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SELENIUM AND OTHER ELEMENTS ACCUMULATION BY HIGHER FUNGI IN ECOSYSTEMS OF THE DNIESTER RIVER VALLEY

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The article presents the results of studying the ability of higher fungi accumulate selenium and other chemical elements. It was established that the mushrooms that grow in the Dniester River valley, accumulate in its fruit body from 0.147 to 24.92 mg Se/kg of dry matter. The concentration of selenium in mushrooms depends on the ecological and geochemical conditions of growth, and the highest concentration observed in the accumulative ecosystems, which are located in the depressions. The content of macro- and microelements in wild and cultivated mushrooms (*Agaricus bisporus*) differs significantly.
Keywords: *higher fungi, chemical elements, selenium, geochemical landscape, ecosystem.*

SELENIUL ŞI ALTE ELEMENTE ACUMULATE DE MACROMICETE ÎN ECOSISTEMELE DIN VALEA FLUVIULUI NISTRU

În articol sunt prezentate rezultatele cercetării capacităţii macromicetelor de a acumula seleniu şi alte elemente chimice. S-a constatat că ciupercile din valea Nistrului acumulează în corpul lor 0,147-24,92 mg Se/kg de masă uscată. Concentraţia de seleniu în ciuperci depinde de condiţiile ecologice şi geochimice de creştere, fiind mai ridicată în ecosistemele acumulative din depresiuni. Conţinutului de macro- şi microelemente în ciupercile sălbatice şi în cele cultivate (*Agaricus bisporus*) diferă în mod semnificativ.
Cuvinte-cheie: *ciuperci, elemente chimice, seleniu, landşaft geochimic, ecosistem.*

Introduction

Fungi provide important biogeochemical functions in ecosystems. They transform organic and inorganic matters as well as actively involved in the biological cycling of chemical elements [4]. Macromycetes are known to accumulate high concentrations of various chemical elements including heavy metals [7], therefore they are used as biological indicators for monitoring of environmental pollution [22]. However, edible mushrooms are significant sources of macro- and micronutrients for human being.

Many researchers consider mushrooms to represent a significant source of essential selenium (Se) [3,8]. Se is included in the active sites of many proteins and serves as one of the antioxidant protection components in both human and animal organisms [14]. At the same time it is believed to be conditionally required for plant nutrition. The ability to reduce the toxic effects of some heavy metals is considered as an important property of Se [10]. It has been demonstrated that if food contains comparable Se concentrations, toxicity of high mercury and cadmium concentrations is generally reduced [5,12].

Currently, there are data on Se concentrations in soils, surface waters, agricultural crops, local foodstuffs and in the blood serum of the Dniester river Valley residents [13,17,19,20] as well as in algae and water plants [18]. However Se concentrations in mushrooms growing in this area remain unknown. Therefore the aim of the present work is assessment of mushroom ability to accumulate Se and other chemical elements in ecosystems of the Dniester River Valley.

Methods and materials

Mushroom samples have been collected in the ecosystems of the Dniester River Valley during autumn 2013. Each of these ecosystems occupies specific relief element and can be represented as elementary geochemical landscape of a certain type [21, p.111-113]. Mushroom samples have been collected within the following types of elementary geochemical landscapes: a) eluvial urbanized landscapes – areas in Tighina (Bender) and Dubăsari; b) transit landscapes – slopes near the villages Severinovca, Raşcov, Beloci, Doibani and near the town Camenca; c) accumulative landscape – the plot of the Dniester central floodplain near Chiţcani village, d) artificial environment – artificial growth medium for mushroom cultivation farms.

All considered transit geochemical landscapes are represented by forest ecosystems with artificial coniferous-deciduous vegetation, which is used for erosion control. Ecosystem of the accumulative landscape in the central floodplain is derived from the floodplain elm oak wood, which is currently represented by tree stand with predominant white poplar.

For each fungus species collected at each site several specimens (5-10) were sampled depending on size and availability. The fungi were cleaned from external impurities, chopped up with plastic knife, dried at room temperature to constant weight, powdered in a porcelain pestle and mortar and kept in closed polyethylene containers till the beginning of the analysis. Thus, a single value for each species represents the average value of specimens collected at given site.

