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The Concentrations and Bioconcentration Factors of Copper and Zinc in Edible

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Mushrooms

Abstract. Copper and zinc contents have been determined in up to 28 species of edible mushrooms from different sites in the province of Lugo (NW Spain). Two hundred thirty-eight collected samples were analyzed by an anodic stripping voltammetric technique using a drop mercury as the working electrode. The results showed that the element concentrations were species-dependent, and the highest metal levels corresponded to the following species: Calvatia utriformis (235.5 mg Cu/kg), Macrolepiota procera (217.8 mg Cu/kg), and Agaricus macrosporus (217.7 mg Cu/kg) and Calvatia utriformis (265.8 mg Zn/kg), Lactarius delicious (231.0 mg Zn/kg), and Agaricus macrosporus (221.3 mg Zn/kg) for Cu and Zn, respectively. All mushroom species bioaccumulated copper and zinc. Nevertheless, some individual samples of the species, such as Hydnum repandum, Cantharellus cibarius, and Coprinus comatus, were bioexclusors (BCF < 1). The hymenophore in mushrooms showed higher mean metal levels than the rest of the fruit bodies, with statistically significant differences. The copper and zinc concentrations were compared to literature data and levels set by legislation. It can be concluded that the consumption of these mushrooms cannot be considered a toxicological risk, and they provide an important nutritional requirement to the diet.

Toxicological and environmental studies have prompted interest in the determination of toxic elements in food. Mushrooms surely do not constitute a significant portion of the human diet, but the consumption of wild and cultivated mushrooms has become increasingly popular in recent years. Galicia (Spain) has a large edible mushroom potential and is becoming an important exporter of wild mushrooms. Though commercial sources may be limited to a few varieties, wild ones provide thousands from which to choose.

There are several reasons why mushroom poisoning can occur among people, and the high heavy metal concentrations in some edible fungi is a known source as chronic poisoning (Tüzen *et al.* 1998a). Higher fungi are able to bioconcentrate or

exclude specific metal ions, and analyzing the fruit body-to-soil ratios of metals it has been found the bioconcentration factor (BCF). The reason of the store or exclusion of the elements present in the ground has been referred to the difference between species, to their behavior (parasitic, saprophytic, or mycorrhizal), and to the environmental contamination, but it has not always been possible to decide on bioaccumulation or bioexclusion only for these reasons (Romeo and del Signore 1994). Many species of mushrooms possess the ability to effectively take up and accumulate heavy metals (Kojo and Lodenius 1989; Kalač *et al.* 1991; Falandysz *et al.* 1993, 1995; Lodenius 1994; Melgar *et al.* 1998; Garcia *et al.* 1998; Alonso *et al.* 2000; Kalač and Svoboda 2000).

Copper is an essential element as nutrient metal for humans, and animal livers are the major contribution to dietary intake. The mean daily intake is 12.5 μ g/kg of body weight (WHO 1996) and the acceptable daily intake (ADI) is 500 μ g/kg of body weight per day (WHO 1982). As with copper, zinc is an essential metal for the correct function of various enzyme systems. In food, the major contributors to the diet are meat and its products, from which zinc is readily absorbed. For adults, intakes of zinc from food and other sources are 0.3 mg/kg of body weight per day, and the ADI is 1 mg/kg of body weight per day (WHO 1982). Some Cu and Zn salts exhibited a protective effect toward cancer; nevertheless, they appear also to be a potential carcinogen, as some of them can accelerate the growth of experimental tumors (Concon 1988; Doyle *et al.* 1994).

The fruit bodies of mushrooms accumulate remarkably high concentrations of Cu and Zn (Byrne *et al.* 1976; Tyler 1980, 1982; Quinche 1980, 1987; Fagot *et al.* 1988; Sugahara *et al.* 1990; Vetter 1989, 1990, 1994; Źródlowski 1995; Vetter *et al.* 1997; Falandysz *et al.* 1993; Kalač *et al.* 1989, 1991, 1996; Jorhem and Sundström 1995; Pop and Nicoara 1996; Kalač and Svoboda 1998; Tüzen *et al.* 1998b; Sesli and Tüzen 1999). It can be due to the influence of some environmental factors (metal concentrations in the soil, pH, organic matter, and contamination by atmospheric deposition) and fungal factors (fungal structure, biochemical composition, decomposition activity, development of mycelium and fruit bodies, morphological portion).

The aim of the present work was to provide the accumulation capacity (bioconcentration or bioexclusion) of copper and zinc

in fruit bodies of some edible mushrooms (cultivated and wild species) collected in the province of Lugo (Galicia, NW Spain), in relation to some factors: substrate (metal content, acidity, and organic matter content), species and ecology (mycorrhizal and saprophite), and morphological portion (hymenophore and rest of the fruit body). Finally, it was also intended to evaluate the contribution of mushrooms to the daily intake of these trace metals.

