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ASSESSMENT OF FACTORS INFLUENCING TRACE ELEMENT CONTENT OF BASIDIAL MUSHROOMS FROM THE EUROPEAN PART OF RUSSIA

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INTRODUCTION

Assessment of trace element uptake by man's organism with foodstuffs is one of the main constituents of the environmental monitoring. It is assumed that edible mushrooms are important suppliers of trace elements in man's organism. According to literature data, among the biotic components of the terrestrial ecosystems it is just mushrooms that can accumulate maximal concentrations of trace elements in fruiting bodies [1–3]. However, in spite of numerous publications over the last decade indicating high concentrations of toxic heavy metals in mushrooms, information on the potential ability of mushrooms for accumulation of trace elements is still controversial [4–6].

Mushrooms belong to a large group of eukaryotic heterotrophic organisms, sectioned into a separate cenosis (*Mycota* or *Fungi*) and taking intermediate place between the cenosis of animals and plants. Mushrooms use ready organic compounds of substrates (leaf fall, humus) as a source of nutrition and biosynthesis of new compounds. Simple compounds translocate directly through cell membranes, more complex ones disintegrate into monomers by means of extra cellular ferments. There is evidence for binding of zinc by organic compounds in the process of metabolism in mushrooms; for inclusion of Co in B_{12} molecule during synthesis of this vitamin; there are also cases of selective accumulation of toxic metals (for example, selenium, lead, cadmium, and mecury) by some mushroom species [7–10]. Taking into consideration numerous literature data, the mere fact of high concentration of different trace elements in mushrooms is beyond question. On this basis, there has been a strong belief that mushrooms are accumulators or concentrators of heavy and toxic elements. It is in the use of terms «accumulation» and «concentration» that the authors see a substantial contradiction. Does the process of accumulation really take place or are high concentrations of trace elements explained by any other reasons?

This study was aimed at assessing the factors influencing accumulation of elements, heavy and toxic elements particularly, by basidial mushrooms. To achieve this goal, it was necessary to complete the following tasks:

1) to determine the range of trace element concentrations in the main species of edible basidiomycets most widespread over the European part of Russia;

2) to assess the difference in the elemental content in mushrooms growing in different environmental and geochemical conditions;

3) to determine concentration levels of bulk and mobile forms of trace elements in the substrate where mycelium is spread;

4) to assess the factors influencing the trace element content of the fruiting bodies of mushrooms.

EXPERIMENTAL

Sampling of the fruiting bodies of mushrooms was carried out in the city of Moscow, in Moscow, Kaluga, Tver, Gor'kii, Tula, and Voronezh Regions, in the Belomorskii state reserved area, and in Karelia. The following species were collected: *Boletus edulis, Leccinum scabrum, Leccinum aurantiacum, Suillus luteus, Russula vesca, Lactarius torminosu, Paxillus involutus, Cantharellus cibarius, Armillariella mellea, Agaricus bisporus, Agaricus campestris,* and *Pleurotus ostreatus*. The sampling of fruiting bodies of boletus was also carried out in the seaside areas of Island. In Tver Region, along with the sampling of fruiting bodies of boletus, soil samples were collected up to the depth of 40 cm.

The elemental content of the samples was determined by means of the instrumental neutron activation analysis (INAA) (Na, Mg, Cl, K, Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Rb, Mo, Ag, Sb, I, Cs, La, W, Au, Hg, and Th) and atomic absorption spectrometry (AAS) (Mn, Ni, Cu, Cd, and Pb) in the analytical laboratories of GIN RAS (Moscow) and JINR (Dubna) [11–13].

RESULTS AND DISCUSSION

The data on the trace element content in mycorhizal mushrooms, soil saprophyte and saprophyte parasitizing on wood are given in Table 1. These data show a considerable excess of maximum permissible levels (MPL) of some toxic elements in mushrooms. Thus, the concentration of Se in boletus (*Boletus edulis*) two times exceeds MPL; of Cd four times, of Hg 1.1 times; in brown cap boletus (*Leccinum scabrum*) and boletus luteus (*Suillus luteus*) the concentration of Cd is twice MPL. The highest saturation with trace elements is observed in boletus; it has high concentrations of Cl, Co, Br, Sb, I, Cs, Rb, and Pb. Brown cap boletus shows high concentrations of Zn, As, Se, Rb, Ag, and Hg, orange-cap boletus (*Boletus versipellis*) of Cu, Zn, Rb, and Cd; in boletus luteus of Cl, Ca, and Cs. Russula (*Anglophile*) concentrate to a great extent such essential elements as Na, Mg, Cl, K, Cr, Co, Ni, and I. Rather high concentrations of Mg, Cl and I are observed in chantarelles (*Cantharellus cibarius*). The concentration of Cd 13 times exceeds MPL in honey agaric (*Armillariella mellea*). In the other mushrooms excess of MPL was not observed. Most probably, due to different ways of taking up nutrients, as well as to different depth of extension of hypha, the accumulation of

