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Concentrations of mercury, cadmium, lead and copper in fruiting bodies of edible mushrooms in an emission area of a copper smelter and a mercury smelter

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Abstract

Four metals were determined by AAS techniques in 56 samples of 23 wild mushroom species collected in a heavily polluted area in eastern Slovakia in 1997 and 1998. The area has been contaminated from historical polymetallic ores mining and smelting and by emissions from a mercury smelter between 1969 and 1993 and from a copper smelter since 1951. No significant differences in metal concentrations ($P < 0.05$) were found in four species when comparing the periods 1992–1993 and 1997–1998. Considerable contamination of most species was observed mainly for mercury and cadmium. The highest levels of mercury, up to 50 mg kg^{-1} dry matter, were found in *Boletus reticulatus*, *Lycoperdon perlatum* and *Marasmius oreades*, and of cadmium up to 20 mg kg^{-1} dry matter in *Xerocomus chrysenteron* and *Lycoperdon perlatum*. The latter species also had extremely high lead and copper concentrations in hundreds of milligrams per kilogram dry matter. Concentrations of mercury and copper in caps of four *Boletaceae* species were significantly ($P < 0.05$) higher than those in stipes.

Keywords: Edible mushrooms; Heavy metals; Mercury; Cadmium; Lead; Copper; Mercury smelter vicinity; Copper smelter vicinity

1. Introduction

Wild mushrooms have been a very popular delicacy especially in some central European countries and yearly consumption may exceed 10 kg for some individuals. Fruiting bodies of many mushroom species accumulate considerable levels of mercury, cadmium, lead, and copper. The element concentrations are primarily species-dependent. Numerous literature data were reviewed (Seeger, 1982; Kalač and Svoboda, 1998; Michelot

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et al., 1998). The reported metal concentrations differ over very wide ranges within a mushroom species and knowledge on factors affecting accumulation rates has been very limited. There has been a consensus that mushroom fruiting bodies are not the appropriate bioindicator of environmental contamination by heavy metals. However, in heavily polluted areas the observed metal concentrations have been considerably elevated.

In our previous study (Kalač et al., 1996) we were interested in mushrooms collected from an area contaminated by emissions from a mercury smelter and a copper smelter between 1990 and 1993. Nevertheless, the mercury smelter was closed in 1993 and the copper smelter decreased its metal emissions during the 1990s. The aims of our present work are to compare levels of four metals in mushroom fruiting bodies in a selected