Materials and Methods

Sampling

Copper and zinc levels in 238 samples of edible mushrooms have been analyzed in 28 species of *Basiodiomycetes* fungi: 13 saprophites (*Agaricus macrosporus*, *Agaricus campestris*, *Agaricus silvicola*, *Calvatia utriformis*, *Clitocybe nebularis*, *Coprinus comatus*, *Lepista nuda*, *Macrolepiota procera*, *Marasmius oreades*, *Fistulina hepatica*, *Agaricus bisporus*, *Agrocybe cylindrica*, and *Pleorotus ostreatus*) and 15 mycorrhizals (*Amanita rubescens*, *Boletus aereus*, *Boletus edulis*, *Boletus aestivalis*, *Boletus pinophilus*, *Cantharellus cibarius*, *Hydnum repandum*, *Lactarius deliciosus*, *Leccinum scabrum*, *Russula cyanoxantha*, *Tricholoma equestre*, *Tricholoma columbetta*, *Tricholoma portentosum*, *Xerocomus badius*, and *Xerocomus chrysenteron*). These species were selected in relation to edible quality, commercialization, and frequency in the areas of the study. These were collected in the province of Lugo (NW Spain) in three different areas: urban, pastureland, and forest areas (Figure 1).

Simultaneously with mushrooms, soil samples of forest upper soil horizon (0-10 cm), after removing superficial layer of organic detritus) were also collected at appropriate sampling places.

Mushroom samples were cleaned (not washed), cut, and separated in two portions (Hawksworth *et al.* 1995): the hymenophore (H) (lamellas in the species of genus *Agaricus*, *Amanita*, *Cantharellus*, *Clitocybe*, *Coprinus*, *Lactarius*, *Lepista*, *Macrolepiota*, *Russula*, and *Tricholoma* and tubes and porus in the species of genus *Boletus* and *Xerocomus*) and the rest of the fruit body (RFB) (the cap, except hymenophore, and the stalk), homogenized, and dried at 110°C for 6 h. Aproximately 3-g aliquots of homogenized dry mushrooms were placed in a porcelain crucible and ashed in an oven at 430°C for 8 h (depending on the species, for a complete mineralization). The filtered product was transferred into a 25-ml volumetric flask making up the level with 0.1 N HCl. All samples were run in triplicate.

Soil samples were dried at room temperature. One gram of soil was heated at 40° C, and, to obtain all Cu and Zn content (both bio- and not bioavailable), the sample digestion was performed using a mixture of HCl:HNO₃ (3:1). After digestion, it was again heated up to 105° C for 90 min, filtered, and brought to a volume of 50 ml Milli-Q water.

Analysis

Contents of copper and zinc in mushrooms and soils were determined employing an anodic stripping voltammetric technique (ASV), with drop mercury as the working electrode, using a Processor VA 693 with Stand VA 647.

The electrolysis was carried out in electrolytical cell, and the analytical conditions were:

- De-aeration time, 180 s
- Accumulation potential, -1,500 mV
- · Accumulation time, 120 s
- Voltammetric sweep, from -1,500 mV to 50 mV

- Sweep rate, 20 mV/s
- Pulse amplitude, 50 mV

The peak voltage for Cu was located around -100 mV and for Zn around -600 mV (Metrohm 1991). The detection limit was 0.990 μ g/L for Cu and 0.738 μ g/L for Zn.

Precision and reproducibility of the method were determined by analyzing 12 replicates of one representative sample and calculating the coefficient of variation, which was 4.15% for Cu and 1.23% for Zn. According to these results, the method can be considered reproducible and precise.

The accuracy of the method was carried out by means of the study of analytical recovery. The mean recovery was 89.26% for Cu and 94.39% for Zn. The epiphytic lichen *Evernia prunastri (L.). Ach* (IAEA-336) was used as the reference material. The recovery of copper was 90.28% and of zinc 97.4%.

The concentration of Cu and Zn in the samples was evaluated by means of standard additions. Metal levels in the samples were calculated by the following formula: mg metal/kg dry weight = $(A\ V)/W$; where $A=\mu g/L$ of metals, V= dilution volume of sample, L, and W= dry weight of sample, g. Heavy metal concentrations were expressed as mg/kg dry weight (mg/kg DW)

Some samples were confirmed using an atomic absorption spectrophotometer (AAS) with graphite furnace, model Z-8100 Polarized Zeeman Hitachi. Zeeman background correction was used. Analytical conditions were: Cu lamp, wavelength 324.8 nm, slit 1.3 nm; Zn lamp, wavelength 213.9 nm, slit 1.3 nm.