Table 1. Trace element content in some basidomycets, $\mu g/g$

Element	Boletus *Boletus edulis* $n = 29$			Brown-cap boletus *Leccinum scabrum* $n = 20$			Orange-cap boletus *Leccinum aurantiacum* $n = 11$			MPL
	Mean	Median	STD	Mean	Median	STD	Mean	Median	STD	
Na	41	37	28	34	37	23	28	24	13	—
Mg	70	73	26	73	70	19	71	69	23	—
Cl	188	145	141	58	48	36	90	95	39	—
K, %	0.16	0.13	0.07	0.19	0.18	0.06	0.19	0.19	0.02	—
Ca	49	45	18	69	68	16	39	38	7	—
Sc	0.0006	0.0004	0.0005	0.0032	0.0035	0.0031	0.0002	0.0002	0.0001	—
Cr	0.044	0.035	0.032	0.067	0.035	0.068	0.024	0.024	0.004	0.2
Mn	0.9	0.7	0.4	0.7	0.6	0.3	0.9	0.9	0.6	—
Fe	5.5	4.7	2.6	6.6	4.7	7.0	2.6	2.1	1.9	—
Co	0.029	0.015	0.030	0.017	0.012	0.013	0.013	0.013	0.003	—
Ni	0.13	0.11	0.07	0.04	0.03	0.01	0.05	0.06	0.01	—
Cu	1.5	1.5	0.8	1.0	0.8	0.7	2.4	2.4	0.4	—
Zn	7.4	5.1	6.9	8.4	5.8	6.9	8.6	9.1	4.2	—
As	0.007	0.006	0.003	0.029	0.016	0.022	0.006	0.005	0.003	0.5
Se	1.08	1.12	0.75	0.21	0.26	0.20	0.04	0.05	0.02	0.5
Br	1.60	1.26	1.28	0.41	0.20	0.40	0.44	0.45	0.05	—
Rb	20.4	12.6	18.5	21.3	11.9	20.7	21.5	20.5	21.6	—
Mo	0.03	0.03	0.01	< 0.01	< 0.01	—	0.02	0.02	0.01	—
Cd	0.13	0.12	0.11	0.06	0.08	0.05	0.04	0.03	0.03	0.03
Ag	0.09	0.04	0.08	0.26	0.09	0.25	0.03	0.03	0.01	—
Sb	0.06	0.03	0.05	0.004	0.003	0.002	0.003	0.003	0.001	0.3
I	0.007	0.005	0.007	0.002	0.002	0.001	0.004	0.003	0.002	—
Cs	0.19	0.16	0.12	0.10	0.07	0.09	0.07	0.04	0.06	—
La	0.004	0.003	0.003	0.009	0.003	0.006	< 0.003	< 0.003	—	—
W	< 0.01	< 0.01	—	< 0.01	< 0.01	—	< 0.01	< 0.01	—	—
Au	0.0003	0.0005	0.0003	0.0003	0.0004	0.0003	0.0002	0.0001	0.0001	—
Hg	0.063	0.052	0.056	0.039	0.024	0.036	0.010	0.009	0.004	0.05
Th	0.001	0.001	0.0005	0.003	0.001	0.002	0.001	0.001	0.001	—
Pb	0.04	0.03	0.02	0.03	0.03	0.004	0.03	0.02	0.006	0.5

Table 1 (continued)

