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Yu. A. Bilyavskyj
Cand. of Agr. Sc.
T. M. Myslyva
Cand. of Agr. Sc.
Zhytomyr National Agroecological University

QUALITY MONITORING OF EDIBLE MACROMYCETES GROWING IN AN ECOLOGICAL CONDITIONS OF ZHYTOMYR POLISSIA REGION

The specific accumulation of heavy metals by various species of the wild edible macromycetes with either tubular or lamellar hymenophore growing within the natural ecosystem zones in Zhytomyr Region, in particular the Polissian part thereof, has been researched hereby. It was ascertained that the qualitative and quantitative composition of pollutants accumulated by macromycetes mainly depends upon ecological condition of its growing environment, existence of contaminants in the soil substrate, wherein the fungi grow, and as well a macromycete itself. The principal contaminants of the mycological products growing within natural woodland ecosystems include lead (Pb), zinc (Zn) and cadmium (Cd), while in some cases – copper (Cu). The mycological products growing in a climate of the region under research are considered to be ecologically hazardous, and its consumption by people might result in escalation of both carcinogenic and not carcinogenic health hazards.

***Key words*:** *heavy metals, forest floor, soil, macromycetes, environmental safety, carcinogenic risk i non-carcinogenic risk.*

A problem statement

Because of current economic situation in Ukraine, the public interest in replenishment of the food ration by means of wild harvest, in particular wild fungi, has been significantly increased to the date. Moreover, such foodstuffs as fungi are considered to be the traditional food for inhabitants of the forest areas of the state, in particular the Polissian part of Zhytomyr Region. Prevalence of various species of the edible fungi in the forests of Zhytomyr Polissia, high yield and traditional consumption thereof by local inhabitants provide for delivery of microelements, inclusive of pollutants, to the organism of a man [1]. However, intensification of the anthropogenic and man-caused environmental impact results in pollution of environment by such chemicals as xenobiotics, which are rather widely represented by heavy metals [1, 4, 8]. Because of unfavourable ecological conditions, the wild fungal cultures may be significantly contaminated and therefore not safe for people as the mycobiota is known for its high pollutant accumulation ability. Therefore, environmental researches of the specific accumulation of various chemicals, in particular heavy metals, by the edible macromycetes have become very actual and reasonable to the date.

Review of recent researches and publications

Regular long-term researches in the field of accumulation of heavy metals by fungi and potential hazard induced by consumption of the mycological products by people have not been effectively described in modern domestic science-oriented literature, except for certain researches performed under local conditions of Rivne [5] and Transcarpathian [2] Regions. The closer attention is paid by modern researchers to the specific accumulation and behaviour of the radioactive elements containing in the mycological products. Results of such researches are published in works of O. Orlov and others [3, 6]. Selection of the declared research is conditioned by the fact that neither research involving assessment of carcinogenic and not carcinogenic hazard of fungi consumption by people living within the residential areas, in particular the Polissian part of Zhytomyr Region has been previously performed.

Purpose, objects and methods of research

The purpose of research assumes assessment of specific accumulation of Cu, Pb, Cd і Zn by various species of the wild edible macromycetes with either tubular or lamellar hymenophore growing within the natural ecosystem zones in Zhytomyr Region, in particular the Polissian part thereof. Also it involves determination of both carcinogenic and not carcinogenic health hazards for rural residents consuming polluted fungi. The objectives of research are as follows: 1) determination of contamination level for the topsoil, forest floor and leaf litter located within the area of natural woodland ecosystems; 2) estimation of contamination level and identification of the specific accumulation of heavy metals in mycothalluses of the edible fungi with either tubular or lamellar hymenophore growing within the areas of natural woodland ecosystems; 3) determination of scale of carcinogenic and not carcinogenic health hazard for people affected by chemicals penetrating into organism through consumption of polluted macromycetes. The said researches were performed in 2011–2013 within the woodland areas of Radomyshl, Korostyshiv, Olevsk and Ovruch districts of Zhytomyr Region. The samples of soil, forest floor and fungal mycothalluses were taken in July and August. The aforesaid samples were taken according to requirements of DSTU (Ukrainian State Standard) ISO 10381-4:2005. (ISO 10381-4:2003, IDT). Sampling depth for soil was 0…20 cm, while for forest floor – 0…5 cm. Carcinogenic and non-carcinogenic health hazard rate was assessed on the basis of the ordinary methodology [7]. Availability of Cd, Cu, Pb and Zn mobile forms in ammonium acetate extraction buffer (pH 4,8) was determined with help of atomic absorption spectrometry. The mycological cultures were taken from the same places as samples of the soil and forest floor. Each sample included at least three mycothalluses. Cd, Cu, Pb and Zn content in fungal mycothalluses was determined by atomic absorption spectrophotometry applied upon dry mineralization. The total of five and eight species of the edible fungi with tubular and lamellar hymenophore accordingly has been examined. In order to assess a rate of hazard connected with the