Results and Discussion

The results showed that the element concentrations were primarily species-dependent, and it has been rather difficult to determine the effects of environmental factors on the concentrations of elements. The amounts of trace element contents are related to species of mushrooms, collecting site of the sample, age of fruit bodies and mycelium, and distance from the source of pollution. In this work, at least four factors could be affect heavy metal concentrations of the edible mushrooms: species, ecology, morphological portion, and soil characters, such as metal levels, pH, and organic matter. These factors influence the metal concentrations and the BCFs, as higher fungi are able to bioconcentrate (BCF > 1) or exclude (BCF < 1) specific metal ions.

The heavy metal concentrations (mg/kg DW) of the edible mushrooms are given in Table 1, where samples number (n), portions, mean concentrations, standard deviations, BCFs, and coefficient of Pearson correlation (r) are indicated.

Species and Ecology

In general, a good correlation between total soil content and fungi uptake has been observed because of the wide area covered by the mycelia and the symbiotic process.

The copper content of the samples (Figure 2) varied a wide range (*P. ostreatus* and *L. deliciosus* contained 26.28 and 32.62 mg Cu/kg, respectively, and *C. utriformis* 251.9 mg Cu/kg), but many species may accumulate it selectively, for example, *C. utriformis*, *A. macrosporus*, and *M. procera*, which presented the highest contents. These levels have been earlier found by Byrne *et al.* (1976) and Vetter (1990). Saprophytic species showed higher mean levels of cooper than mycorrhizal ones

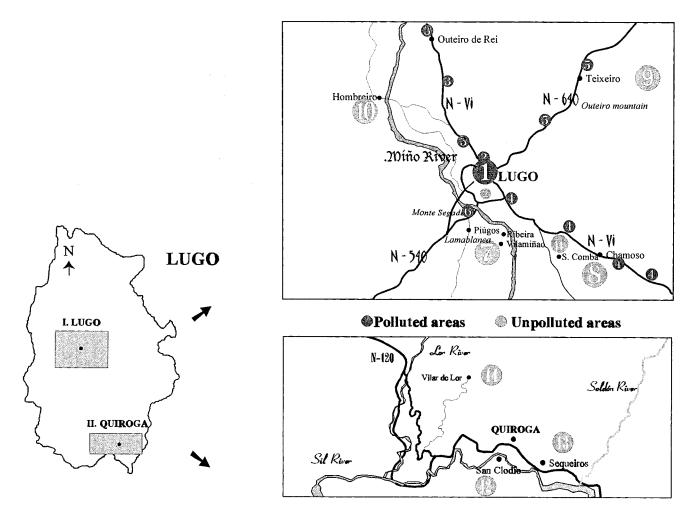


Fig. 1. Sampling areas in Lugo (NW Spain)

with statistically significant differences (p < 0.001), specifically *C. utriformis* (H: 251.9 mg/kg; RFB: 219.2 mg/kg), *A. macrosporus* (H: 242.4 mg/kg; RFB: 193.0 mg/kg), and *M. procera* (H: 235.8 mg/kg; RFB: 199.9 mg/kg), which reached the highest contents, always over 200 mg/kg DW. These results were similar to the other authors for *A. macrosporus* and *M. procera*.

Elevated copper concentrations, considerably higher than those in vegetables, should be considered as a nutritional source of the element. Nevertheless for humans, bioavailability from mushrooms was reported to be low due to limited absorption from the small intestine (Kalač *et al.* 1996).

In this work, all species of mushrooms bioaccumulated copper, and the BCFs were significant higher in the saprophytic species than in the mycorrhizal ones, especially *M. procera* and *A. macrosporus*, which presented the highest BCFs. So *M. procera* was the species that accumulated more copper according to other authors (Sugahara *et al.* 1990; Vetter 1990, 1994; Pop and Nicoara 1996; Jorhen and Sundström 1995; Kalač and Svoboda 1998, 2000). The lowest BCF values of cooper corresponded to *L. deliciosus*.

The levels of zinc found were significant different (p < 0.001) between saprophite and mycorrhizal species (Figure 3),

showing higher mean levels in saprophite species than mycorrhizal ones, probably because the former have higher decomposing activity. *C. utriformis*, *L. deliciousus*, and *A. macrosporus* reached the highest mean contents. Vetter *et al.* (1997) also found similar concentrations for these elements, but Byrne *et al.* (1976) and Sesli and Tüzen (1999) obtained lower concentrations.

All the species bioaccumulated zinc; the highest levels were for L. deliciosus, C. utriformis, and A. macrosporus. Nevertheless, in some individual samples of the species, such as H. repandum, C. cibarius, and C. comatus, the BCFs were < 1 (bioexclusor).