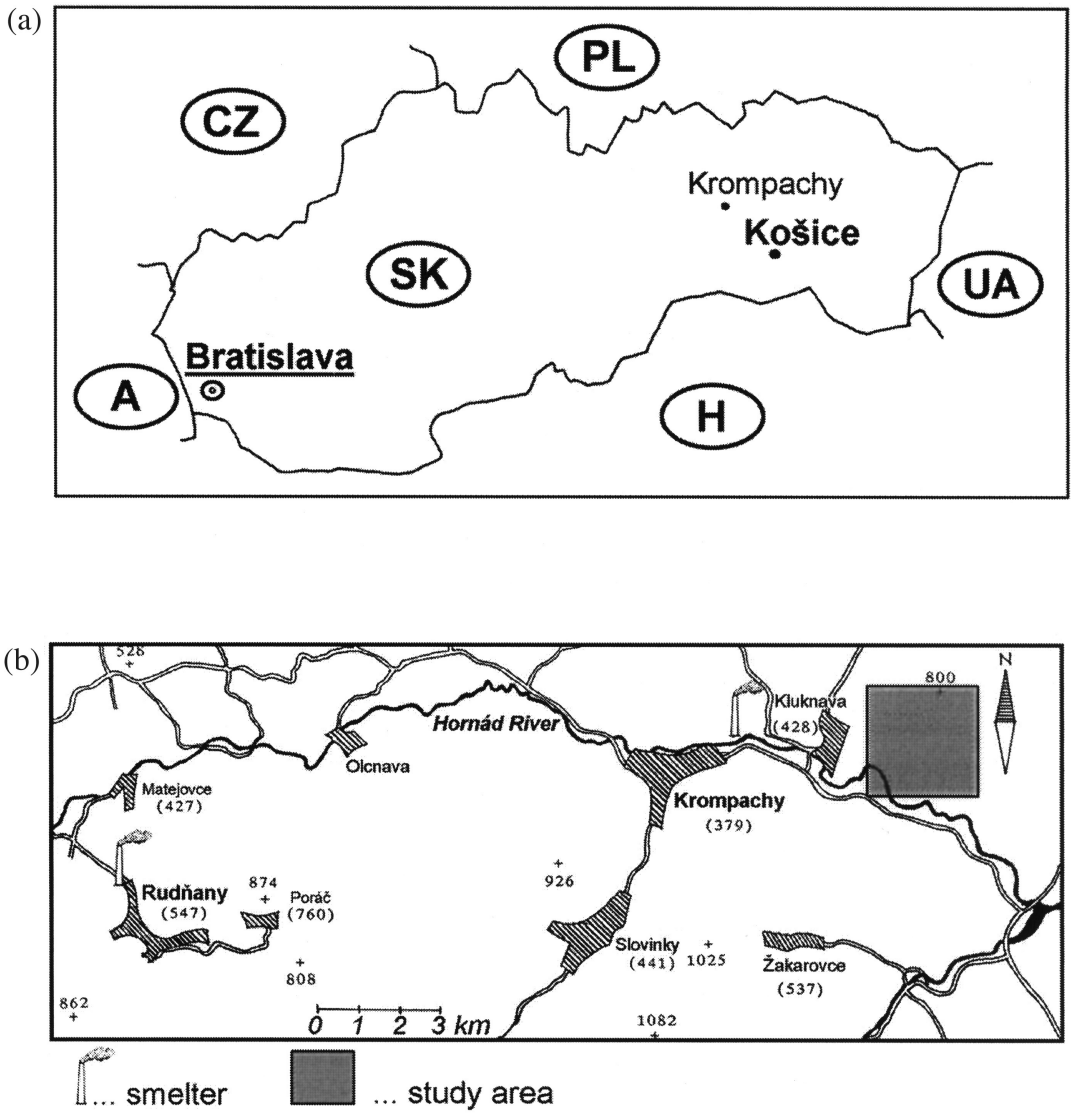

Fig. 1. Maps of study area.

emission area in during the periods 1992–1993 and 1997–1998 and to survey further edible mushroom species for the metal concentrations.

2. Materials and methods

The study was carried out in eastern Slovakia, near the village Kluknava situated 30 km northwest of Košice (Fig. 1a). The observed area of 2×2 km has been contaminated by emissions from the adjacent copper smelter at Krompachy and the mercury smelter at Rudňany 15 km apart (Fig. 1b). Both smelters are located in the Slovak ore-yielding mountains area, where polymetallic ores have been exploited since the Bronze Age. Iron, copper, and silver were produced with a large development during the Middle Ages.

Small-scale copper smelters have operated in the Krompachy region for several centuries. The present smelter has been operating since 1951 and it has processed ore concentrates and recycled copper materials. Annual copper emissions from its stack height of 200 m have been between 40 and 55 tons, lead emissions decreased from some 50 t to 20 t since 1990.

Mercury was produced from a sulphide concentrate in Rudňany at a composite plant since 1963 and the smelter since 1969. Annual emissions were approximately 4 t of mercury. Both plants were closed in 1993. However, a limited release of contaminated dust from spoil heaps continues. Nevertheless, many thousands of tons of mercury are estimated to have been released into the environment during seven centuries of polymetallic ores mining and smelting in the region.

