *Thelephora terrestris*. Caps of *Boletus cavipes* were further divided into lamellas and the body of the caps.

Total arsenic in caps, stems, and lamellas of mushrooms

Total arsenic was determined by the standard addition method in all caps, in some stems, and in a few lamellas by graphite furnace atomic absorption spectrometry after mineralisation with concentrated nitric acid and further treatment with concentrated perchloric acid in a closed-pressurised microwave system. Under these conditions arsenite is oxidised to arsenate. Methylarsonic acid and dimethylarsinic acid are also converted to arsenate as ascertained through digestion of solutions of these compounds. In the digests, 98% of the arsenic was recovered.

The signals for arsenate produced by the graphite furnace atomic absorption spectrometer are influenced by the concentration of nitric acid and of sodium nitrate in the analysed solutions (Figure 2). To prevent such influences and other interferences (Chakraborti *et al.*, 1980, 1984; Irgolic, 1992) from affecting the results, the standard addition technique employing aqueous solutions of arsenate was used for the quantification of arsenic in the digests. Calibration curves were linear to 2 ng arsenic (injection volume 20 μ L) with a slope of 0.17 absorption units per ng As supplied as arsenate. The 3σ -detection limit for the solutions introduced into the furnace is 0.04 ng As. Because the mass that can be digested should not exceed 0.5 g, the digests were diluted to 10 mL to reduce

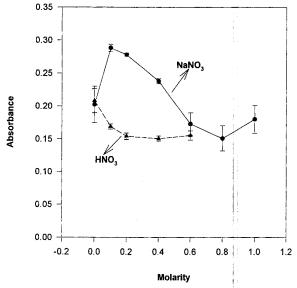


Figure 2 The influence of the concentrations of nitric acid and of sodium nitrate on the absorption signal of 4 ng As (as arsenate).

the nitric acid concentration (nitric acid at high concentrations attacks the surfaces of the graphite tube), and a five-fold dilution is necessitated by the standard addition method, the method detection limit based on dry mushrooms is 0.2 mg As/kg [0.04 ng \times (10 mL/0.02 mL) \times (1000 g/0.5 g) \times 5 \times 10⁻⁶ (mg ng⁻¹) mg kg⁻¹].

Arsenic in caps and stems of L. laccata, L. amethystea and B. cavipes

Caps and stems of Laccaria laccata, Laccaria amethystea, and Boletus cavipes were analysed separately for total arsenic. The arsenic concentrations in the caps were 2–3-times higher than in the stems (Table 1). The woody structure of many stems makes grinding and homogenisation difficult. For this reason, and because the concentrations of arsenic in the stems were low, the stems of all other mushrooms were discarded and total arsenic was determined only in the caps.

Arsenic in lamellas and caps of Boletus cavipes

The lamellas could be easily separated from the caps of a dried specimen of *B. cavipes*. The arsenic concentration in the lamellas $(3.6 \pm 0.4 \text{ mg kg}^{-1}, n = 3, \text{ samples from one specimen})$ was not quite twice the concentration $(2.1 \pm 0.3 \text{ mg kg}^{-1})$ in the lamella-free cap.

Dependence of the arsenic concentrations on the age of *Laccaria laccata* and *L. amethystea*

Mushrooms may accumulate arsenic with time. Older and presumably larger specimens may have higher arsenic concentrations than younger and smaller specimens. Caps of *L. laccata* and *L. amethystea* collected in the same location at the same time were divided into three groups according to their mass. Several low-mass caps had to be combined to obtain approximately 0.4 g for digestion. The concentrations of arsenic (Figure 3). are clearly higher in the heaviest and probably oldest caps (~50 mg kg⁻¹) than in the light and probably younger caps(~30 mg kg⁻¹).

Table 1 Concentrations of arsenic in caps and stems of Laccaria laccata, Laccaria amethystea, and Boletus cavipes.