Comparing fungi values with soil contents (data not shown), Cu and Zn were accumulated in fungi, and in general, the BCFs were higher in the mycorrhizal species than the saprophytes ones, but there were not a significant difference.

Fungi possess a very effective mechanism that enables them to take up some trace elements from the substrate more readily. This mechanism may be more effective in the parasitic and saprophytic fungi trophic groups than in the mycorrhizal fungi group. Fungal species growing on wood generally contain lower concentrations of heavy metals than fungi growing on soil, probably due to limited content of

Table 1. Heavy metal concentrations (mg/kg DW) in the different species of mushrooms

			Copper			Zinc				
Species	n	Portion	Mean	SD	BCF	r	Mean	SD	BCF	r
Agaricus bisporus	6	H RFB	72.81 65.80	20.1 12.7	(1)		75.83 62.44	30.0 22.0	(1)	
Agaricus	9	Н	126.8	50.4	6.66	0.560	215.0	67.4	5.72	0.859**
campestris		RFB	104.2	39.7	4.67	0.520	149.3	25.9	5.01	0.787*
Agaricus	13	Н	242.4	61.2	22.30	0.325	267.0	74.1	10.36	0.210
macrosporus		RFB	193.0	56.0	17.10	0.320	175.7	63.3	6.81	0.176
Agaricus silvicola	6	Н	193.5	64.0	6.40	-0.027	209.4	62.7	18.58	0.987**
		RFB	129.6	46.4	4.17	0.486	130.8	30.3	12.70	0.888**
Amanita	12	Н	63.93	16.2	9.26	0.091	195.9	43.4	9.06	0.116
rubescens		RFB	49.80	23.8	6.34	0.003	133.0	38.4	6.28	0.438
Agrocybe	6	Н	42.24	10.7	(1)	0.000	79.29	21.7	(1)	000
cilindrica		RFB	32.07	11.2	(-)		53.34	9.37	(-)	
Boletus aereus	6	Н	80.07	21.3	6.47	0.837*	160.0	51.6	5.00	0.820*
Boicius acreus	O	RFB	68.18	23.5	4.01	0.571	96.54	38.1	4.43	0.325
Boletus edulis	10	Н	85.76	31.1	6.94	-0.264	133.4	40.7	11.66	0.681*
Doleius edulis	10	RFB	51.99	16.6	3.33	-0.193	63.70	23.6	7.28	0.386
Boletus pinophilus	13	Н	85.76	45.2	7.13	0.355	146.4	65.4	9.70	0.631*
Doieius pinopniius	13	RFB								
D 1 1 .			49.84	33.9	4.04	0.185	81.44	46.7	5.60	0.504
Boletus reticulatus	6	H	69.56	18.9	7.51	-0.183	195.4	45.1	5.06	0.781
G 1	_	RFB	52.75	23.7	4.46	0.201	119.9	34.2	3.73	0.747
Calvatia	7	Н	251.9	80.6	10.16	0.293	281.1	46.7	13.28	0.961*
utriformis		RFB	219.2	66.9	8.79	0.409	250.5	73.6	11.54	0.941**
Cantharellus	13	Н	70.39	32.4	4.72	-0.123	108.2	50.2	6.77	0.650*
cibarius		RFB	52.70	21.8	3.30	-0.252	71.41	33.5	5.63	0.484
Clitocybe	9	H	92.35	24.6	4.78	0.559	158.3	76.7	8.83	0.599
nebularis		RFB	72.54	29.0	2.94	0.769*	100.6	66.0	6.35	0.826**
Coprinus comatus	10	Н	147.3	63.5	4.51	-0.212	139.7	30.4	9.38	0.077
		RFB	95.32	32.2	2.57	0.457	88.18	29.2	5.72	0.814**
Fistulina hepatica	6	Н	39.51	15.2	(1)		50.33	17.8	(1)	
		RFB	32.33	12.0			35.83	13.3		
Hydnum	8	Н	42.83	8.69	1.74	0.549	52.50	12.9	7.47	0.574
repandum		RFB	35.38	13.4	1.59	0.217	30.00	7.44	5.85	0.553
Lactarius	9	Н	32.62	12.3	18.46	-0.204	309.8	54.5	5.06	-0.059
deliciosus		RFB	18.55	8.25	9.06	-0.277	152.2	29.7	2.79	0.163
Leccinum scabrum	6	Н	49.67	26.5	7.23	-0.893*	142.8	43.4	5.62	0.262
		RFB	41.88	23.8	2.94	-0.581	58.53	23.5	4.96	0.277
Lepista nuda	9	Н	117.7	45.2	10.69	0.224	182.1	36.8	6.32	0.511
Depisia maa		RFB	119.2	39.9	10.39	0.665	108.9	36.1	3.67	0.478
Macrolepiota	12	Н	235.8	109	20.78	0.371	106.8	24.5	4.38	0.321
procera	12	RFB	199.9	77.1	18.64	0.465	78.18	23.1	3.345	-0.163
Marasmius	6	Н	116.1	19.6	11.11	0.312	152.9	23.3	5.37	0.412
oreades	U	RFB	107.3	25.8	9.58	0.744	84.06	12.4	2.94	0.734
Pleurotus	6	Н	26.28	7.84		0.744	96.56	27.7		0.734
	O	п RFB	24.16	7.64 7.61	(1)		68.88	27.7	(1)	
ostreatus	10				7.01	0.561			4.67	0.102
Russula	12	H	85.18	29.7	7.91	0.561	112.5	47.8	4.67	-0.102
cyanoxantha	-	RFB	59.58	16.6	5.92	0.235	80.46	50.9	3.39	-0.078
Tricholoma	7	Н	91.68	39.2	7.13	0.689	238.0	86.2	7.61	-0.156
columbetta	_	RFB	61.11	22.8	4.73	0.917**	166.0	54.5	5.29	-0.095
Tricholoma	6	H 	72.14	25.7	11.94	0.556	233.5	73.6	13.98	0.982**
equestre		RFB	34.24	16.6	6.25	0.093	106.1	57.6	6.17	0.774
Tricholoma	10	H	66.76	21.0	9.28	0.222	164.6	45.4	8.43	0.112
portentosum		RFB	48.18	23.3	6.67	0.306	83.56	33.1	4.44	-0.077
Xerocomus badius	9	Н	61.58	28.9	9.80	0.372	225.7	75.3	11.24	0.269
		RFB	48.39	22.0	8.88	-0.321	162.3	60.8	7.99	0.370
Xerocomus	6	Н	77.56	31.6	7.81	0.785	162.3	61.1	7.16	0.306
crysenteron		RFB	66.09	28.7	6.77	0.521	111.9	38.1	4.43	-0.100