Both smelters are situated in valleys of submontane landscape covered with forests. The prevailing winds are north-westerly and westerly. The observed area (Fig. 1b) is formed by four forested valleys with orientation from north-east to southwest. Spruce (*Picea abies*) is the prevailing tree in coniferous and mixed forests at an altitude between 400 and 800 m above sea level. Exposure of the area to metal pollution for centuries is reflected in high soil contamination. Metal concentrations vary widely in the forest soils between 0.01 and 0.32, 0.25 and 10, 15 and 2200 and 10

Table 1
Metal concentrations (mg kg^{-1} dry matter) in four species given as 1997–1998/1992–1993 data and background mean values from several European countries

Metal	Parameter	*Xerocomus badius* (M)[a]	*Leccinum rufum* (M)[a]	*Leccinum griseum* (M)[a]	*Macrolepiota procera* (S)[a]
	n	3/4	5/3	3/3	4/6
Hg	x	3.95/4.77	2.41/4.85	1.92/2.36	40.6/31.3
	S_x	2.38/3.62	1.25/4.30	0.33/1.53	32.1/31.0
	Background	0.61[b]	–	0.80[e]	5.03[b], 2.91[d]
Cd	x	1.15/5.85	0.19/1.87	5.01/4.44	7.72/11.2
	S_x	0.41/4.56	0.10/2.01	3.64/2.90	7.57/13.2
	Background	0.89[b]	–	1.0[f]	1.82[b], 1.9[c]
Pb	x	1.39/4.04	3.92/1.04	1.58/3.83	62.4/29.9
	S_x	0.77/2.22	4.08/1.33	0.54/1.76	39.9/34.4
	Background	1.26[b]	–	–	4.87[b], 7.4[c]
Cu	x	41.4/42.9	91.6/32.2	36.1/52.2	324/228
	S_x	1.8/10.4	93.4/9.9	8.6/22.3	148/60.2
	Background	39.8[b]	–	–	155[b], 200[c]

[a] M, mycorrhizal species; S, saprophytic species.
[b] Bohemia (Kalač et al., 1989a,b; Kalač and Šlapetová, 1997).
[c] Sweden (Jorhem and Sundström, 1995).
[d] Hungary (Vetter and Berta, 1997).
[e] Bavaria (Seeger, 1976a).
[f] Bavaria (Seeger, 1978).

Table 2
Metal concentrations (mg kg^{-1} dry matter) in 19 mushroom species and background mean levels from several European countries