Element	Boletus luteus *Suillus luteus* $n = 17$			Russula *Russula vesca* $n = 15$			Coral milky cap *Lactarius torminosus* $n = 6$			MPL
	Mean	Median	STD	Mean	Median	STD	Mean	Median	STD	
Na	41	42	10	74	74	39	19	20	5	—
Mg	76	103	56	1734	1754	98	103	105	35	—
Cl	122	101	39	1878	1872	523	39	37	20	—
K,%	0.13	0.11	0.04	0.42	0.37	0.12	0.16	0.16	0.07	—
Ca	80	82	6	47	44	14	54	56	4.8	—
Sc	0.0003	0.0003	0.0001	0.003	0.003	0.002	0.002	0.001	0.001	—
Cr	0.029	0.028	0.008	0.10	0.09	0.07	0.06	0.04	0.05	0.2
Mn	0.5	0.5	0.1	1.7	1.5	1.1	1.3	1.5	0.5	—
Fe	4.5	4.6	0.7	9.9	9.4	4.3	8.4	9.3	3.2	—
Co	0.009	0.008	0.002	0.05	0.04	0.04	0.023	0.027	0.012	—
Ni	0.06	0.06	0.01	0.19	0.22	0.13	0.15	0.11	0.05	—
Cu	0.7	0.6	0.3	2.2	2.1	0.3	1.1	1.1	0.31	—
Zn	4.8	5.0	0.8	8.0	7.6	1.1	5.6	5.9	0.8	—
As	< 0.003	< 0.003	—	0.01	0.01	0.01	0.04	0.04	0.01	0.5
Se	0.02	0.02	0.01	0.02	0.02	0.01	0.05	0.03	0.04	0.5
Br	0.05	0.05	0.02	0.20	0.22	0.08	0.07	0.06	0.05	—
Rb	16.2	15.7	2.1	2.2	2.1	0.4	47	60	36	—
Mo	< 0.01	< 0.01	-	0.007	0.007	0.003	< 0.01	< 0.01	—	—
Cd	0.06	0.05	0.02	0.023	0.021	0.009	0.02	0.02	0.01	0.03
Ag	< 0.01	< 0.01	—	0.10	0.12	0.06	0.02	0.02	0.007	—
Sb	0.002	0.002	0.001	0.010	0.007	0.010	0.007	0.008	0.004	0.3
I	0.003	0.003	0.002	0.074	0.071	0.006	0.005	0.005	0.004	—
Cs	0.21	0.22	0.03	0.01	0.01	0.004	0.97	1.23	0.78	—
La	< 0.003	< 0.003	—	0.013	0.013	0.006	0.005	0.005	0.002	—
W	< 0.01	< 0.01	—	0.031	0.022	0.03	< 0.01	< 0.01	—	—
Au	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	1E-04	0.0001	0.0001	—
Hg	0.010	0.010	0.003	0.005	0.005	0.002	0.008	0.008	0.004	0.05
Th	< 0.001	< 0.001	—	0.002	0.002	0.0006	0.001	0.001	0.001	—
Pb	< 0.02	< 0.02	—	0.05	0.06	0.005	0.09	0.10	0.03	0.5

Table 1 (continued)

Element	Flat-cap mushroom *Paxillus involutus* $n = 22$			Chanterelle *Cantharellus cibarius* $n = 17$			Honey agaric *Armillariella mellea* $n = 13$			MPL
	Mean	Median	STD	Mean	Median	STD	Mean	Median	STD	
Na	29	23	19	52	42	34	16	15	5.5	—
Mg	121	109	57	1431	1302	283	127	121	25	—
Cl	25	18	25	1133	1034	386	57	40	48	—
K,%	0.33	0.33	0.15	0.22	0.22	0.04	0.31	0.34	0.13	—
Ca	55	53	28	45	44	7	46	55	16	—
Sc	0.002	0.002	0.0015	0.001	0.001	0.001	0.0003	0.0003	0.0002	—
Cr	0.05	0.03	0.04	0.05	0.05	0.01	0.03	0.03	0.01	0.2
Mn	1.47	0.74	1.50	3.3	2.9	1.3	1.54	1.51	0.02	—
Fe	13	13	4.0	11.6	10.3	7.9	10	9.1	4.9	—
Co	0.032	0.039	0.023	0.03	0.02	0.01	0.005	0.005	0.002	—
Ni	0.10	0.10	0.05	0.08	0.11	0.07	0.09	0.11	0.02	—
Cu	3.2	2.9	0.95	3.7	2.6	1.4	2.1	2.0	0.04	—
Zn	10	11.7	3.6	6.8	6.1	2.9	8.0	7.9	1.7	—
As	0.04	0.04	0.03	0.02	0.01	0.02	< 0.005	< 0.005	—	0.5
Se	0.07	0.07	0.02	0.04	0.04	0.05	0.011	0.007	0.008	0.5
Br	0.37	0.21	0.35	0.14	0.12	0.07	0.04	0.04	0.02	—
Rb	14	11	15	52	53	8.1	2.8	2.8	0.9	—
Mo	0.02	0.01	0.02	0.02	0.02	0.03	0.01	0.01	0.005	—
Cd	0.02	0.01	0.01	0.020	0.017	0.006	0.4	0.6	0.15	0.03
Ag	0.05	0.06	0.03	0.012	0.011	0.007	0.04	0.04	0.02	—
Sb	0.003	0.003	0.002	0.007	0.007	0.005	0.003	0.003	0.001	0.3
I	0.006	0.005	0.003	0.095	0.073	0.052	0.018	0.011	0.015	—
Cs	0.22	0.25	0.02	0.65	0.62	0.21	0.043	0.049	0.019	—
La	0.026	0.027	0.013	0.009	0.013	0.007	0.004	0.007	0.003	—
W	< 0.01	< 0.01	—	< 0.01	< 0.01	—	0.013	0.013	0.007	—
Au	0.0019	0.0030	0.0013	0.0002	0.0002	0.0001	0.0003	0.0002	0.0001	—
Hg	0.006	0.005	0.003	0.008	0.007	0.006	0.003	0.003	0.002	0.05
Th	0.006	0.007	0.005	0.002	0.002	0.001	0.002	0.001	0.002	—
Pb	0.09	0.09	0.03	0.17	0.19	0.04	0.08	0.07	0.02	0.5