^{*} Significant difference, p < 0.05; ** significant difference, p < 0.01. (1)Wood-decaying and cultivated fungal species.

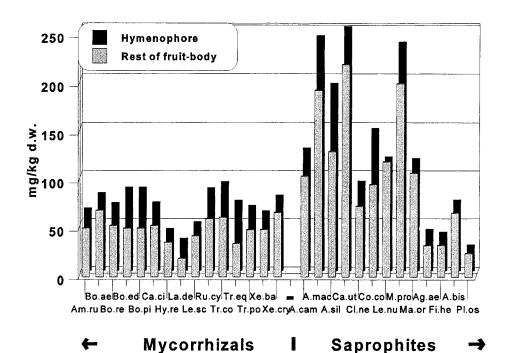


Fig. 2. Mean levels of copper in the studied mushroom species in relation to ecology and morphological portion

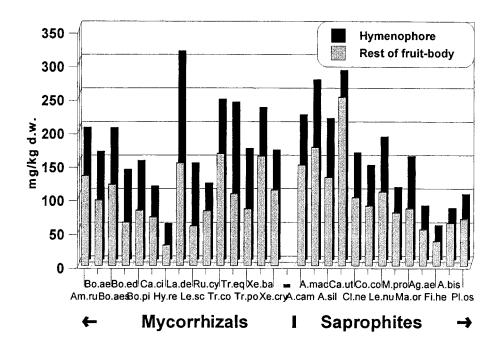


Fig. 3. Mean levels of zinc in the studied mushroom species in relation to ecology and morphological portion

mycelia with the soil. Most macrofungi contain significantly more zinc than copper.

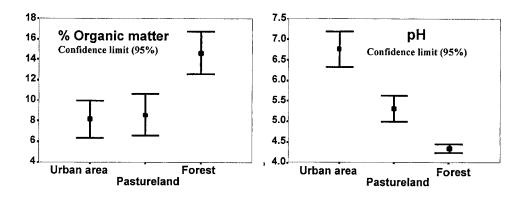
Morphological Portion

The BCFs and the hymenophore in mushrooms showed higher mean levels of cooper and zinc (Tables 1, 2) than the rest of the fruit bodies with statistically significant differences (p > 0.001 for Zn, p < 0.01 for Cu). In the case of Zn, only 8 samples of mushrooms (3.36%) presented higher levels in the rest of the

Table 2. Relationship between hymenophore (H) and rest of the fruit body (RFB)

Metal	Н	RFB	H/RFB
Cu	97.97	76.19	1.29
Zn	164.12	103.70	1.58

fruit body than the hymenophore, and, in the case of Cu, 42 samples (17.64%). It can be due to the higher biological activity that presents the hymenophore respect to the rest of the fruit-body (Chang and Chan 1973).