Selenium content was determined by fluorometric method, based on wet digestion of samples with a mixture of HNO_3 and $HClO_4$, reduction of Se^{+6} to Se^{+4} and formation of fluorescent complex between selenic acid and 2,3-diaminonaphtalene [1]. All samples were analyzed in duplicate. Reference-standards of lyophilized cabbage, wheat flour and dry milk with regulated selenium levels (150, 57 and 115 μg/kg respectively) were used in each determination. For estimation of elemental composition of champignons samples were digested in microwave oven using a mixture of HNO_3, H_2O_2 and $HClO_4$. The resulting HNO_3 solutions were subjected to ICP-MS (Al, As, B, Ca, Cd, Co, Cr, Cu K, Hg, Li, Mg, Mn, Na, Ni, Pb, Sn, Sr, V, Zn) and AES-ICP (Si, P, Fe) analysis on quadruple mass-spectrometer Nexion 300D and atomic-emission spectrometer Optima 2000DV (Perkin Elmer, USA).

Results and discussions

Se concentrations have been analyzed in fruit bodies of 12 fungi species from 4 families: Boletaceae, Suillaceae, Agaricaceae and Tricholomataceae. Displayed in figure 1 mean Se concentrations give an overview of Se accumulation by mushrooms of these families.

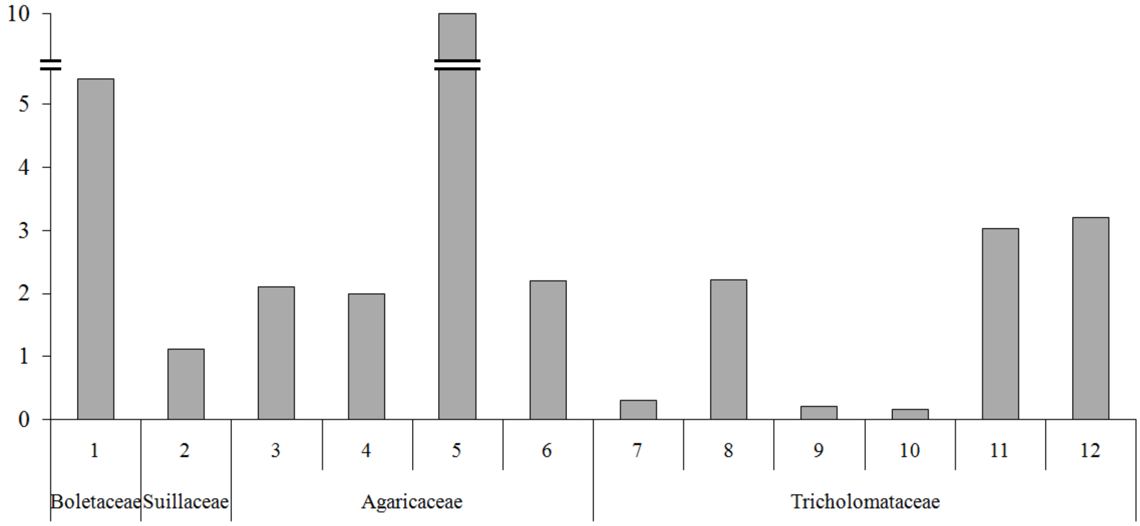

Fig.1. Se concentrations in basidiomycetes from the Dniester river Valley:
Boletaceae: 1 – *Boletus pulchrotinctus*; Suillaceae: 2 – *Suillus luteus*; Agaricaceae: 3 – *Lepiota aspera*, 4 – *Leucoagaricus leucothites*, 5 – *Agaricus bisporus*, 6 – *Lycoperdon perlatum*; Tricholomataceae: 7 – *Clitocybe nebularis*, 8 – *Lepista inversa*, 9 – *Armillaria mellea*, 10 – *Armillaria gallica*, 11 – *Tricholoma populinum*, 12 – *Lepista nuda*.

Se concentration range in mushrooms of the Dniester river valley is 0.147–24.920 mg/kg that is comparable with the values detected in mushrooms of Switzerland – 0.012–20.0 mg/kg [9], and Finland – 0.01–36.0 mg/kg [8]. First of all, one should indicate interspecies differences in Se content that is obvious both for whole samples and in separate families. Besides, Se accumulation differences apparently occur at the level of families. Particularly, Agaricaceae family mushrooms accumulate Se from 1.980 to 24.920 mg/kg, whereas Tricholomataceae family mushrooms – from 0.150 to 3.200 mg/kg. Evidently, Agaricaceae family mushrooms accumulate Se more intensively than Tricholomataceae family mushrooms. A significant amount of Se has been demonstrated in samples of *Boletus pulchrotinctus* from Boletaceae family (5.40±0.37 mg/kg). T. Stijve [9] also indicates high Se levels in mushrooms from Agaricaceae and *Boletaceae* families growing in Switzerland.