Table 2. Comparison of trace element content of cultivated and field mushrooms, μg/g

Element	Cultured champignon *Agaricus bisporus*, agrofirm, $n = 11$			Field champignon *Agaricus campestris*, $n = 21$		
	Mean	Median	STD	Mean	Median	STD
Na	56	61	22	63	41	61
Mg	143	126	38	159	130	70
Cl	189	135	140	300	242	197
K,%	0.44	0.46	0.11	0.37	0.39	0.07
Ca	43	43	18	50	47	21
Sc	0.0002	0.0003	0.0002	0.0004	0.0003	0.0003
Cr	0.02	0.02	0.01	0.05	0.04	0.03
Mn	0.54	0.60	0.05	0.67	0.73	0.09
Fe	3.7	3.7	0.7	5.6	4.2	2.9
Co	0.004	0.004	0.001	0.060	0.040	0.060
Ni	0.03	0.03	0.004	0.08	0.09	0.04
Cu	2.0	2.1	0.3	14.1	10.1	8.1
Zn	4.9	4.9	0.4	7.3	6.2	2.1
As	0.02	0.02	0.01	0.13	0.13	0.09
Se	0.19	0.15	0.14	0.65	0.52	0.55
Br	0.19	0.20	0.07	0.37	0.24	0.33
Rb	0.81	0.87	0.19	0.43	0.40	0.31
Mo	< 0.01	< 0.01	—	0.01	0.01	0.005
Cd	0.009	0.007	0.001	1.80	1.41	1.40
Ag	0.01	0.01	0.003	1.23	0.97	0.81
Sb	0.002	0.002	0.001	0.007	0.009	0.006
I	0.006	0.008	0.004	0.011	0.006	0.009
Cs	0.002	0.002	0.001	0.003	0.003	0.002
La	0.004	0.003	0.001	0.009	0.007	0.008
W	< 0.01	< 0.01	—	< 0.01	< 0.01	—
Au	0.0001	0.0002	0.0001	0.019	0.028	0.021
Hg	0.012	0.013	0.004	0.60	0.62	0.55
Th	< 0.001	< 0.001	—	0.006	0.006	0.002
Pb	< 0.05	< 0.05	—	0.10	0.08	0.05

Table 2 (continued)

Element	Cultured oyster *Pleurotus ostreatus*, argofirm, $n = 10$			Field oyster *Pleurotus ostreatus*, $n = 11$		
	Mean	Median	STD	Mean	Median	STD
Na	9.2	9.0	1.0	9.0	8.6	1.1
Mg	129	103	22	133	121	48
Cl	36	25	5.6	35	27	8
K,%	0.36	0.36	0.08	0.48	0.47	0.09
Ca	79	80	57	99	88	32
Sc	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001
Cr	0.01	0.01	0.01	0.02	0.02	0.01
Mn	0.46	0.45	0.06	1.03	0.90	0.29
Fe	8.8	9.0	1.0	8.9	9.0	0.9
Co	0.01	0.01	0.00	0.01	0.01	0.00
Ni	< 0.03	< 0.03	—	0.035	0.041	0.02
Cu	0.7	0.7	0.1	1.0	0.9	0.2
Zn	4.9	4.8	0.3	6.1	6.3	0.8
As	0.01	0.01	0.002	0.01	0.01	0.001
Se	0.03	0.04	0.03	0.06	0.06	0.01
Br	0.05	0.04	0.01	0.05	0.05	0.02
Rb	1.17	1.10	0.21	1.09	1.10	0.21
Mo	< 0.01	< 0.01	—	< 0.01	< 0.01	—
Cd	0.017	0.015	0.003	0.26	0.19	0.11
Ag	0.03	0.03	0.01	0.03	0.03	0.01
Sb	0.001	0.001	0.001	0.001	0.001	0.001
I	0.002	0.002	0.001	0.005	0.003	0.003
Cs	0.007	0.010	0.006	0.033	0.034	0.007
La	0.002	0.002	0.00	0.014	0.008	0.01
W	< 0.01	< 0.01	—	< 0.01	< 0.01	—
Au	0.0002	0.0003	0.0001	0.0001	0.0001	0.0001
Hg	0.030	0.028	0.008	0.019	0.021	0.008
Th	< 0.001	< 0.001		0.0008	0.0007	0.0003
Pb	< 0.05	< 0.05	—	< 0.05	< 0.05	—

trace elements by different mushrooms differs considerably. Due to weak metal uptake by roots of host plants, the lowest concentrations of trace elements are observed in saprophytic mushrooms fed with wood and in parasites. The highest concentrations of trace elements were revealed in saprophytes forming mycelium in the uppermost humus layers. Mycorhizal mushrooms take some intermediate place in this system. Besides, it is worth noting that mushrooms of one and the same species can grow on roots of different plants and reflect accessibility of elements in different soil horizons.

The results obtained for field mushrooms are very important for understanding the levels of trace element intake in man's organism. However, residents of large cities mainly consume cultured mushrooms.