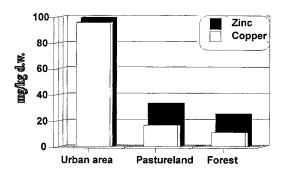


Fig. 4. Percentage of the organic matter, pH, and metal levels (mg/kg DW) in different zones from soils

Table 3. Pearson correlations to determine the significant differences of the Cu and Zn levels between total metal content in soil and fruit body

Correlation		Total Species	Saprophite Species	Mycorrhizal Species	
Cu soil–Cu fruit body ^a	Pearson coef.	0.508***	0.331***	0.481***	
	Significance	0.000	0.000	0.000	
Zn soil-Zn fruit body	Pearson coef.	0.140**	0.112^{NS}	0.064^{NS}	
	Significance	0.008	0.157	0.299	

^a Except A. macrosporus and A. silvicola levels.

The Zn mean ratio of H/RFB obtained in the samples analyzed as a whole was 1.58 (Table 2), but it may be noted the value of the *L. deliciosus* (2.1) is very similar to that obtained by Alonso *et al.* (2000) for the mercury in more species.

Soil Factors

The mycelia of higher fungi spread over large areas (several square meters) and their intimate association with soil and dead organic matter and/or symbiotic association with plant roots offer conditions for intensive exchange with substrates. Heavy metal content in many terrestrial fungi correlates with metal concentration in the soil in which they grow. In the case of edible fungi, toxic metals may be incorporated into food chains (Gabriel *et al.* 1997). In the other hand, heavy metal concen-

tration in the mushrooms are hardly affected by pH and organic matter content of the soil (Gast et al. 1988).

In this work, we investigated the uptake of cooper and zinc in mushrooms and their relationship with soil characteristics. According to the soil characteristics, we can establish three soil groups: urban area, pastureland, and forest (Figure 4). In general, it must be noted that the soil pH was acid, being the highest level (7) for Lugo City and the lowest value (4) for forest zone. With respect to the organic matter, the major values were found in the forest area. The statistical study with ANOVA (Table 3) showed a great significant difference for copper (p < 0.001). Nevertheless, Tyler (1982) observed that the soil parameters were not the determinant for the uptake of heavy metals by mushrooms in contrast with plants.

Substrates composition is an important factor, but great differences exist in uptake of individual metals. Copper is

^{NS} No significative correlation.

^{**} Significant correlation, p < 0.01; *** significant correlation, p < 0.001.

	Table 4	 Pearson correlations t 	to determine the significant	differences of the	Cu and Zn levels	between total metal co	ontent in soil and BCF
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Correlation		Total Species	Saprophite Species	Mycorrhizal Species
Cu soil–Cu BCF ^a	Pearson coef. Significance	-0.533*** 0.000	-0.805*** 0.000	-0.603*** 0.000
Zn soil–Zn BCF	Pearson coef. Significance	-0.528*** 0.000	-0.628*** 0.157	-0.489*** 0.000

^a Except A. macrosporus and A. sylvicola levels.

^{***} Significant correlation, p < 0.001.

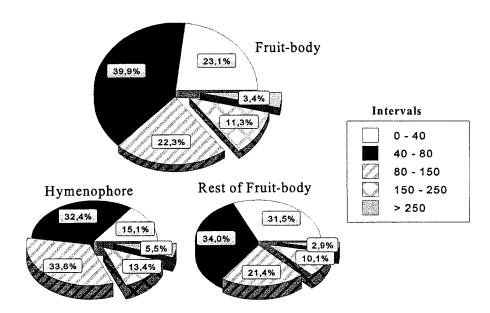


Fig. 5. Percentages of copper concentration intervals in mushroom samples

accumulated in fruit bodies, and levels of zinc are comparable in the fruit body and in the relevant substrate (Kalač and Svoboda 2000)

The BCFs also showed a clear correlation for copper and zinc (Table 4). These results indicated that the higher metal concentrations in the soil, the higher metal concentrations in the fruit bodies and lower BCFs. Similar results were observed by other authors (Brunnert and Zadrazil 1981; Favero et al. 1990; Falandysz et al. 1994, 1995; Falandysz and Chwir 1997; Rácz et al. 1995, 1996; Tüzen et al. 1998b). A lower efficiency in the accumulation at high concentrations may be due to the toxic effects of the metal ions (Brunnert and Zadrazil 1981; Favero et al. 1990; Gadd 1993; White and Gadd 1987).