	Arsenic concentration* (mg kg ⁻¹ dry mass)				
Mushroom	Cap		Stem		
	Body	Lamellas			
Laccaria laccata	20.6 19.8		10.0 10.0		
Laccaria laccata	32.5 33.5		16.2 15.4		
Laccaria laccata	20.6 21.4		10.4 9.6		
Laccaria amethystea	23.0 24.0		8.8 7.5		
Laccaria amethystea	30.9 31.2		12.2 12.5		
Boletus cavipes	2.1 2.3 1.9	3.6 3.8 3.3	1.0 0.8 1.2		

^{*} Duplicate or triplicate analyses of the same cap, stem or lamellas.

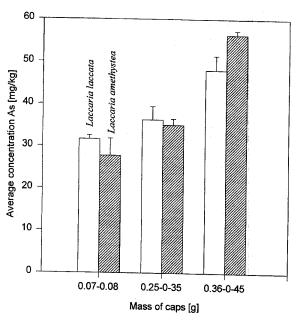


Figure 3 Averages and average deviations (n = 2 or 3) for arsenic concentrations in light (young), medium, and heavy (old) caps of Laccaria amethystea and Laccaria laccata.

Arsenic concentrations in mushroom caps

Among the 36 families and 83 species of mushrooms collected, the following species had arsenic concentrations below the method detection limit of 0.2 mg kg⁻¹ (abbreviations E, I, CE, P, DP explained in footnotes to Table 2):

Albatrellus: confluens (E); Aleuria: aurantia (E); Amanita: citrica (I), spissa (E), rubescens (E), fulva (E), virosa (DP); Armillariella: mellea (E); Calvatia: excipuliformis (E); Cantharellus: tubaeformis (E), lutescens (E), cornucopioides (E); Clitocybe: odora (E), nebularis (CE); Collybia: fusipes (E); Coprinus: micaceus (E), comatus (E); Cortinarius: delibutus (I), armilatus (E), mucosus (E); Geastrum: triplex (I); Hydnum: repandum (E), umbilicatum (E); Hygrocybe: coccinea (E); Hygrophorus: eburneus (E), marzuolus (E); Lactarius: torminosus (P), blennius (CE), salmonicolor (E), chrysorrheus (I), vellereus (I), volemus (E), scrobitulatus (P); Leccinum: crocipodium (E), scabrum (E); Lepista: caespitosa (E), nebularis (E); Lyophyllum: fumosum (E); Marasmius: alliaceus (E); Microlepiota: procera (E); Oudemansiella: radicata (E); Psathyrella: hydrophilla (E); Rozites: caperata (E); Russula: virescens (E), cyanoxantha (E), ochroleuca (E), nigricans (E), lepida (E), olivacea (E), delica (E); Scleroderma: citrinum (E); Sparassis: crispa (E); Suillus: variegatus (E), grevillei (E), bovinus (E); Tricholoma: columbeta (E), sciodes (P), vaccinum (CE), pessundatum (P), portentosum (E); Xerocomus: parasiticus (E), chrysenteron (E), badius (E), subtomentosus (E).

Only 19 species belonging to 13 families had arsenic concentrations above the detection limit (Table 2). The highest concentrations were found in *Laccaria amethystea* (25–128 mg kg⁻¹), *Thelephora terrestris*

(37–39 mg kg⁻¹), Laccaria laccata (11–33 mg kg⁻¹), Boletus cavipes (~11 mg kg⁻¹), and Ramaria botrytis (~10 mg kg⁻¹).

No correlation exists between the concentrations of arsenic and the edibility or degree of toxicity of the mushrooms. All poisonous (P, DP) have low arsenic concentrations (Table 2). Among the 61 species of edible mushrooms, only eleven had arsenic concentrations above the detection limit of 0.2 mg kg⁻¹ (Table 2). The concentration of arsenic in the mushrooms of the same family may vary considerably as shown by specimens of Laccaria amethystea, L. laccata, and L. proxima (Table 2) collected at different sites. How much arsenic is taken up by a mushroom will be influenced by the total arsenic concentration in the soil, by the nature of the arsenic compounds present in the soil, by the properties of the soil (affecting the bioavailability of the arsenic compounds), by the biochemical reactions, through which a mushrooom processes arsenic compounds, and probably likely several other factors.

