

Concentrations of trace elements in wild edible mushrooms

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Received 3 May 2000; received in revised form 29 August 2000; accepted 29 August 2000

Abstract

The concentrations of Cu, Cd, Co, Ni, Mn, Pb, Zn and Fe in 66 samples of mushroom fruiting bodies, representing seven species, mainly all edible, were determined by atomic absorption spectrophotometry. The mushrooms were collected from near roads and inner parts of forest and lawns in Balıkesir in the north western part of Turkey. The results indicate that the Fe level in the species *Volvariella speciosa* (Fr.) Sing. from near the road was the highest with a mean of 6990 mg/kg. The level of Ni was the highest in *Clitocybe flaccida* (Sow.: Fr.) Kummer, from near road with a mean of 3.32 mg/kg. Cu levels were almost similar for both areas within a range of 35–89 mg/kg in the different species. The Cd was accumulated mostly by *Lactarius sanguifluus* (Paulet: Fr.) Fr. and *V. speciosa* from near road with a mean of 1.60 mg/kg. Concentration of Mn, Pb, Co and Zn in *L. sanguifluus* from near road were the highest with means of 63.6, 7.66, 6.03 and 149 mg/kg, respectively. © 2001 Published by Elsevier Science Ltd.

Keywords: Edible mushrooms; Trace element; Turkey

1. Introduction

Wild growing macrofungi have been a favourite delicacy in many countries. Some people collect macrofungi to make a substantial contribution to food intake. Therefore, it is necessary to know the levels of toxic and essential elements in edible mushrooms.

Accumulation of heavy metals by mushrooms has been known for a few decades and a number of works describing metal content in fruit bodies have been published (Gabriel, Baldrian, Rychlovsky & Krenzelok, 1997; Garcia, Alonso, Fernandez & Melgar, 1998; Gast, Jansen, Bierling & Haanstra, 1988; Jorhem & Sundström, 1995; Kalac, Niznanska, Bevilaqua & Staskova, 1996; Sesli & Tüzen, 1999; Vetter, 1994; Yoshida & Muramatsu, 1997). The strong accumulation of cadmium, lead and mercury in some edible mushrooms is of great interest when considering human health. In the case of edible fungi, toxic metals may be incorporated into food chains. Edible mushrooms may contain higher amounts of heavy metals than plants, especially in the vicinity of highways subject to heavy traffic (Demirbas, 2000; Lepsova and

Kral, 1988; Liukkonen-Lilja, Kuusi, Laaksovirta, Lodenius, & Piepponen, 1983; Liukkonen, Kuusi, Laaksovirta, Lodenius, & Piepponen, 1981; Tyler, 1982).

The element concentrations are primarily species-dependent. It has been rather difficult to determine the effects of environmental factors on the concentrations of elements.

The purpose of this study is to evaluate the concentrations of toxic and essential elements in several species of edible wild higher mushrooms collected from near the highway and inner part areas of forests and lawns in Balıkesir, in the north-western part of Turkey. Also, an additional objective of this survey was to enlarge existing data on essential and trace elements in edible mushrooms.

2. Materials and methods

The macro fungi were collected in Balıkesir, in the northwestern part of Turkey, in autumn 1998 and winter 1999. The area of this study (Fig. 1) included forest and lawns which had been exposed to pollutants of automobile traffic for many years. The collected samples were classified and evaluated in two categories: near