Food Repercussions

In Spain, there is no recommendation about the concentration of copper and zinc in mushrooms. The Czech safe minimum limit is 80 mg/kg DW for copper. In the case of zinc, only the Slovak legislation has a limit of 10 mg/kg DW for cultivated mushrooms.

In our study, according to the concentration intervals (Figure 5), 37.0% of samples exceeded 80 mg Cu/kg DW. All sa-

prophite species (except *C. nebularis*) showed higher levels than 10 mg Cu/kg DW. These concentrations are higher than those of other foods (Cuadrado *et al.* 1995; Kalač and Svoboda 2000) and the consumption of uncultivated mushrooms with copper concentrations of 300 mg/kg DW but it does not represent a sanitary risk because the ADI has been established in 500 µg Cu/kg DW (WHO 1982). So copper is an essential element food and the recommended doses per day for an adult varied between 1.5 and 3 mg (NRC 1989). It can be concluded that the consumption of mushrooms cannot be considered a toxicological risk, but yes an important supply of copper to the diet.

In the case of zinc (Figure 6), only nine samples presented higher levels than 250 mg/kg DW (3,8%): the species *C. utriformis, L. deliciosus*, and *A. macrosporus*. The cultivated species showed lower contents of Zn up to the limit established by the Polish legislation (100 mg Zn/kg DW). The ADI was established in 1 mg Zn/kg DW (WHO 1982), and the recommended dose per day for an adult is 15 mg.

The consumption of these mushrooms does not represent a toxicological risk, and they are an important nutritional requirement to the diet. So the zinc is an antagonist of other metals (Cd, Pb, Ni), and its presence in some mushrooms reduces the risks associated at high concentrations of other toxic metals (WHO 1996).

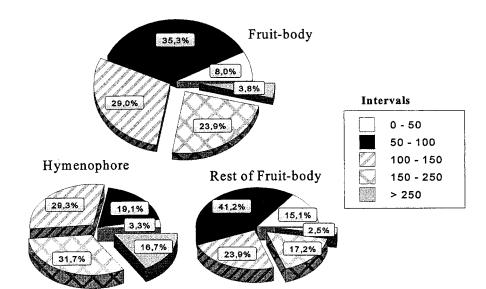


Fig. 6. Percentages of zinc concentration intervals in mushroom samples

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References

Alonso J, Salgado MJ, García MA, Melgar MJ (2000) Accumulation of mercury in edible macrofungi: influence of some factors. Arch Environ Contam Toxicol 38:158–162

Brunnert H, Zadrazil F (1981) Translocation of cadmium and mercury into the fruiting bodies of *Agrocybe aegerita* in a model system using agar platelets as substrate. Eur J Appl Microbiol Biotechnol 12:179–182.

Byrne AR, Ravnik V, Kosta L (1976) Trace element concentrations in higher fungi. Sci Total Environ 6:65–78

Chang ST, Chan KY (1973) Quantitative and qualitative changes in proteins during morphogenesis of the basidiocarp of *Volvariella* volvacea. Mycol 65:355–364

Concon JM (1988) Food toxicology. Part B: contaminants and additives. Marcel Dekker, New York

Cuadrado C, Kumpulainen J, Moreiras O (1995) Contaminants and nutrients in total diets in Spain. Eur J Clin Nutr 49:767–778

Doyle ME, Steinhart CE, Cochrane BA (1994) Food safety 1994. Marcel Dekker, New York

Fagot J, Guillitte O, Delcarte E (1988) Contamination en métaux lourds de champignos supérieurs sur sites industriels et naturels Belgique. Arch Int Phys Biochimic 96:36

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

Falandysz J, Niestój M, Danisiewicz D, Pempkowiak J, Bona H (1993) Cadmium and lead content of wild mushrooms Agaricus campestris L. collected from different locations in northern Poland. Bromat Chem Toksykol 26:275–280

Falandysz J, Bona H, Danisiewicz D (1994) Silver content of wildgrown mushrooms from northern Poland. Z Lebensm Unters Forsch 199:222–224

Falandysz J, Danisiewicz D, Galecka K (1995) Mercury in mushrooms and underlying soil in the city of Gdańsk and in the adjacent area. Bromat Chem Toksykol 28:155–159

Favero N, Bressa G, Costa P (1990) Response of *Pleurotus ostreatus* to cadmium exposure. Ecotoxicol Environ Saf 20:1–6

Gabriel J, Baldrian P, Rychlovský P Krenželok M (1997) Heavy metal content in wood-decaying fungi collected in Prague and in the National Park Š umava in the Czech Republic. Bull Enrivon Contam Toxicol 59:595–602