Species	Hg		Cd		Pb		Cu	
	Area	Background	Area	Background	Area	Background	Area	Background
Boletus reticulatus (*B. aestivalis*) (M)[i]	55.3	2.39[a], 2.20[g]	6.81	2.50[a] 1.8[h]	6.0	1.48[a]	90.4	27.3[a]
Xerocomus chrysenteron (M)	2.81, 5.7	0.66[a] 0.34[f] 0.56[g]	16.5, 19.2	1.35[a] 2.1[h]	1.03, 3.34	1.12[a]	36.4, 46.1	32.1[a] 31.5[b]
X. subtomentosus (M)	2.97	0.57[a] 0.33[g]	0.45	1.13[a] 0.5[h]	0.93	0.42[a]	35.0	14.9[a] 41.9[b]
Boletellus fragilipes (M)	2.49, 1.86	–	1.55, 1.78	–	2.84, 1.97	–	31.3, 32.2	–
Leccinum scabrum (M)	0.68, 1.92	0.28	0.45, 2.96	–	0.23, 13.1	–	22.1, 45.5	21.8[b]
L. quercinum (M)	2.69	–	0.47	–	5.82	–	50.5	–
Suillus luteus (M)	5.35, 11.3	0.15[g]	1.58, 0.75	0.13[e] 0.2[h]	5.47, 4.46	0.24[e]	66.5, 52.3	7.9[e]
Cantharellus cibarius (M)	0.60, 0.33, 0.58	0.07[a] 0.02[c] 0.11[g]	1.43, 0.57, 0.91	0.29[a] 0.5[c] 0.84[e]	3.13, 12.7, 9.11	1.58[a] 0.7[c] 0.84[e]	99.6, 81.7, 85.2	38.8[a] 40[b] 46[e]
Hydnum repandum (M)	10.5, 9.07, 9.29	0.9[d] 0.6[g]	0.37, 0.32, 0.52	0.3[c] 0.2[d] 0.4[h]	1.42, 1.10, 2.55	0.9[c] 1.3[d]	32.2, 24.3, 24.0	35[d]
Russula aeruginea (M)	5.71	0.19[a] 0.67[g]	0.99	0.55[a] 0.2[h]	2.58	3.76[a]	50.7	33.4[a]
R. lepida (M)	4.0	–	0.56	–	1.93	–	47.3	45[b]
R. vesca (M)	17.6	0.62[g]	0.34	9.0[h]	1.12	–	52.4	58.7[b]
R. paludosa (M)	0.04, 0.11	–	1.45, 1.20	–	1.89, 1.52	–	15.8, 14.2	–
R. polychroma (M)	2.15	–	1.67, 7.49	–	17.2, 7.77	–	75.3, 54.6	–
Lactarius deliciosus (M)	4.79, 3.97	0.53[f] 0.35[g]	2.77, 3.16	5.7[h]	1.79, 4.19	–	34.5, 22.6	16.9[b]
L. pinicola (M)	3.08	–	2.9	–	2.01	–	23.8	–
Marasmius oreades (S)	33.0	1.7[c] 8.5[d] 3.0[g]	9.41	0.3[c] 1.4[h] 0.9[d]	28.7	1.8[c] 1.0[d]	263	81[b] 120[d]
Ramaria aurea (M)	11.2	0.27[g]	4.57	1.9[h]	16.8	–	86.8	–
Lycoperdon perlatum (S)	22.9, 44.5	2.9[f] 3.3[g]	16.5, 10.9	2.1[h]	223, 145	–	505, 347	–

[a]Bohemia (Kalač et al., 1989a,b; Kalač and Šlapetová, 1997).
[b]Austria (Mutsch et al., 1979).
[c]Finland (Kuusi et al., 1981).
[d]Danmark (Andersen et al., 1982).
[e]Sweden (Jorhem and Sundström, 1995).
[f]Hungary (Vetter and Berta, 1997).
[g]Bavaria (Seeger, 1976a).
[h]Bavaria (Seeger, 1978).
[i]M, mycorrhizal species; S, saprophytic species.

and 730 mg kg^{-1} for mercury, cadmium, lead, and copper, respectively.

For a sample, one to four complete fruiting bodies of a species were collected from a place of diameter up to 5 m. The prevailing nutritional strategy of the individual mushroom species (saprophytic or mycorrhizal) (Keizer, 1998) is given in Tables 1–3. Fruiting bodies were cleaned by a stainless knife from all surface contamination in a manner usual for the preparation of mushroom for culinary purposes. No washing or caps peeling was used. Fruiting bodies were sliced and dried at ambient temperature.

Sample homogenization and ashing, and cadmium, lead and copper determination by atomic absorption spectrometry measurements, were the same as described in our previous work (Kalač et al., 1996). Mercury was determined in the homogenized dried samples (0.1–0.2 g) using a cold-vapour AAS analyzer (AMA 254, Altec Prague) with a detection limit of 0.5 ng g^{-1}. Mean differences between duplicates were up to 5%. Blank background levels were below the detection limits for all determined elements. The green alga *Chlorella kessleri,* P-ACHK (Institute of Radioecology and Applied Nuclear Techniques, Košice, Slovakia) was used as the reference material. Differences between experimentally determined and certified concentrations were up to 2% for mercury and up to 5% for the other metals.

Differences between metal mean concentrations in the periods 1992–1993 and 1997–1998 were tested by *t*-test and regression analysis was used for testing of differences in metal concentrations in caps and stipes.