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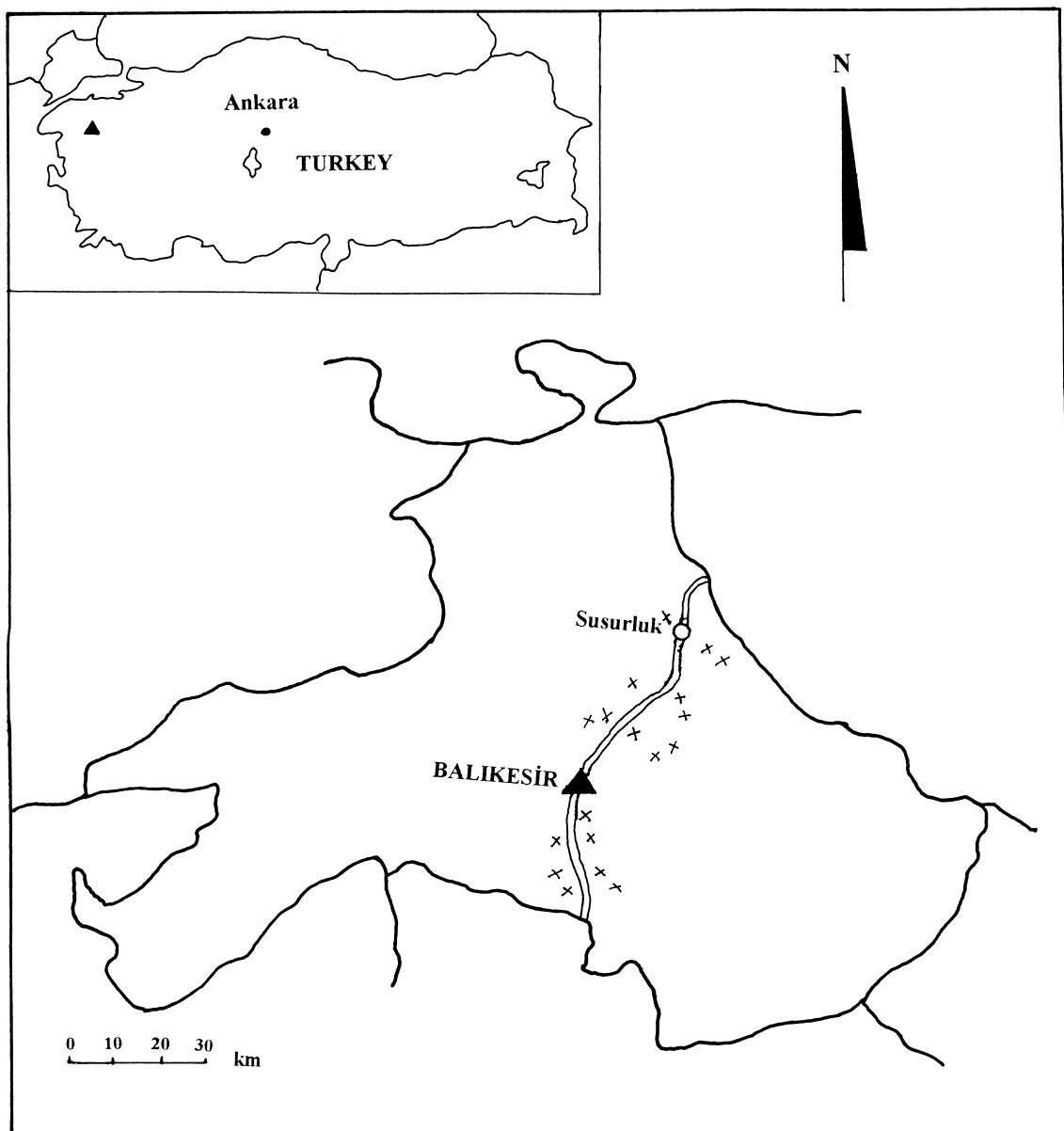


Fig. 1. Map of the study area.

highway area and inner part area. The sampling distance for near road area is 0–100 m from the road and, for the inner part area, was beyond 100 m. In addition to these wild edible macrofungi, samples of *Agaricus bisporus* were also obtained commercially. Metal levels in 66 samples of seven species of edible mushrooms were analysed.

For the identification of specimens, the habitat and morphological characteristics of the macrofungi found in the localities were recorded and photographed. The macro fungus specimens were then carried to the laboratory. Their spore prints were extracted and spore measurements were determined. Finally, each species was identified using reference books (Moser, 1983; Phillips, 1981).