Gadd GM (1993) Interactions of fungi with toxic metals. New Phytol 124:25-60

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

Gast CH, Jansen E, Bierling J, Haanstra L (1988) Heavy metals in mushrooms and their relationship with soil characteristics. Chemosphere 17:789–799

Hawksworth DL, Kirk PM, Sutton BC, Pegler DN (1995) Dictionary of the fungi, 8th ed. Cab International, Wallingford

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

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

Kalač P, Svoboda L (2000) A review of trace element concentrations in edible mushrooms. Food Chem 69:273–281

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

Kalač P, Burda J, Stašková I (1991) Concentrations of lead, cadmium, mercury and copper in mushrooms in the vicinity of lead smelter. Sci Total Environ 105:109–119

Kalač P, Nižnanská M, Bevilaqua D, Štašková I (1996) 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 177:251–258

Kojo MR, Lodenius M (1989) Cadmium and mercury in macrofungi. Mechanisms of transport and accumulation. Angew Botanik 63: 279–292

Lodenius M (1994) Mercury in macrofungi: natural or anthropogenic?
Ed. S. Varnavas. Proc. Environmental Contamination, 6th Int. conf, Delphi (Greece). Edinburgh

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

Metrohm (1991) Application bulletin. Determination of zinc, cad-

- mium, lead, copper, thallium, nickel and cobalt in water samples after DIN 38406 E16
- NRC (National Research Council) (1989) Recommended dietary allowances, 10th ed. National Academy Press, Washington, DC
- Pop A, Nicoara A (1996) Heavy metals in three species of edible mushrooms. Studia Univ Babes-bolyai Biologia 41:93–96
- Quinche JP (1980) Les teneurs en quelques éléments traces de l'*Agaricus campester*. Bull Romand de Mycol 2:20
- Quinche JP (1987) Les teneurs en huit éléments traces de *Lepista nuda*. Mycol Helv 2:173–181
- Rácz L, Papp L, Fodor P (1995) Migration analysis of elements from compost and casing material to the fruit bodies in cultivated mushrooms (*Agaricus bisporus*). Acta Alimen 24:161–166
- Rácz L, Papp L, Prokai B, Kovács Z (1996) Trace element determination in cultivated mushrooms: an investigation of manganese, nickel, and cadmium intake in cultivated mushrooms using ICP atomic emission. Microchem J 54:444–451
- Romeo F, del Signore A (1994) La presenza di micro e macroelementi nei funghi: una rassegna. Riv Merceol 33:255–308
- Sesli E, Tüzen M (1999) Levels of trace elements in the fruiting bodies of macrofungi growing in the East Black Sea region of Turkey. Food Chem 65:453–460
- Sugahara T, Kawai H, Matsuzawa M, Fujishiro S, Aoyagi Y, Hosogai Y (1990) Mineral contents in edible mushrooms growing in soil. Nippon Shokuhin Kogyo Gakkaishi 37:540–546
- Tüzen M, Özdemir M, Demirbas A (1998a) Study of heavy metals in some cultivated and uncultivated mushrooms of Turkish origin. Food Chemistry 63:247–251

- Tüzen M, Özdemir M, Demirbas A (1998b) Heavy metal bioaccumulation by cultivated *Agaricus bisporus* from artificially enriched substrates. Z Lebensm Unters Forsch A 206:417–419
- Tyler G (1980) Metals in sporophores of basidiomycetes. Trans Br Mycol Soc 74:41–49
- Tyler G (1982) Accumulation and exclusion of metals in *Collybia* peronata and *Amanita rubescens*. Trans Br Mycol Soc 79: 239–245
- Vetter J (1989) Comparison of mineral elements in Agaricus and Pleurotus fruit bodies, Z Lebensm Unters Forsch 189:346–350
- Vetter J (1990) Mineral element content of edible and poisonous macrofungi. Acta Alimen 19:27–40
- Vetter J (1994) The copper, manganese and zinc content of some edible mushrooms. Z Lebensm Unters Forsch 198:469-472
- Vetter J, Siller I, Horváth Z (1997) Zinc content of sporocarps of basidiomycetous fungi. Mycologia 89:481–483
- White C, Gadd GM (1987) Inhibition of H⁺ efflux and K⁺ uptake and induction of K⁺ efflux in yeast by heavy metals. Tox Assess 2:437–444
- World Health Organization (1982) Evaluation of certain food additives and contaminants. 26th report of the Joint of FAO/WHO Expert Committee of Food Additives. WHO Technical Report Series, No. 683, Geneva
- World Health Organization (1996) Trace elements in human nutrition and health. Geneva
- Źródłowski Z (1995) The influence of washing and peeling of mushrooms *Agaricus bisporus* on the level of heavy metal contaminations. Pol J Food Nutr Sci 4/45:26–33