Arsenic in soils

The dried, ground, and sieved soil samples were digested in a closed pressurised microwave system with concentrated nitric acid and with a mixture (4:1) of concentrated nitric and hydrofluoric acids. Total arsenic was determined in the digests by graphite furnace atomic absorption spectrometry (standard addition). The concentrations of arsenic in the soils based on nitric-acid-only digests are 60-70% of the concentrations based on the HNO₃/HF digests. Consequently, the total arsenic concentrations in soils were calculated based on the results obtained with the HNO₃/HF digests. The arsenic concentrations in the soils, in which the investigated mushrooms grew, ranged from 6.5 to 65 mg kg⁻¹ (Table 3). Among the 28 soils, ten have concentrations of total arsenic higher than 20 mg kg-1. The highest concentrations were found in soils, on which Laccaria amethystea had been growing. Soils not influenced by human activities have arsenic concentrations in the range $0.1-40 \text{ mg kg}^{-1}$ with an average of 5 mg kg⁻¹ (Woolson, 1983; Tanaka, 1989; US Academy of Sciences, 1977). Although the Slovenian soils associated with mushrooms have arsenic concentrations higher than the average, all but two of the concentrations are within the normal range. The highest concentration of arsenic (65.5 mg kg-1) was found in a soil derived from granite in an unpolluted area near Areh on the Pohorje mountain at ~1,200 m altitude. Granitic soils are generally low on arsenic (Kabata-Pedias and Pedias, 1984). Because the soil sample was taken among a patch of growing Laccaria amethystea with high arsenic concentrations in their tissues, the soil could have become enriched with arsenic through decay of the mushrooms. The soil sample probably contained mycelium that might also have high concentrations of arsenic. The mycelium with a lifespan up to 100 years and extending from a few to approximately 100 m² (Ingaro et al., 1992) might collect arsenic from a wider area and concentrate it in the short-lived aerial parts.

Table 2 Concentrations of arsenic in mushroom caps*.

	As (mg kg-1, dry mass)		
 Mushroom (location)	This work**	Literature	
Amanita phaloides (4), (DP) Amanita muscaria (3), (P)	0.8 1.0 0.8 1.2	0.2–1.9 0.1–1.8 0.3–2.1	
Boletus cavipes (4), (E)	12.4 11.9 10.7 11.3		
Cantharellus cibarius (2), (E)	1.8 1.8	0.07-1.3	
Collybia butiracea (5), (E) Collybia peronata (3), (I)	4.2 4.8 1.5 1.9		
Cortinarius xantochephalus (3), (P) Cortinarius xantochephalus (3), (P) Cortinarius trivialis (4), (E)	2.8 3.2 1.1 1.5 0.9 1.0	0.8–2.2 0.8–1.2	
Dermocibes semisangvinea (6), (P) Dermocibes semisangvinea (3), (P)	4.3 4.4 4.8		
Laccaria amethystea (3), (E) Laccaria amethystea (6), (E) Laccaria amethystea (5), (E)	122.6 128.5 55.4 56.8 26.9 26.4 26.5 25.2	6–250 41–182	
Laccaria laccata (5), (E) Laccaria laccata (2), (E) Laccaria laccata (4), (E)	31.2 33.4 32.9 25.9 26.3 26.9 27.4 11.5 11.9	0.4–81	•
Laccaria proxima (3), (E) Laccaria proxima (4), (E) Laccaria proxima (5), (E)	3.9 4.3 2.1 2.5 0.8 1.2	0.2-0.7	
Lepista inversa (4), (E) Lepista nuda (5), (CE) Lepista nuda (1), (CE)	2.6 2.8 3.9 4.5 6.2 5.8	3–5 5.4	
Lyophyllum connatum (4), (E)	2.1 2.5		
Paxilus involutus (2), (P)	5.7 5.9		
Ramaria botrytis (2), (E)	9.6 10.4	1.5	
Sarcodon imbricatus (5), (E)	1.7 1.5		
Thelephora terresris (6), (I)	36.9 37.4 38.6 38.9		

^{*(}E) Edible, (CE) conditionally edible, (I) inedible, (P) poisonous, (DP) deadly poisonous.