Samples were cleaned without washing, cut and dried at 40°C in an oven for 48 h after drying in air for 5 days. The sample of mass 0.5–2 g was weighed and placed in a porcelain crucible and ashed at 450°C for 15–24 h, then the ash was dissolved in 2 ml conc. HNO₃, evaporated to dryness, heated again at 450°C for 3 h and dissolved in 1 ml conc. H₂SO₄, 1 ml conc. HNO₃ and diluted with deionized water up to a volume of 25 ml. All samples were run in duplicate.

A Perkin-Elmer model SIM AA 900 graphite furnace atomic absorption spectrophotometer with Zeeman background correction at wavelengths of 283.3 nm for Pb, 228.8 nm for Cd, 232.0 nm for Ni and 240.7 nm for Co, and a Pye Unicam 929 flame atomic absorption spectrophotometer with deuterium background correction

at 213.9 nm for Zn, 279.5 nm for Mn, 248.3 nm for Fe and 324.8 nm for Cu were used.

Correlations between concentrations of the metals were tested by regression analysis. Concentrations of metals from the test were compared statistically by two-tailed tests.

Green alga (MBH, certified reference material) was used as the reference material.

The detection limit is defined as the concentration value that corresponds to three times the absorbance obtained from 10 replicated measurements of the blank. Detection limits determined accordingly, and the equivalent concentrations in mushroom, are given in Table 1.

3. Results and discussion

The result of the analysis of the CRM showed good agreement with the certified levels (Table 2).

Element concentrations in the mushroom species, when at least four samples except *Volvariella speciosa* from inner part area, were analysed, are given in Table 3.

Table 1
Detection limits and equivalent concentrations in mushroom

Element	Detection limits ($\mu\text{g/l}$)	Equivalent conc. in mushroom (mg/kg)
Fe	0.085	1.06E-3
Cu	0.009	1.12E-4
Zn	0.038	4.75E-4
Mn	0.015	1.88E-4
Co	0.009	1.12E-4
Ni	0.010	1.25E-4
Cd	2.2E-4	2.75E-6
Pb	0.0048	6.02E-5

Table 2
Levels of elements in certified reference material analysed as sample (results in mg/l)

Metal	Green algae ($n = 5$)
Cu found	18.9 \pm 1.2
Certified	19.6
Cd found	0.042 \pm 0.006
Certified	0.045
Ni found	1.28 \pm 0.15
Certified	1.23
Pb found	1.26 \pm 0.22
Certified	1.23
Co found	19.1 \pm 1.3
Certified	19.9
Zn found	41.5 \pm 1.7
Certified	40.2
Mn found	34.5 \pm 2.3
Certified	32.8
Fe found	352 \pm 13
Certified	339

The uptake of metals in mushrooms is in many respects different from that of plants. Reasons for the variations in the concentrations of all metals could be considered to be mushroom species, distance from polluted area and age of mycelium. The latter factor seems to be of great importance, but it is very difficult to determine its effect (Seeger, 1982).

Zinc is widespread among living organisms due to its biological significance. Mushrooms are known as zinc-accumulators and sporophore:substrate ratio for Zn ranges from 1 to 10 (Bano, Nagaraja, Vibhakar & Kapur, 1981). Minimum and maximum values of Zn samples were 60.4 and 158 mg/kg from near road area and 55.7 and 158 mg/kg from inner part area. The lowest mean level was found in *L. semisanguifluus* Heim & Lecl. from near road area and in *Lepista inversa* (Scop.:Fr) Pat. from inner part area and the highest in *Lactarius sanguifluus* from near road area and in *L. semisanguifluus* from inner part area (Fig. 2). The difference between the two studied areas for six investigated species was fairly low.