pollutant in valid manner, the toxic properties of soil were determined as the zinc equivalent. The test data were statistically processed with help of application software package, inclusive of Microsoft Excel and Statistica 10.0.

Research results

The quantitative and qualitative composition of pollutants accumulated by macromycetes mainly depends upon ecological condition of its growing environment and existence of contaminants in the soil substrate, wherein the fungi grow. Concentration of chemicals in fungal mycothalluses depends upon content of chemical elements in the parent rocks and mineral composition thereof; soil type, its agrochemical, physical & chemical properties, and as well chemical composition of the forest floor.

The soils located within the area under research are generally known for concentration of copper and zinc found in the top genetic horizon. The above is also evidenced by the value of elluvial accumulative coefficient thereof. The closer to parent rock, the higher concentration of cadmium, while lead is being concentrated within the top part of illuvial horizon. Migration of cadmium within the profile of soddy-podzolic soils is of clear elluvial-illuvial character. Cadmium that has previously penetrated to the soil exists there mainly in condition inherent to the plants, thus affecting the environment. The mobile form stimulates rather high migrating ability of the said element through the whole landscape, thus resulting in higher contamination of the flow of substances that have been getting to the plants from soil [4]. It shall be noted that chemical and physical properties of the soils within the area under research are considered to be rather favourable for intensified soil-to-plant or soil-to-water migration of the heavy metals. Therefore, contaminated mycological products can be found even on less-polluted soils.

It is ascertained in the course of research that content of either whole or mobile forms of copper, zinc, lead and cadmium in soils within natural woodland ecosystems does not generally exceed maximum permissible limits as per applicable regulations, except for the content of Cd mobile forms, the concentration of which in the topsoil within the area of certain woodlands has been 1,3–1,7 times more than MAC. Upon calculation of the zinc equivalent of toxic properties it has been ascertained that the topsoil contamination (in terms of the zinc equivalent) is of less- to medium-polluted character, while the forest floor contamination has predominantly medium-polluted level (except for certain woodlands within the area of Radomyshl district) (Table 1).

Content of heavy metals in the leaf and coniferous litter, which is a base for substrate, wherein the edible macromycetes grow, generally has average values specified in professional bibliographic sources [2] and is differentiated depending on woody plant species – edificators of the plant groups in the woodland ecosystems.

Table 1. **Level of pollutants (heavy metals) content in soil (layer depth 0…20 cm) and forest floor (layer depth 0…5 cm) within woodland ecosystems of Zhytomyr Polissia in terms of the zinc equivalent of toxic properties**