Mushroom-soil concentration ratios

The ratios of the arsenic concentrations in the mushrooms and in the soils, [As]_M/[As]_S, provide some information about the mushroom-soil interaction. Among the 19 species of mushrooms listed in Table 3 only three species (Laccaria amethystea, Laccaria laccata, Thelephora terrestris) had mushroom/soil ratios higher than one (range 1.13-2.37). These ratios are characteristic of the places, at which the mushrooms grew, but not necessarily of other sites even when populated by the same mushrooms. The ratios in Table 3 are based on concentrations of total arsenic and not on concentrations of arsenic compounds. The bioavailability will certainly depend on the nature of the arsenic compounds present in the soil and on the soil properties. For example, experiments with the mycelium of Agaricus placomyces clearly showed, that among seven arsenic compounds arsenobetaine and tetramethylarsonium iodide were taken up most efficiently from a potato-dextrose agar medium (Sljekovec et al., 1996).

A correlation between the concentrations of arsenic in

mushroom species and in the soils they grew on is unlikely and was not observed for 17 of the 19 species listed in Table 3. In addition to differences in soil properties and the likely presence in the soils of several arsenic compounds (that determine the bioavailability of arsenic) at different concentration ratios, the individual manner in which mushroom species biochemically process arsenic compounds mitigate against such a correlation. However, good correlations were found for specimens of Laccaria amethystea and Laccaria laccata (Figure 4) collected at different sites. Laccaria amethystea has almost exclusively dimethylarsinic acid in its tissues (Byrne et al., 1991) and L. laccata dimethylarsinic acid and arsenate (Slekovec et al., 1996).

Acknowledgements

The financial support for the purchase of a microwave digestion system by the Jubiläumsfond der Österrreichischen Nationalbank is gratefully acknowledged. We thank Mr A. Poler for the identification of the mushrooms.

^{**}The results refer to the duplicate analysis of different mushroom caps collected at the same location.

Table 3 Concentrations of As in soils and mushroom caps and mushroom-soil concentration ratios

	Mushroom	Total arsenic*(mg kg-1 dry mass) in			
		Mushroom cap	Soil	As _M /As _S	
	Amanita				
	Amanita phaloides (DP)	0.9	6.5	0.14	
	Amanita muscaria (P)	1.0	27.4	0.14	
	Boletus		21.4	0.04	
	Boletus cavipes (E)	11.6	• • •		
	Cantharellus	11.0	34.8	0.33	
	Cantharellus cibarus (E)	1.8	10.3	0.12	
	Cortinarius				
	Cortinarius xantochephalus (P)	3.0	11.6	0.26	
	Cortinarius xantochephalus (P)	1.3	10.4	0.12	
	Cortinarius trivialis (E)	1.0	29.3	0.03	
	Collybia		27.3	0.03	
	Collybia butiracea (E)	4.5	32.6	0.14	
	Collybia peronata (I)	1.7	17.4	0.14	
	Dermocybe	1.,	17.4	0.10	
	Dermocibes semisangvinea (P)	4.2			
	Dermocibes semisangvinea (P)	4.3	6.5	0.66	
		4.6	10.8	0.43	
	Laccaria				
	Laccaria amethystea(E)	125.6	65.4	1.92	
	Laccaria amethystea(E)	56.1	49.5	1.13	
	Laccaria amethystea (E)	26.1	31.0	0.84	
	Laccaria laccata (E)	32.4	23.3	1.39	
	Laccaria laccata (E) Laccaria laccata (E)	26.6	18.9	1.41	
	Laccaria manina (E)	11.7	10.1	1.16	
	Laccaria proxima (E) Laccaria proxima (E)	4.1	18.2	0.22	
	Laccaria proxima (E)	2.3	10.4	0.22	
		1.0	9.8	0.10	
	Lepista				
	Lepista nuda (CE)	4.2	18.2	0.22	
	Lepista inversa (E)	6.0	20.9	0.28	
	Lepista inversa (E)	2.7	9.1	0.29	
	Lyophyllum connatum (E)	2.3	26.5	0.09	
	Paxilus involutus (P)	5.8	7.8	0.09 0.74	
	Ramaria botrytis (E)	10.0	11.3	0.74	
	Sarcodon imbricatus (E)	1.9	19.2		
	Thelephora terrestris (I)	38.0	16.0	0.10 2.37	

^{*}Values listed are average concentrations for mushroom caps from Table 2.