Content of copper in mushrooms ranged from 26.3 to 87.7 mg/kg (near road area) and from 28.3 to 95.9 mg/kg (inner part area). The variation within two categories of collected samples was also low. The lowest mean levels for both areas were seen in *L. semisanguifluus* and the highest in *Clitocybe alexandri* (Gill.) Konr. (Fig. 3). Copper concentrations, considerably higher than those in vegetables, should be considered as a nutritional source of the element. Nevertheless, for man, bioavailability from mushrooms was reported to be low, due to limited absorption from the small intestine (Schellman, Hilz & Opitz, 1980).

The iron concentrations were fairly high in *V. speciosa* from both areas (Fig. 4). Values ranged from 220 to 7162 mg/kg (near road area) and from 246 to 6473 mg/kg (inner part area). However, the variation within the species was low.

Content of manganese in mushrooms ranged from 7.45 to 66.2 mg/kg (near road area) and from 8.91 to 54.7 mg/kg (inner part area). The lowest mean levels were found in *L. semisanguifluus* for both areas and the highest in *L. sanguifluus* from near road area and *C. flaccida* from inner part area (Fig. 5).

Correlation coefficients were calculated for all pairs of eight investigated elements. The significant linear correlation between concentrations of copper–zinc ($r: 0.755$, $P: 0.02$), copper–manganese ($r: 0.673$, $P: 0.05$), copper–iron ($r: 0.786$, $P: 0.02$), manganese–cobalt ($r: 0.718$, $P: 0.02$) and manganese–nickel ($r: 0.737$, $P: 0.02$) was found only for *L. sanguifluus*. At the given significance level, P , in linear correlation, the presence of manganese in *L. sanguifluus* shows the presence of copper, nickel and cobalt; the presence of copper shows the presence of manganese and iron, and so on.

The highest mean level of Ni by far was found in *L. sanguifluus* with a mean of 13.5 mg/kg (near road area)

Table 3
Concentrations of all studied elements from near highway and inner part areas in mg/kg dry weight