Place of researches	Soil type	Description of the place of researches	Character of the contamination	
			soil	forest floor
Slovechne, Ovruch district	Soddy less podzolic sandy loam soil on water-glacial deposits	coniferous forest (pine)	LP	MP
		mixed forest (birch+pine)	LP	MP
		mixed forest (oak+pine)	LP	MP
Budky, Olevsk district	Soddy medium podzolic sandy loam soil on fluvioglacial sands	coniferous forest (pine)	LP	MP
Bilokorovychi, Olevsk district	Soddy medium podzolic sandy soil on fluvioglacial sands	mixed forest (oak+pine)	LP	LP
		mixed forest (birch+pine)	LP	LP
Gumennyky, Korostyshiv district	Soddy less podzolic sandy loam soil on moraine	mixed forest (oak+aspen+ birch)	MP	MP
		coniferous forest (pine)	MP	MP
Menkivka, Radomyshl district	Soddy medium podzolic sandy loam soil on water-glacial deposits	mixed forest (oak+aspen)	LP	LP
		coniferous forest (pine)	LP	LP
Krasnobirka, Radomyshl district	Soddy less podzolic sandy loam soil on water-glacial deposits	mixed forest (oak+birch)	MP	HP
		mixed forest (oak+pine)	MP	MP

Note: LP – less pollution; MP – medium pollution; HP – high pollution.

Contained in macromycetes heavy metals are distributed in uneven manner, in which connection the position and concentration of certain element are dependable either upon fungus growing locality or it species and hymenophore structure as the most fungi pollutants are accumulated in specific tissues of mycothalluses, i. e. lamellas and tubes. Upon the results of performed researches there have been determined intensity-based sequences of copper, zinc, lead and cadmium accumulation in mycothalluses of the edible fungi with either lamellar or tubular hymenophore (Table 2).

Table 2. **Intensity-based sequences of heavy metals accumulation in edible mushroom mycothalluses**

Name of the mushroom	Sequence of accumulation
Tubular hymenophore	
Boletus edulis Bull. ex Fr.	Zn > Cu > Pb > Cd
Leccinum aurantiacum (Bull. ex Fr.) S. F. Gray)	Zn > Cu > Pb > Cd
Leccinum scabrum (Fr.) S.F. Gray	Zn > Cu > Pb > Cd
Suillus luteus (Fr.) S.F. Gray	Zn > Cu > Pb > Cd
Suillus variegatus (Fr.) Kuntze	Zn > Cu > Pb > Cd
Lamellar hymenophore	
Lactarius torminosus (Fr.) S. F. Gray	Zn > Pb > Cu > Cd
Lactarius deliciosus Fr.	Zn > Cu > Pb > Cd
Lactarius volemus Fr.	Zn > Cu > Pb > Cd
Tricholoma flavovirens (Fr.) Lund. et Nannf.	Zn > Cu > Pb > Cd
Tricholoma terreum **(**Fr.) Kumm	Zn > Cu > Pb > Cd
Paxillus involutus (Batch.) Fr.	Zn > Cu > Pb > Cd
Agaricus campestris Fr.	Zn > Cd > Cu > Pb
Russula xerampelina **(**Schff) Fr.	Zn > Cd > Cu > Pb

In general, the macromycetes with tubular hymenophore are specifically known for more intensive accumulation of copper and zinc, while the macromycetes with lamellar hymenophore – lead and cadmium. It is ascertained that copper is predominantly concentrated by such macromycetes with tubular hymenophore as *Suillus luteus* (Fr.) S. F. Gray and *Suillus variegatus* (Fr.) Kuntze (Table 3). Zinc, as much as possible, is accumulated by *Leccinum aurantiacum* (Bull. ex Fr.) S. F. Gray; lead – by *Suillus luteus* (Fr.) S. F. Gray and *Suillus variegatus* (Fr.) Kuntze, while cadmium – by all species under research, except for *Boletus edulis* Bull. ex Fr.

Table 3. **Data on heavy metal accumulation ability of edible macromycetes with tubular hymenophore**

Type of mushroom and amount of the analysed standards	Name of the element			
	Cu	Zn	Pb	Cd
Boletus edulis Bull. ex Fr., n=75				
Leccinum aurantiacum (Bull. ex Fr.) S. F. Gray, n=60				
Leccinum scabrum (Fr.) S.F. Gray, n=30				
Suillus luteus (Fr.) S.F. Gray, n=30				
Suillus variegatus (Fr.) Kuntze, n=30				

Note:

– weak concentrator

– medium concentrator

– strong concentrator

Lead concentrators are considered to be all species of macromycetes with lamellar hymenophore under research, except for *Agaricus campestris* Fr. and *Russula xerampelina* (Schff) Fr., while cadmium concentrators – all species, except for *Lactarius torminosus* (Fr.) S. F. Gray and *Paxillus involutus* (Batch.) Fr. (Table 4).