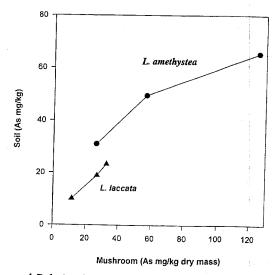


Figure 4 Relationship between arsenic concentrations in soils and in mushroom caps for Laccaria amethystea and Laccaria laccata.

REFERENCES

Byrne, A.R., Ravnik V. and Kosta, L. 1976. Trace element concentrations in higher fungi. Sci.Tot.Environ., 6, 65-78.

Byrne, A.R. and Tušek-Znidaric, M. 1983. Arsenic accumulation in the mushroom *Laccaria amethystina*. *Chemosphere*, **12**, 1113–1117.

Byrne, A.R., Tušek-Znidaric, M., Puri, B.K.and Irgolic, K.J. 1991. Studies of the uptake and binding of trace metals in fungi; Part II. Arsenic compounds in *Laccaria amethystina*. *Appl. Organomet. Chem.*, **5**, 25–32.

Chakraborti, D., De Jonghe, W. and Adams, F. 1980. The determination of arsenic by electrothermal atomic absorption spectrometry with a graphite furnace. Part 1. Difficulties in the direct determination. *Anal. Chim. Acta*, 119, 331–340.

Chakraborti, D., Irgolic, K. J. and Adams, F. 1984. Matrix interferences in arsenic determinations by graphite furnace atomic absorption spectrometry: Recommendations for the determination of arsenic in water samples. *Int. J. Environ. Anal. Chem.*, 17, 241–256.

- Ingaro, G., Belloni, P. and Santaroni, G.P. 1992. Mushrooms as biological monitors of trace elements in the environment. *J. Radioanal. Nucl. Chem.*, **161**, 113–120.
- Irgolic, K. J. 1992. Arsenic. In: Stoeppler, M. (ed.), *Hazardous Metals in the Environment*, pp. 287-350. Elsevier, Amsterdam.
- Kabata-Pendias, A. and Pendias, H. 1984. *Trace Elements in Soils and Plants*, pp. 171–177. CRC Press, Boca Raton, Florida, USA.
- Kalac P., Burda, J. and Staškova, I. 1991. Concentration of lead, cadmium, mercury and copper in mushrooms in the vicinity of a lead smelter. *Sci.Tot. Environ.*, **105**, 109–119.
- Slejkovec, Z., Byrne, A. R., Goessler, W., Kuehnelt, D., Irgolic, K. J. and Pohleven, F., 1996. Methylation of Arsenic in *Pleurotus sp.* and *Agaraicus placomyces*. Acta Chim. Sloven. 43, 269–283 (1996).
- Slekovec, M., Goessler, W. and Irgolic, K. J., 1996; in preparation.
- Stijve, T., 1977. Selenium content in mushrooms. Z. Lebensm. Unters. Forsch., 164, 201–203.
- Stijve, T., Vellinga, E. C. and Herrmann, A. 1990. Arsenic

- accumulation in some higher fungi. Persoonia, 14, 161-166.
- Stijve, T. and Bourgui, B. 1991. Arsenic in edible mushrooms. *Deutsch. Lebensm. Rundsch.*, **10**, 307–310.
- Tanaka, T. 1989. Distribution of arsenic in the natural environment with emphasis on rocks and soils. Appl. Organomet. Chem., 2, 283–295.
- US Academy of Sciences, 1977. p. 18, *Arsenic*, Washington, D. C.
- Vetter, J. 1989. Vergleichende Untersuchung des Mineralstoffgehaltes der Gattungen Agaricus (Champignon) und Pleurotus (Austernseitling). Z. Lebensm. Unters. Forsch., 189, 346–350.
- Vetter, J. 1990. Mineral element content of edible and poisonous macrofungi. *Acta Aliment.*, 19, 27–40.
- Woolson, E. A. 1983. Emissions, Cycling and Effects of Arsenic in Soil Ecosystems. In: Fowler, B. E. (ed.), Biological and Environmental Effects of Arsenic, pp. 51–139, Elsevier, Amsterdam.

Paper received 29 July; accepted 22 August 1996.