Family and species	Area	Value	Element							
			Cu	Zn	Mn	Fe	Co	Cd	Ni	Pb
<i>Tricholomataceae</i>										
<i>Clitocybe alexandri</i>	NR ^a (7)	Mean	83.0	74.4	26.2	242	1.49	0.79	2.98	3.15
		S.D.	2.6	9.1	2.4	19	0.92	0.81	2.08	1.65
		Range	76.6–87.7	63.9–79.7	23.9–28.6	220–255	0.85–2.82	0.15–2.12	1.35–5.72	1.35–5.12
	IP ^b (5)	Mean	88.8	81.8	51.4	634	1.5	0.54	3.38	3.05
		S.D.	9.3	3.7	3.3	11	0.33	0.35	0.53	0.42
		Range	78.3–95.9	79.3–86.0	48.1–54.7	623–644	1.25–1.91	0.38–0.88	2.89–3.95	2.57–3.37
<i>Clitocybe flaccida</i>	NR(7)	Mean	50.0	134	23.5	295	2.14	0.60	3.32	4.16
		S.D.	3.6	9	2.2	5	0.25	0.13	0.15	1.08
		Range	45.9–53.1	125–143	21.2–26.1	290–300	1.96–2.42	0.51–0.81	3.17–3.47	7.07–3.22
	IP(8)	Mean	51.8	120	52.6	1476	3.35	0.70	2.88	4.69
		S.D.	5.3	7	2.0	28	0.55	0.22	1.61	1.58
		Range	46.7–56.8	112–126	51.2–54.5	1452–1507	2.83–3.93	0.45–0.93	1.61–3.58	6.13–3.66
<i>Lepista inversa</i>	NR(6)	Mean	44.9	76.0	26.9	996	1.72	0.62	2.91	2.43
		S.D.	3.9	20.5	4.7	189	0.71	0.35	0.91	1.44
		Range	41.2–49.0	60.4–99.2	22.3–31.8	790–1162	0.87–2.68	0.08–1.50	2.14–4.57	0.54–4.95
	IP(6)	Mean	40.2	59.8	27.3	1274	1.47	0.65	3.45	2.55
		S.D.	4.1	6.3	2.3	172	0.48	0.11	1.34	1.13
		Range	35.2–43.7	55.7–67.2	25.5–30.4	1149–1471	0.97–2.31	0.50–0.81	2.27–5.87	1.26–4.38
<i>Pluteaceae</i>										
<i>Volvariella speciosa</i>	NR(4)	Mean	64.2	97.5	30.4	6990	1.98	1.60	3.96	4.28
		S.D.	4.5	32.1	2.9	242	0.55	0.25	1.05	1.60
		Range	59.3–68.2	60.7–118	27.8–33.5	5703–7162	1.57–3.02	1.37–2.02	2.79–5.80	2.78–6.88
	IP(2)	Mean	67.2	103	29.8	5896	3.80	1.33	2.73	2.98
		S.D.	4.4	6	2.8	817	1.12	0.43	0.59	0.40
		Range	64.1–70.3	99–107	27.9–31.8	5318–6473	3.00–4.59	1.02–1.64	2.31–3.15	2.70–3.26
<i>Russulaceae</i>										
<i>Lactarius sanguifluus</i>	NR(4)	Mean	43.8	149	63.6	646	6.03	1.05	13.5	7.66
		S.D.	6.1	12	3.6	40	1.64	0.30	1.79	2.12
		Range	42.9–54.3	135–158	61.0–66.2	612–680	4.04–7.49	0.77–1.37	12.0–15.5	4.64–9.48
	IP(4)	Mean	58.5	135	14.5	252	1.94	3.15	19.4	2.79
		S.D.	14.2	16	2.5	10	0.51	0.35	2.0	1.51
		Range	46.9–74.3	121–142	11.4–18.5	246–264	1.36–2.30	2.70–3.52	17.7–21.6	1.47–4.55
<i>Lactarius semisanguifluus</i>	NR(4)	Mean	40.0	74.3	14.5	586	2.39	0.48	6.42	3.44
		S.D.	14.0	12.8	8.4	35	0.92	0.17	1.19	0.42
		Range	26.3–55.0	62.5–94.1	7.45–22.1	552–623	1.67–3.42	0.38–0.74	5.44–7.75	3.10–3.91
	IP(4)	Mean	34.7	154	10.9	341	2.09	0.49	5.05	2.40
		S.D.	7.1	12	6.9	68	1.35	0.01	0.25	0.66
		Range	28.3–42.2	139–158	8.91–17.7	293–389	1.14–3.05	0.49–0.50	4.87–5.23	1.93–2.86
<i>Agaricaceae</i>										
<i>Agaricus bisporus</i>	n = 5	Mean	34.5	33.2	6.78	87.2	0.15	0.34	3.76	0.55
		S.D.	4.9	4.7	2.62	34.8	0.07	0.09	0.94	0.12
		Range	28.2–38.8	29.3–38.7	4.67–10.3	56.1–135	0.09–0.25	0.25–0.46	2.50–4.74	0.44–0.67

^a NR, near road.

^b *IP, inner part.

and 19.4 mg/kg (inner part area). The lowest mean levels, 2.91 and 2.75 mg/kg were found in *Lepista inversa* from near road area and *V. speciosa* from inner part area, respectively (Fig. 6). The minimum and maximum values of Ni for samples are 1.35;15.5 mg/kg from near road area and 1.61;21.6 mg/kg from inner part area.

The cobalt levels were generally low. Relatively higher levels of Co were found in *L. sanguifluus* from near road area and *V. speciosa* and *C. flaccida* from inner part

area — 6.03, 3.80 and 3.35 mg/kg, respectively (Fig. 7). Variation of the mean of species from two categories was not very high, except *L. sanguifluus*.