Table 4. **Data on heavy metal accumulation ability of edible macromycetes with lamellar hymenophore**

Type of mushroom and amount of the analysed standards	Name of the element			
	Cu	Zn	Pb	Cd
Tricholoma flavovirens (Fr.) Lund. et Nannf., n=60				
Lactarius deliciosus Fr., n=30				
Tricholoma terreum (Fr.) Kumm, n=30				
Lactarius volemus Fr., n=30				
Lactarius torminosus (Fr.) S. F. Gray, n=30				
Paxillus involutus (Batch.) Fr., n=60				
Agaricus campestris Fr., n=30				
Russula xerampelina (Schff) Fr., n=60				

Note:

– weak concentrator

– medium concentrator

– strong concentrator

Ecological safety of the macromycetes under research significantly differs depending upon chemical element and fungus itself (Figure 1). It is found that the maximum specific quantity of samples with exceeded copper content (as compared with applicable MAC) taken from mycothalluses of macromycetes with tubular hymenophore falls within *Suillus variegatus* (Fr.) Kuntze (42±1,3 %) and *Leccinum aurantiacum* (Bull. ex Fr.) S. F. Gray (38±0,9 %), while as concerns mycothalluses of *Boletus edulis* Bull. ex Fr., the exceeded MAC of copper has been revealed only in each tenth sample.

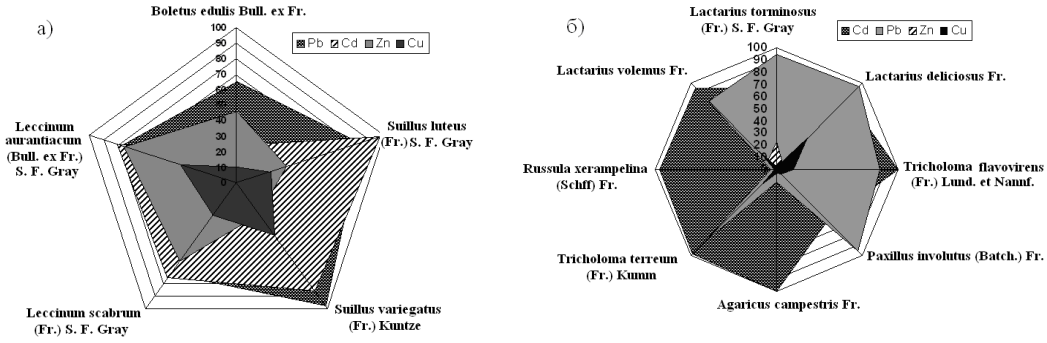

Figure 1. **Percentage of samples with exceeded MAC of heavy metals taken from mycological products – macromycetes with tubular (a) and lamellar (b) hymenophore, averaged values for 2011–2013**

The number of samples with exceeded MAC of zinc taken from mycothalluses of macromycetes with tubular hymenophore differs within the range 25±1,1 % … 76±3,4 %. Macromycetes with tubular hymenophore are found to be contaminated with lead and cadmium. Mycothalluses are found to have higher concentration of lead and cadmium (65±2,6 % … 98±5,4 % and 24±0,6 % … 97±5,1 % of the total quantity under test accordingly). It is found upon research of five species of macromycetes with tubular hymenophore that mycothalluses of *Boletus edulis* Bull. ex Fr. have the minimum content of heavy metals, while the same of *Leccinum aurantiacum* (Bull. ex Fr.) S. F. Gray and *Suillus variegatus* (Fr.) Kuntz are contaminated to the maximum.