3. Results and discussion

A possible decrease in the metal levels in fruiting bodies following closure of the mercury smelter in 1993 and a decrease of copper smelter emissions since the start of the 1990s was tested for four mushroom species with at least three samples from the observed area from both periods 1992–1993 and 1997–1998. Results are given in Table 1. Differences of mean values tested by *t*-test are not statistically significant at level $P < 0.05$. However, the limited number of samples and the great variance of metal concentrations must be taken into consideration.

Metal concentrations in 19 mushroom species with only one, two or three samples are given in Table 2. Mean values, published for mushrooms collected from unpolluted or mildly polluted areas of several European countries are shown for comparison as background levels. Differences between experimentally determined and published background concentrations were not statistically tested due to the low number of samples. Unfortunately, information on background levels is lacking for many species. As can be seen from

Table 3
Distribution of metals within fruiting bodies in four mycorrhizal Boletaceae species

Species	Stipe (mg kg^{-1} dry matter)				Cap (relative conc., stipe = 1.0)			
	Hg	Cd	Pb	Cu	Hg	Cd	Pb	Cu
Boletus edulis	29.1	7.50	1.53	62.7	1.84	3.20	0.55	2.09
	10.3	0.89	0.78	23.0	1.83	3.89	1.17	1.98
Boletus reticulatus	17.9	2.82	1.24	72.4	1.93	3.37	0.62	0.98
	20.3	9.60	1.17	71.8	1.45	2.48	1.97	2.26
	13.6	1.54	0.75	51.0	1.54	5.13	2.80	1.90
	23.5	0.81	0.40	27.5	1.70	2.16	0.60	2.17
Leccinum scabrum	1.32	1.23	1.94	25.4	2.86	2.08	2.04	2.69
	1.95	2.73	1.09	30.7	2.19	3.85	0.83	2.15
	1.56	1.49	0.46	17.1	2.08	1.82	2.13	2.06
Leccinum griseum	1.09	1.43	1.44	28.2	1.96	1.50	1.17	1.79

Tables 1 and 2, mercury, followed by cadmium, show the highest level of fruiting bodies contamination as compared to background, while for copper the concentrations are comparable for most species.

Within the observed species, *Macrolepiota procera, Boletus* spp., *Marasmius oreades* and *Lycoperdon perlatum* are known as mercury accumulators. Similarly, *Boletus* spp. accumulate cadmium, *Macrolepiota procera* lead and *Macrolepiota procera* and *Marasmius oreades* copper. Their accumulation ability was illustrated by very high levels of those metals in all these species from the observed area. Moreover, high accumulation of mercury was also observed in *Suillus luteus*, *Hydnum repandum, Russula vesca, Ramaria aurea* and *Lycoperdon perlatum*, that of cadmium in widely consumed *Xerocomus chrysenteron* and in *Lycoperdon perlatum*, and that for lead and copper in *Lycoperdon perlatum* and in *Marasmius oreades*.

Different soil contamination with metals has been only one of numerous factors affecting metal levels in fruiting bodies. There are two important factors: the age of mycelium and the interval between fructifications. Direct contamination of fruiting bodies by emissions seems to be of less importance due to the short life span of only some 10–14 days development. Some species are typical accumulators (Tyler, 1980; Seeger, 1982; Kalač and Svoboda, 1998; Michelot et al., 1998). As concluded in a review (Wondratschek and Röder, 1993), no mushroom species can be considered as a precise indicator of environmental pollution with heavy metals but fruiting bodies can be useful for distinguishing between polluted and unpolluted areas.

From the toxicological point of view, many of the observed samples exceeded Czech statutory limits for wild growing mushrooms 5.0, 2.0, 10.0 and 80.0 mg kg^{-1} dry matter for mercury, cadmium, lead and copper, respectively, valid since 1999. Thus, some mushroom species from the polluted area should not be consumed at all.

It has been known that most metals are distributed unevenly within the fruiting body with higher concentrations in caps than in stipes. Results for four species are given in Table 3. Differences between metal concentrations in caps and stipes are significant at $P < 0.05$ only for mercury and copper. Comparable results were observed in different mushroom species from unpolluted areas for mercury (Seeger, 1976b; Falandysz and Chwir, 1997), cadmium (Melgar et al., 1998) and lead (García et al., 1998). Thus, similar distribution seems to occur also in the contaminated fruiting bodies.