Cadmium content ranged from 0.08 to 3.52 mg/kg in samples from near road area and from 0.38 to 1.64 mg/kg in samples from inner part area. The ability to accumulate cadmium appears lowest for *L. semisanguifluus* and relatively higher for *V. speciosa* and *L. sanguifluus* (Fig. 8). The mean values were similar for near road and inner

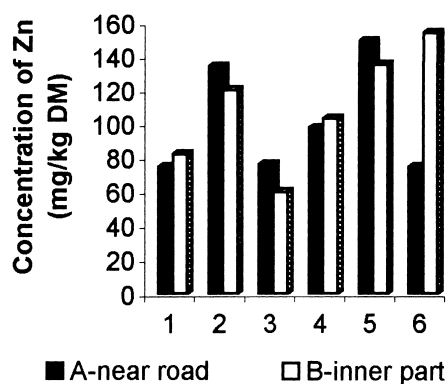


Fig. 2. Comparison of mean concentrations of Zn (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

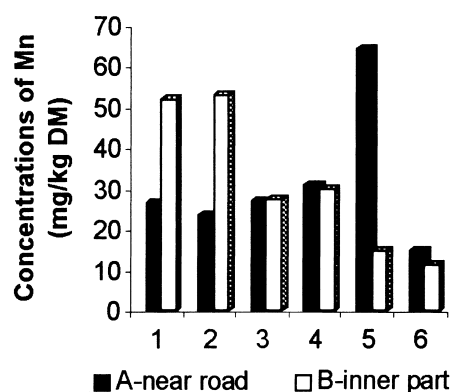


Fig. 5. Comparison of mean concentrations of Mn (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

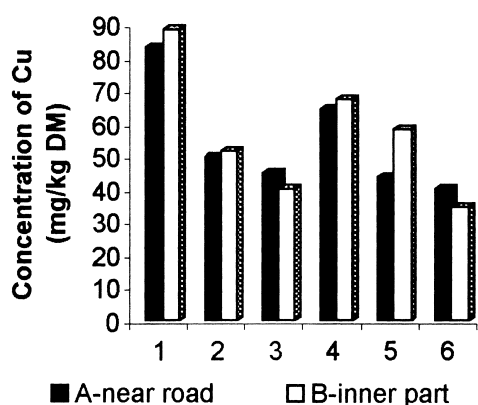


Fig. 3. Comparison of mean concentrations of Cu (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

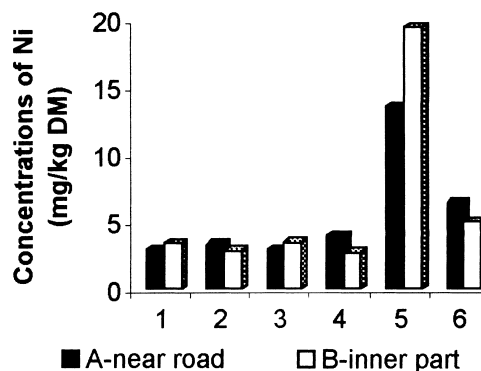


Fig. 6. Comparison of mean concentrations of Ni (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

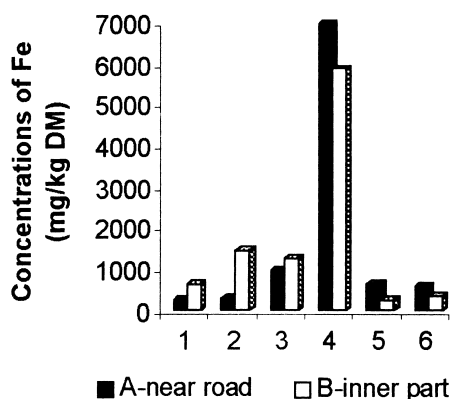


Fig. 4. Comparison of mean concentrations of Fe (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