Table 2 contains concentrations of trace elements in wild growing and cultivated champignons and oysters. It follows from Table 2 that concentrations of toxic metals in field champignons exceeds MPL for Se 1.3 times; for Cd 60 times, and for Hg 12 times. Concentrations of As and Pb are close to MPLs. It is necessary to note that the major element contents in cultivated and field champignons are approximately equal, whereas concentrations of nearly all the trace elements are considerably higher in field champignons. Thus, the concentration of Co in field champignons exceeds an analogous concentration of Co in cultivated champignons 12 times, Cu 7 times, As 6 times, Cd 200 times, Ag 123 times, Au 190 times, and Hg 50 times.

Concentrations of major and trace elements in field and cultivated oysters are quite similar except for Cd whose concentration in field oysters exceeds MPL 8.6 times. Concentrations of toxic elements in cultivated mushrooms do not exceed established standards. One may note that concentrations of trace elements in oyster mushrooms are in general substantially lower than those in champignons. This is apparently typical for xylophytes for which wood serves the substrate for mycelium extension.

The data presented in Tables 1 and 2 show that nearly all the investigated wild growing mushrooms are characterized by high concentrations of trace elements. Moreover, thus is equally true both for essential and for toxic elements. The level of concentrations of the latter may reach in some mushroom species the values hazardous for life.

Analyzing the data presented in Tables 1 and 2, one may note two peculiarities:

— difference in concentrations of one and the same element in one and the same mushroom species reaches 100–200 times;

— set of trace elements whose concentration is high in any mushroom species could be large enough, but elements with higher mobility in soil solutions are prevailing.

One may presuppose that in the accumulation of trace elements by mushrooms, of first importance is not the accumulative ability of the mushroom

Table 3. Trace element content of champignons (*Agaricus campestris*) in relation to their site of growth, μg/g

Element	Collection place				
	Moscow, north	Moscow, centre	Moscow, south-east	Moscow Region, south 10 km from MARR	Moscow Region, south 160 km from MARR
Na	34	205	41	15	17
Mg	100	87	274	130	150
Cl	350	388	644	488	81
K,%	0.28	0.31	0.40	0.40	0.38
Ca	79	46	54	34	28
Sc	0.0001	0.0001	0.0002	0.0023	0.0001
Cr	0.03	0.06	0.05	0.05	0.03
Mn	0.5	0.4	1.1	1.9	1.0
Fe	3.3	3.4	4.6	8.7	6.4
Co	0.01	0.01	0.05	0.60	0.01
Ni	0.03	0.03	0.09	0.24	0.05
Cu	4.4	23	8.7	21	4.7
Zn	7.0	9.9	6.1	12	5.7
As	0.28	0.05	0.17	0.16	0.04
Se	1.4	0.2	1.3	0.2	0.8
Br	0.1	0.2	0.3	0.3	0.7
Rb	0.1	0.1	0.5	1.0	0.3
Mo	<0.01	<0.01	<0.01	0.01	0.01
Cd	0.94	0.20	0.17	3.4	0.18
Ag	0.4	33	19	3.0	0.7
Sb	0.002	<0.01	0.007	0.011	0.001
I	0.006	0.004	0.017	0.014	0.034
Cs	0.002	<0.001	0.003	<0.001	0.003
La	0.01	< 0.01	0.01	0.01	0.01
W	<0.01	<0.01	<0.01	0.04	<0.01
Au	<0.0001	0.017	0.081	0.0028	0.001
Hg	0.03	1.14	1.28	0.87	0.08
Th	<0.001	<0.001	<0.001	0.003	0.001
Pb	0.10	0.18	0.05	0.19	0.05

mycelium itself, but chemical features of the substrate of its extension, namely the presence of mobile forms of trace elements. This statement could be checked by analysis of one and the same mushroom species collected in different environmental and geochemical conditions.

Trace element contents of wild champignons growing in different conditions are presented in Table 3. Sampling was carried out in the same climatic zone in a large city (Moscow), in districts with different level of technogenic impact, as well as in Moscow Region. Samples were collected in the north of Moscow in the region of north Medvedkovo (the lowest level of technogenic pollution), in the center of Moscow in Shabolovskaya Street (high level of technogenic pollution), in the south-east of Moscow in the district Pechatniki (most contaminated district), 10 km from the Moscow Automobile Ring Road (MARR), in forest belt of Simferopol highway and in the south of Moscow Region 160 km from Moscow in the district with predominant agricultural activity.

The results obtained illustrate well the dependence of trace element concentrations in mycelium on the environmental and geochemical situation in the places of sampling fruiting bodies of mushrooms.