The maximum specific quantity of samples with exceeded copper content (as compared with applicable MAC) taken from mycothalluses of macromycetes with lamellar hymenophore falls within *Lactarius deliciosus* Fr., the each third sample of which has been found to be contaminated with the said element. The mycothalluses of *Lactarius torminosus* (Fr.) S. F. Gray and *Russula xerampelina* (Schff) Fr. have been found to be almost uncontaminated. It is found that only mycothalluses of *Lactarius torminosus* (Fr.) S. F. Gray have zinc content that is 1,1–1,2 times more than the applicable MAC, while the other species of macromycetes with lamellar hymenophore under research have no excessive content of the said element. However, only mycothalluses of *Russula xerampelina* (Schff) Fr. have been found to be almost uncontaminated with lead, while 79±2,6% … 96±4,9 % of the other tested species have demonstrated exceeded content of lead (as compared with applicable MAC).

The excessive content of cadmium has been revealed in mycothalluses of all species of macromycetes with lamellar hymenophore, and moreover, 100 % of tested mycothalluses of *Tricholoma flavovirens* (Fr.) Lund. et Nannf. and *Agaricus campestris* Fr. have been found to have such content even higher that applicable MAC. Other species under test (in amount of 59±1,4 % … 98±4,8 %) have demonstrated exceeded content of cadmium.

It is found upon research of eight species of macromycetes with lamellar hymenophore that mycothalluses of *Agaricus campestris* Fr. та *Russula xerampelina* (Schff) Fr. have the minimum content of heavy metals, while the same of *Lactarius deliciosus* Fr. and *Lactarius volemus* Fr. are contaminated to the maximum.

In the course of research there have been determined certain hazards connected with penetration of chemicals, inclusive of carcinogenic agents, to the organism of a man as a result of consumption of the mostly polluted macromycetes by residents of the rural settlements located within the Polissian part of Zhytomyr Region. We have calculated the rate of not carcinogenic hazard connected with consumption of four mostly contaminated species of macromycetes: *Lactarius deliciosus* Fr., *Lactarius volemus* Fr., *Leccinum aurantiacum* (Bull. ex Fr.) S. F. Gray) and *Suillus variegatus* (Fr.) Kuntze (Table 5).

Table 5. **Rate of non-carcinogenic risk connected with penetration of chemicals to the organism of a man as a result of macromycetes consumption**

Name of substance	Average daily dose (ADD), мг/(кг день)	Reference dose for chronic oral ingestion RfD, мг/кг	Hazard quotient HQ	Organs and systems of organism which are struck
Copper	$4{,}6–9{,}9 \cdot 10^{-4}$	0,019	0,024-0,052	Gastrointestinal tract, liver
Lead	$0{,}9–1{,}9 \cdot 10^{-4}$	0,0035	0,026-0,054	Central nervous system, blood, developmental defects, reproductive system, hormonal disorders
Cadmium	$2{,}1–4{,}6 \cdot 10^{-5}$	0,0005	0,042-0,092	Kidneys, hormonal disorders
Zinc	$0{,}9\text{-}2{,}9 \cdot 10^{-3}$	0,3	0,003-0,009	Blood
Cumulative risk	HQ general		0,365-0,413	
	HQ developmental defects		0,026-0,054	
	HQ gastrointestinal tract		0,024-0,052	
	HQ liver		0,024-0,052	
	HQ blood		0,035-0,060	
	HQ hormonal disorders		0,085-0,118	
	HQ central nervous system		0,026-0,054	
	HQ reproductive system		0,026-0,054	
	HQ kidneys		0,042-0,092	

The hazard has been assessed according to the Hazard Quotient (HQ), with help of which it shall be possible to define the admissible level of penetration of chemicals to the organism of a man. Such a factor in no case has exceeded value of 1.0, while depending on type of element or settlement it has varied within the following ranges of values: for copper – 0.024 … 0.052; for lead – 0.026 … 0.054; for cadmium – 0.042 … 0.092 and for zinc – 0.003 … 0.009. All above shall be interpreted as evidence of low probability of adverse effect progress through daily penetration of the said substances to the organism of a man because of long life consumption of macromycetes.