However, Se accumulation differences appear more specifically at the species level rather than at the family level. The leader in Se accumulation is white button mushroom (*Agaricus bisporus*), which accumulates about 10.00±13.05 mg Se/kg dry weight. The smallest Se content is found in fruit bodies of honey mushrooms (*Armillariella mellea* – 0.19±0.07 mg/kg and *Armillariella gallica* – 0.16±0.02 mg/kg), that is comparable to Se concentrations in honey mushrooms from Moscow region (0.050–0.201 mg/kg) [15]. Furthermore, Se concentrations vary significantly in fruit bodies of fungi belonging to the same species. These variations are not caused by accumulation ability of mushroom mycelium itself, but mainly for the presence of soluble forms of trace element in the habitat [16]. Se accumulation by mushrooms growing in different ecological and geochemical conditions is shown in Table 1.

Table 1

Se accumulation by mushrooms (mg/kg dry weight) in different ecological and geochemical conditions of the Dniester River Valley

Mushroom species	Type of elementary geochemical landscape			
	eluvial	transit	accumulative	artificial
Boletus pulchrotinctus	–	5.403±0.367	–	–
Suillus luteus	–	1.116±0.334	–	–
Lepiota aspera	–	2.097±0.143	–	–
Leucoagaricus leucothites	–	1.982±0.190	–	–
Agaricus bisporus	–	2.528±2.470	24.921±0.540	0.706±0.173
Lycoperdon perlatum	2.200±0.055	–	–	–
Clitocybe nebularis	–	0.302±0.010	–	–
Lepista inversa	–	0.194±0.010	4.224±0.347	–
Armillariella mellea	0.150±0.018	0.180±0.074	–	–
Armillariella gallica	–	0.158±0.016	–	–
Tricholoma populinum	–	–	3.030±0.230	–
Lepista nuda	–	–	3.202±0.600	–

The greatest number of fungi species is presented in transit and accumulative ecosystems. Transit ecosystems that are the link between the eluvial and accumulative elements of geochemical catena are characterized by high dynamics of chemical migration and reducing of their concentration as soils wash from the slopes off. Chemical elements accumulate in depressions (accumulative ecosystems) with pit-run fines, which are carried from the slopes [21].

Se is actively redistributed over the relief elements of the Dniester Valley. Thus, Se concentrations in alluvial soils near the village Hrușca are twice more than in soils of the upper terrace above the floodplain [19]. Elevated levels of this trace element in floodplain soils are inherent to the whole the Dniester–Prut interfluve [13]. This Se distribution pattern on the relief elements is reflected in Se accumulation by mushrooms from different geochemical catenae. Despite the small considered sample the average Se concentrations in mushrooms collected in accumulative ecosystem are definitely higher than in mushrooms growing in the eluvial and transit ecosystems (Table 1). The widest Se concentration range is observed for *Agaricus bisporus*. These mushrooms accumulate from 0.782 to 4.275 mg Se/kg in transit ecosystems, up to 24.921 mg/kg in alluvial ecosystems and about 0.583–0.828 mg/kg under artificial growing conditions. Mushrooms tend to accumulate much more Se amounts than crop plants, for which average Se concentrations are (mg/kg): sorghum – 0.147, sunflower – 0.125, maize – 0.117, clover – 0.111, alfalfa – 0.110, oat – 0.107, barley – 0.106, wheat – 0.106 [19]. Comparable amounts of Se are accumulated by algae (up to 3.0 mg/kg) and hydrophytes (up to 1.7 mg/kg) [18].

The above data show that some fungi in the Dniester River Valley are able to accumulate Se concentrations exceeding the safe level of consumption. Calculation of daily Se consumption level with 300 g of fresh *Agaricus bisporus* reveals the value (0.75 mg) that exceeds the adequate daily consumption level of the element by 10.7 times and maximum permissible consumption level by 1.67 times. However, the issue of Se bioavailability from mushrooms to human organism remains controversial. Experiments on rats and humans have shown that 'mushroom selenium' is poorly absorbed by organism [2,6]. Along with Se mushrooms are nutritional source of other chemical elements for human body. A.Gorbunov et al. [16] have shown that macroelement content in cultivated and wild growing mushrooms is approximately equal while trace element concentrations are significantly higher in wild ones.