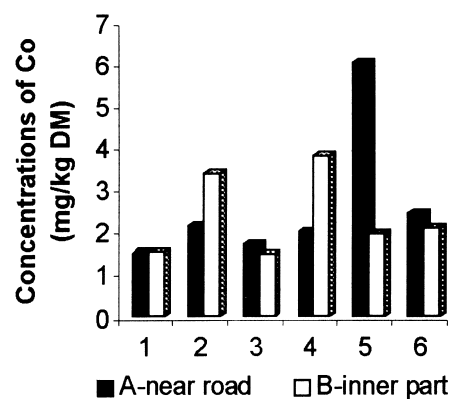


Fig. 7. Comparison of mean concentrations of Co (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

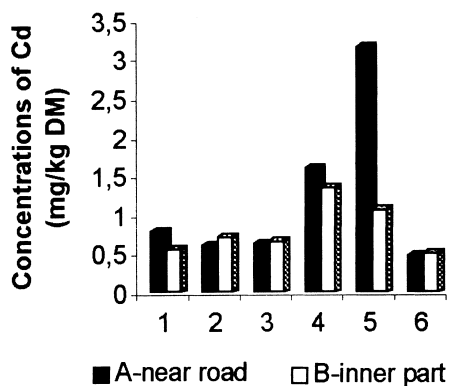


Fig. 8. Comparison of mean concentrations of Cd (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

part area except *L. sanguifluus* and *V. speciosa*. Traffic pollution factors did not show significant differences. High Cd concentrations were probably not caused by pollution but by species-dependent factors.

The minimum and maximum values of Pb were 0.54 and 9.48 mg/kg for samples from near road area and 1.26 and 6.13 mg/kg for samples from inner part area. The highest mean levels were found in *L. sanguifluus* and *V. speciosa* from near road area as 7.66 and 4.28 mg/kg and the lowest in *L. inversa* from near road area and *L. semisanguifluus* from inner part area as 2.43 and 2.40 mg/kg, respectively (Fig. 9).

The lowest mean level was found in the commercially cultivated *Agaricus bisporus*. In the commercially cultured *A. bisporus*, cobalt, cadmium and lead values were low. The values of Mn, Cu, Zn and Fe, known as essential elements, are good agreement with other studies (Jorhem & Sundström, 1995; Sesli & Tüzen, 1999).

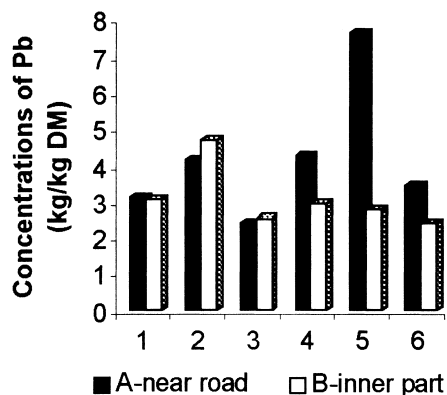


Fig. 9. Comparison of mean concentrations of Pb (mg/kg dry wt.) in six species of mushrooms from (A) near highway area and (B) inner part area: 1, *Clitocybe alexandri*; 2, *Clitocybe flaccida*; 3, *Lepista inversa*; 4, *Volvariella speciosa*; 5, *Lactarius sanguifluus*; 6, *Lactarius semisanguifluus*.

In this study, it was found that the trace metal concentrations were mostly highest in *L. sanguifluus* and the lowest in *L. semisanguifluus*.

In relation to the pollution source in main roads, Jorhem and Sundström (1995) concluded that lead was derived mainly from the contaminated roadside soil rather than from atmospheric deposition. The exposure time for many mushrooms is very short, which makes deposition of Pb from vehicle exhaust a small problem that is continuing to decrease as is the use of leaded petrol.

The occurrence and distribution of different toxic components in certain mushrooms is not only a theoretical mycological problem, but also has practical environmental and toxicological aspects (Vetter, 1994). According to FAO/WHO (1989, 1993) acceptable weekly intakes of cadmium and lead for adults are 0.42–0.49 and 1.5–1.75 mg, respectively. The Pb and Cd levels in all studied species from both areas can be considered as high and mushrooms should not be consumed.

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