However, considering the fact that pollutants might penetrate to the organism of rural residents not only upon consumption of fungi, but also potatoes and vegetables grown by them at home grounds, the probability of not carcinogenic impacts shall be accordingly increased. When reviewing the structure of not carcinogenic hazard origination, it should be stressed that despite of observation point, the maximum specific quantity falls within hazard connected with hormonal disorders (HQ = 0.085 … 0.118) and renal diseases (HQ = 0.042 … 0.092).

The carcinogenic risk (for the purpose of this work shall be understood as probability of increase in frequency of neoplasm development in people because of

oral ingestion of hazardous chemical carcinogens) has been assessed through calculation of individual, cumulative and population risk rates. The chemicals under test have included lead and cadmium selected as substances with proven carcinogenic effect (Table 6).

It has been found that the rate of individual carcinogenic risk connected with long life consumption of contaminated macromycetes for lead is 3.5-7.2 x 10^{-5}. Pursuant to the international criterion scale it is assessed as low (admissible) risk (the risk that as a rule requires setting specific safety hygienic regulations for population). Rate of individual carcinogenic risk for cadmium has varied within the range 1.5-3.4 x 10^{-4}. Pursuant to the international criterion scale it is assessed as medium risk admissible for production conditions, however in case of residential exposure, it shall be subject to dynamic control and comprehensive examination of the sources and potential consequences of the hazardous effects required for making appropriate managerial decisions in the field of hazard management.

Table 6. **Rates of individual and population risks connected with oral ingestion of chemicals upon consumption of macromycetes**

Carcinogen	Individual carcinogenic risk ICR	Population carcinogenic risk PCR	Level of individual carcinogenic risk
Budky, Olevsk district			
Lead	$5,7 \cdot 10^{-5}$	0,016	low
Cadmium	$1,5 \cdot 10^{-4}$	0,044	medium
Cumulative risk	$2,1 \cdot 10^{-4}$	0,060	medium
Menkivka, Radomyshl district			
Lead	$7,2 \cdot 10^{-5}$	0,021	low
Cadmium	$2,1 \cdot 10^{-4}$	0,061	medium
Cumulative risk	$2,8 \cdot 10^{-4}$	0,082	medium
Krasnobirka, Radomyshl district			
Lead	$3,5 \cdot 10^{-5}$	0,034	low
Cadmium	$3,4 \cdot 10^{-4}$	0,33	medium
Cumulative risk	$3,7 \cdot 10^{-4}$	0,36	medium
Gumennyky, Korostyshiv district			
Lead	$4,6 \cdot 10^{-5}$	0,023	low
Cadmium	$2,5 \cdot 10^{-4}$	0,12	medium
Cumulative risk	$2,9 \cdot 10^{-4}$	0,15	medium

Findings and prospects of the further researches

It is found on the basis of the research results that: 1) zinc and cadmium (while in some cases – copper) are considered to be the principal pollutants of the mycological products grown in areas of natural woodland ecosystems within the Polissian part of Zhytomyr Region; 2) copper and zinc are more intensively accumulated by macromycetes with tubular hymenophore, while lead and cadmium – by macromycetes

with lamellar one; 3) mycothalluses of *Leccinum aurantiacum* (Bull. ex Fr.) S. F. Gray) and *Suillus variegatus* (Fr.) Kuntze have the maximum rate of contamination with heavy metals among macromycetes with tubular hymenophore, while mycothalluses of *Lactarius deliciosus* Fr. and *Lactarius volemus* Fr. have the maximum rate of contamination among macromycetes with lamellar hymenophore; 4) the rate of cumulative non-carcinogenic health risk connected with long life consumption of polluted macromycetes is 0.365-0.413 (being assessed as low), while the rate of cumulative carcinogenic risk is 2.1-3.7 x 10^{-4} (being assessed as medium). The further researches shall involve review of specific accumulation by macromycetes of Co, Ni, Cr and As.

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