Elemental analysis of *Agaricus bisporus* samples collected in accumulative ecosystem of Dniester floodplain and those grown under artificial conditions shows that Na and Ca concentrations are approximately equal. At the same time, cultivated mushrooms contain higher concentrations of K, Mg and P (Table 2).

Table 2

Macroelement concentrations in white button mushrooms (*Agaricus bisporus*) under the different growth conditions (mg/kg dry weight)

Element	Growth conditions:	
	artificial	wild
Na	1049±105	1053±105
K	36536±3654	24397±2440
Ca	528±53	721±72
Mg	1136±114	830±83
P	10229±1023	5694±569

Trace element ratio in cultivated and wild white button mushrooms shown on fig. 2 demonstrates enhanced accumulative ability of wild growing mushrooms in contrast with cultivated ones. Indeed, concentrations of Fe, Cr, Li, Sn, I in mushroom samples collected in the floodplain forest are twice higher, Cu, Al, Ni, V – more than 4 times higher, Co and Hg more than 20 times higher than in mushrooms cultivated in the local farms. Only Zn, Si, Mn, Sr, As content is similar in both samples.

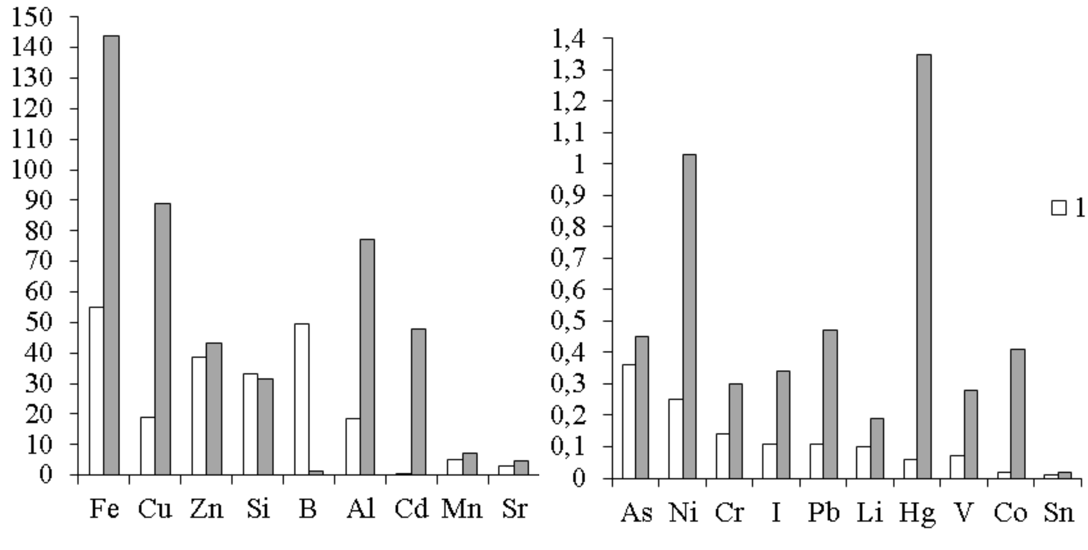

Fig.2. Trace element concentrations (mg/kg) in white button mushrooms (*Agaricus bisporus*) grown in artificial conditions (1) and collected in natural habitats (2).

It should be particularly noted that Cd concentration in wild mushrooms (47.69±4.77 mg/kg) is almost 1,000 times higher than in cultivated ones. Nevertheless, Cd is shown to be low in soils (0.4±0.2 mg/kg) and plants (1.0±0.1 mg/kg) of the Dniester river Valley [17]. This fact requires additional studies to identify the source of toxicant entrance in the ecosystem. Notably, Cd, Mn and Zn content in canned mushrooms almost is not changed. Contrary, canned mushrooms lose large amount of B, Cu, Mg, Se, however high Cr, Ni, Hg concentrations are persisted [11].

Conclusions

1. Mushrooms growing in the Dniester River Valley usually accumulate Se much more active than agricultural crops ranging from 0.147 to 24.92 mg Se/kg dry matter.

2. Se accumulation differences among fungi appear more specifically at the species level rather than at the family level.

3. Se concentrations vary significantly in fungi fruit bodies even in the same species growing in different ecological and geochemical conditions. The average Se content in fungi collected in accumulative ecosystem is higher than in mushrooms grown in eluvial and transit ecosystems.

4. Macro- and trace element content in fruit bodies of cultivated mushrooms (*Agaricus bisporus*) and wild growing ones differs significantly.

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