Champignons vegetating in the north of Moscow feature a high concentration of Se and Cd. Mushrooms collected in the centre of Moscow are characterized by a high concentration of Na, Cu, Zn, Cd (6.7 times MPL); Ag, Hg (23 times MPL) and Pb. Champignons collected in the south-east of Moscow are characterized by high concentrations of Mg, Cl, Mn, Co, Ni, As, Se, Cd, Ag, Sb, I, and Hg. Champignons collected in the forest belt of Simferopol highway exhibit high concentrations of Cl, Sc, Cr, Fe, Co, Ni, Cu, Zn, As, Rb, Cd (113 MPL); I, Hg (17 MPL), Pb. In the agricultural district in the south of Moscow Region only Cd is 16 times MPL. It is necessary to note that the changing environmental and geochemical conditions produce changes both in the concentration of some trace elements and in their enumeration. In the given case, champignons are in fact a peculiar kind of indicator of the environmental and geochemical situation in the place where they were sampled.

Table 3 contains data on trace element variation in mushrooms typical of the region with rather intense technogenic impact on the environment. However, the investigation of trace element variation in mushrooms vegetating in the regions less affected by the technogenic activity is also of great importance.

Table 4 contains data on elemental content in boletus collected in Tver Region, in the south of Moscow Region, in the White Sea Reserve (Arkhangelsk Region), Karelia, and Island. One takes note of a far less range of elemental concentrations. The range of concentration values for most of the trace elements collected in Moscow Region, the White Sea Reserve, and in Karelia is not too large and varies within the range of 1.5–2.5 times.

Excess over MPL for Cr, As, Sb, and Pb was not observed. The Se concentration in mushrooms exceeds MPL three times in the south of Moscow Region and in Karelia; the content of Hg is no greater than MPL. The Cd content in boletus is higher or equal to MPL everywhere except for Island. Elevated con-

Table 4. Trace element content of boletus (*Boletus edulis*) in relation to the site of growth, $\mu g/g$

Element	Place of collection				
	Moscow Region, south	Tver Region	White Sea Reserve	Karelia	Island
Na	47	28	15	17	35
Mg	68	84	57	22	81
Cl	98	264	203	130	55
K,%	0.15	0.13	0.27	0.11	0.23
Ca	54	47	37	32	46
Sc	0.0003	0.0003	0.0002	0.0005	0.0017
Cr	0.04	0.03	0.02	0.05	0.03
Mn	0.59	0.98	0.58	0.59	0.43
Fe	4.6	3.8	3.9	6.2	9.8
Co	0.017	0.026	0.008	0.022	0.008
Ni	0.13	0.13	0.08	0.08	0.06
Cu	1.82	1.75	3.43	0.64	0.98
Zn	9.1	4.0	9.7	4.6	8.9
As	0.008	0.005	0.007	0.005	0.003
Se	1.6	0.3	0.1	1.4	0.1
Br	1.1	3.1	3.0	2.7	0.1
Rb	42	13	10	5.8	3.5
Mo	0.03	<0.01	0.03	0.02	0.05
Cd	0.27	0.13	0.05	0.03	0.02
Ag	0.29	0.16	0.091	0.023	0.007
Sb	0.004	0.002	0.002	0.001	0.001
I	0.002	0.005	0.008	0.005	0.004
Cs	0.35	0.11	0.14	0.04	<0.01
La	<0.01	<0.01	<0.01	<0.01	<0.01
W	<0.01	<0.01	<0.01	<0.01	<0.01
Au	0.0002	0.0002	0.0002	0.0003	0.0002
Hg	0.07	0.07	<0.005	0.05	0.007
Th	0.001	<0.001	<0.001	<0.001	0.001
Pb	<0.05	0.05	<0.05	<0.05	<0.05

centrations of halogens characteristic of the White Sea Reserve are most probably a result of sea salt fractionization. The trace element concentration in mushrooms collected in Island is minimal; it is the authors' opinion that these values may be considered as baseline values for the given mushroom species. The high concentration of Sc determined in the mushrooms fruiting bodies collected in Island most probably reflects the regional peculiarities of the geochemical background in this territory [14].

Mushrooms possess high metabolic activity; the growth rate of mycelium hypha may be in the range of 0.1-6 mm/hr depending on the intake rate of nutrients. Mushrooms hypha extends over large areas of substrates, and high ratio of extension area to mycelium volume favours conditions for intense exchange of major and trace elements. Since the main source of trace elements for mushrooms is the upper soil horizon and leaf fall, the data on their chemical content are necessary.

Table 5 contains data on the gross concentration, the concentration of mobile forms of Ni, Cu, Zn, Cd, Pb, organic matter and acidity in the soil profile situated in the environmentally pristine district of Tver Region (distance to the nearest industrial enterprise is 60 km). The fruiting bodies of edible boletus were collected at the same site (Table 4, Tver Region).