References

Andersen A, Lykke S-E, Lange M, Bech K. Trace elements in edible mushrooms. Publ 68. Danmark: Stat Levnedsmiddelinst, 1982:1–29 (in Danish).

Falandysz J, Chwir A. The concentrations and bioconcentration factors of mercury in mushrooms from the Mierzeja Wiślana sand-bar, Northern Poland. Sci Total Environ 1997;203:221–228.

García MA, Alonso J, Fernández MI, Melgar MJ. Lead content in edible wild mushrooms in Northwest Spain as indicator of environmental contamination. Arch Environ Contam Toxicol 1998;34:330–335.

Jorhem L, Sundström B. Levels of some trace elements in edible fungi. Z Lebensm Unters Forsch 1995;201:311–316.

Kalač P, Šlapetová M. Mercury contents in fruiting bodies of wild growing edible mushrooms. Potrav Vědy 1997;15: 405–410.

Kalač P, Svoboda L. Heavy metals in edible mushrooms. Czech J Food Sci, 1998;16:110–116 (in Czech).

Kalač P, Nižnanská M, Bevilaqua D, Stašková I. Concentrations of mercury, copper, cadmium and lead in fruiting bodies of edible mushrooms in the vicinity of a mercury smelter and a copper smelter. Sci Total Environ 1996; 177:251–258.

Kalač P, Wittingerová M, Stašková I. The contents of seven biogenic trace elements in edible mushrooms. Potrav Vědy 1989a;7:131–136 (in Czech).

Kalač P, Wittingerová M, Stašková I, Šimák M, Bastl J. Contents of mercury, lead and cadmium in mushrooms. Čs Hyg 1989b;34:568–576 (in Czech).

Keizer GJ. Mushrooms encyclopedia. Prague: REBO Prod, 1998:1–288 (in Czech).

Kuusi T, Laaksovirta K, Liukkonen-Lilja H, Lodenius M, Piepponen S. Lead, cadmium, and mercury contents of fungi in the Helsinki area and in unpolluted control areas. Z Lebensm Unters Forsch 1981;173:261–267.

Melgar MJ, Alonso J, Pérez-López M, García MA. Influence of some factors in toxicity and accumulation of cadmium from edible wild macrofungi in NW Spain. J Environ Sci Health 1998;B33:439–455.

Michelot D, Siobud E, Dore JC, Viel C, Poirier F. Update of metal content profiles in mushrooms — toxicological impli-

cations and tentative approach to the mechanisms of bioaccumulation. Toxicon 1998;36:1997–2012.

Mutsch F, Horak O, Kinzel H. Spurenelemente in höheren Pilzen. Z Pflanzenphysiol, 1979;94:1–10 (in German).

Seeger R. Quecksilbergehalt der Pilze. Z Lebensm Unters Forsch, 1976a;160:303–312 (in German).

Seeger R. Die Verteilung des Quecksilbers in den Fruchtkörpern von Steinpilzen und Champignons. Z Lebensm Unters Forsch, 1976b;161:115–117 (in German).

Seeger R. Cadmium in Pilzen. Z Lebensm Unters Forsch, 1978;166:23–34 (in German).

Seeger R. Toxische Schwermetalle in Pilzen. Dtsch Apoth Z, 1982;122:1835–1844 (in German).

Tyler G. Metals in sporophores of basidiomycetes. Trans Br Mycol Soc 1980;74:41–49.

Vetter J, Berta E. Mercury content of some wild edible mushrooms. Z Lebensm Unters Forsch 1997;205: 316–320.

Wondratschek I, Röder U. Monitoring of heavy metals in soils by higher fungi. In: Markert B, editor. Plants as biomonitors. Indicators for heavy metals in the terrestrial environment. Weinheim: VCH, 1993:345–363.