Table 5. Distribution of some trace elements in soil profile

Horizon (cm)	Bulk content and mobile forms, μg/g				
	Ni	Cu	Zn	Cd	Pb
Leaf fall (0–3)	4.6/0.54*(12%)**	8.2/6.8(83 %)	150/90(60 %)	0.81/0.35(43 %)	9.4/1.8(19 %)
A_0–A_1 (3–10)	4.3/0.46(11 %)	4.1/2.9(71 %)	34/18(53 %)	0.45/0.18(40 %)	12.3/1.7(14 %)
B (10–40)	2.1/0.13(6.2)	1.8/1.6(89 %)	9.6/0.5(5 %)	0.07/0.02(28 %)	10/1.1(11 %)

Horizon (cm)	C org %	pH
Leaf fall (0–3)	3.55	4.6
A_0–A_1 (3–10)	0.99	4.7
B (10–40)	0.1	5.32

* Buffered extract pH 4.8.

** % to bulk content.

The given data show that the maximal concentration of bulk content, as well as of mobile forms of metals, is observed in the upper horizon, in so-called litter (leaf fall), which is in good agreement with literature data [15, 16]. However, a question arises in this connection: Why are such high concentrations of heavy metals in the litter (for example, content of Zn exceeds MPL for soil 1.5 times) observed in the relatively background district where technogenic fallout is almost absent? It is also difficult to explain the high percent ratio of mobile forms of metals to their bulk content.

To answer these questions, one should try to calculate theoretically the normal background concentration of Ni, Cu and Zn in the leaf fall horizon. In our case, the leaf fall represents deciduous-coniferous-grass-wood conglomerate 3 cm in depth, the lower layer of which gradually decomposes into humus. The duration

of the whole decomposition is 3–7 years, and the ceaseless accumulation of new material takes place in the upper layer.

The bulk mass in mixed forests assuming grass and shrubby vegetation is 2–5 kg/m^2 per year (on average 3.5 kg/m^2 per year). We know the content of Ni, Cu, Zn in pine needles and birch leaves, which on average is 20, 30 and 100 mg/kg respectively for the «background» districts [13, 14]. Assuming minimal time for material accumulation as 3 years and considering mean density of leaf fall (0.8 g/cm^3), one shall obtain the concentration of Ni equal to 8.7 mg/kg, Cu 13.1 mg/kg, and Zn 44 mg/kg, which is rather close to the values given in Table 5. These are very rough estimations. They do not consider, in particular, the set of factors influencing the concentration of trace elements in the upper horizon: namely, straightforward deposition of atmospheric aerosols, non-constant density of the litter; considerable seasonal variation of trace element content of deciduous and coniferous leaves (3–5 times) [14], etc.

Nevertheless, the results obtained through calculation are comparable to those obtained through experiment. An analogous approach seems to be fair for the majority of the rest trace elements. That is why we can state that the natural process of many years' consequent accumulation of trace elements takes place in the litter. Even in the background districts a five- to ten-fold accumulation of metals relative to low-lying horizons is observed during three years.

The high percent ratio of mobile forms of metals and their bulk content is also explained by natural reasons. In the terrestrial biocenos, the main mass of mushrooms vegetates in the upper soil horizon. As an environmental clustering (grouping), mushrooms are typical decomposers of organic matters. Mushrooms synthesize extra-cellular hydrolytic ferments, which decompose such complicated components of leaf fall as pectin, cellulose and lignin. During twenty-four hours they decompose 2–7 times more organic matter than consume it. Besides, microorganisms participate in this process [15].

Thus, the process of life-sustaining activity of mushrooms promotes transformation of inaccessible organic mineral forms of leaf fall trace elements into easily accessible mobile forms.

The districts with intense technogenic contamination experience several additional factors promoting the accumulation of trace elements in the upper soil horizon:

— a significantly higher, as a rule, concentration of trace elements in vegetative organs of the vegetation in these districts;

— more intensive dying-off processes of organic matter and hence increased leaf fall mass as a result of technogenic impact;

— processes of biogenic formation of acids resulting in an increase of acidity of soil solutions;

— direct deposition of technogenic aerosols on the soil surface;

— acidic rains that also lead to an increase of soil acidity;

— all the above factors considered, an increase in the constituent part of mobile forms of trace elements in the upper horizon.

One may say that in technogenically contaminated districts the upper soil horizon undergoes a many-fold enhancement of factors influencing the trace composition of mushrooms mycelium: the concentration of trace elements increases; the mass of leaf fall increases; the acidity of soil solutions increases; the concentration of mobile forms of metals increases, too.

Taking into consideration the data from Table 5, one can calculate the expected concentration of Ni, Cu, Zn, Cd, and Pb in mushrooms vegetating on these soils. Assuming that at this site we have collected species of mycorizoide mushrooms, arithmetic mean values of the content of movable forms of Ni, Cu, Zn, Cd, and Pb in two lower soil layers were calculated.

These calculations resulted in the following expected concentration values: Ni – 0.29; Cu – 1.5; Zn – 9.2; Cd – 0.1; Pb – 1.4 μg/g. The data given in the second column of Table 4 (Tver Region) relate to the boletus collected in the soil the analysis results of which are given in Table 5. Comparison of both sets of data clearly shows that the theoretically calculated concentration is rather close to data from Table 4, and for Cu and Cd the concentrations of these metals in the mushrooms are identical. This is evidence that our hypothesis on the identity of trace element concentrations in mushroom mycelium with concentrations of their mobile forms in the substrate of mycelium extension is correct, at least in the conditions described in this study.

CONCLUSIONS

1. Mushrooms are not active accumulators of trace elements. The high concentration of trace elements, including heavy and toxic elements, in mushrooms is a sequence of their high concentration in soil in the mobile forms of these elements accessible for mushrooms.

2. The high concentration of mobile forms of metals in the upper soil horizon is due to natural many years' accumulation of leaf fall and because of decomposition by mycelium of hard-to-decompose organics (lignin, cellulose) of different mushroom species possessing a system of extracellular enzyme digesting, which is accomplished by transmission of trace elements into the upper soil horizons from hard available organomineral forms into easily accessible mobile forms.

3. In the regions with intense technogenic contamination, additional superposition and summing of a few factors take place promoting increase of concentrations of mobile forms in the upper soil horizon.

REFERENCES

1. *Burn A. R., Ravnik B., Kosta L.* Trace element concentrations in fungi // Sci. Total Environ. 1976. V. 6. P. 65–78.

2. *Kalac P, Burda J., Staskova I.* Concentrations of lead, cadmium, mercury and copper in mushrooms in the vicinity of a lead smelter // Sci. Total Environ. 1991. V. 105. P. 109–119.
3. *Bagalyi R.* Biogeochemistry of terrestrial plants. Moscow, Geos, 2005. 457 p. (in Russian).
4. *Tarit Roychowdhury, Hiroshi Tokunaga, Masanori Ando.* Survey of arsenic and other heavy metals in food composites and drinking water and estimation of dietary intake by the villagers from an arsenic-affected area of West Bengal, India // Sci. Total Environ. 2003. V. 308. P. 15–35.
5. *Randa Z., Soukal L., Mizera J.* Possibilities of the short-term thermal and epithermal neutron activation for analysis of macromycetes (mushrooms) // J. Radioanal. Nucl. Chem. 2005. V. 264, No. 1. P. 67–76.
6. *Randa Z., Kucera J.* Trace elements in higher fungi (mushrooms) determined by activation analysis // J. Radioanal. Nucl. Chem. 2004. V. 259, No. 1. P. 99–107.
7. *Muller E., Leffler B.* Mycology. Moscow: Mir, 1995. 341 p. (in Russian).
8. *Mirchink G. T.* Soil Mycology. Moscow: MSU, 1996. 210 p. (in Russian).
9. *Lozovskaya I. N., Orlov D. S., Sadovnikova L. K.* Ecology and preservation of biosphere from chemical contamination. Moscow, 1998. 284 p. (in Russian).
10. *Domoradsky I. V., Gradova N. B.* Essay on mycology for environmental scientists. Moscow: Istoki, 2007. 86 p. (in Russian).
11. *Frontasyeva M. V., Pavlov S. S.* REGATA experimental setup for air pollution studies // Problems of Modern Physics / Editors: A. N. Sissakian, D. I. Trubetskov. Dubna, JINR, 1999. P. 152–158.
12. *Gorbunov A. V., Gundorina S. F., Onischenko T. L., Frontasyeva M. V.* Development of a combined method to carry out a multielement analysis for environment preservation // J. Radioanal. Nucl. Chem. Articles. 1989. V. 129, No. 2. P. 443–451.
13. Collection of methodical essays on determination of heavy metals in soil, hothouse bed and products of plant cultivation. RF Minselkhozprod, Moscow, 1998. P. 27–82 (in Russian).
14. *Geptner A. P., Ivanovskaya T. A., Pokrovskaya E. V., Lyapunov S. M., Okina O. I., Gorbunov A. V.* Hydrothermally changed giapoclastides in the earth surface in the riftzone of Island (problem of trace element biogenic accumulation) // Lythology and Natural Resources. 2007. No. 5. P. 503–529 (in Russian).
15. *Loukina N. V., Nikonov V. V.* Nutritional regime of north taiga forests. Apatity, 1998. 316 p. (in Russian).
16. *Loukina N. V., Nikonov V. V.* Biogeochemical cycles in north forests in the conditions of aerotechnogenic contamination. Apatity, 1996. Parts 1, 2. 216 p., 194 p. (in Russian).
17. *Gorbunov A. V., Lyapunov S. M., Okina O. I., Frontasyeva M. V.* Seasonal variation of trace element content of vegetative organs of wood vegetation // Environmental Chemistry. St. Petersburg, 2005. V. 14, No. 4. P. 258–266 (in Russian).
18. *Bab'eva I. P., Zenova G. M.* Soil biology. MSU, 1983. 285 p. (in Russian).

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