

## THE STUDY OF HEAVY METAL FROM ENVIRONMENTAL SAMPLES BY ATOMIC TECHNIQUES

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**Rezumat.** Prin tehnicile Spectrometriei de Absorbție Atomică (AAS) și Spectrometriei Razelor X de Fluorescență cu Dispersie în Energie (EDXRF) am analizat conținutul de metale grele (Cd, Cr, Ni, Pb, Ti, Sr, Co, Bi) din opt specii de ciuperci sălbatice (*Amanita vaginata*, *Amanita rubescens*, *Amanita phalloides*, *Armillariella mellea*, *Armillariella tabescens*, *Agaricus campestris*, *Hypholoma fasciculare*, *Hypholoma pudorinus*) și probe de sol substrat, colectate din zece site-uri forestiere ale județului Dâmbovița, România. S-a determinat că elementele, în special metalele grele în sol erau caracteristice solurilor acide din terenurile forestiere românești care sunt influențate de poluarea industrială. S-a studiat transferul metalelor grele de la substraturi la ciuperci și s-a calculat coeficientul de acumulare al metalelor grele analizate prin tehnicile AAS și EDXRF. Valorile concentrațiilor metalelor grele din probele de ciuperci analizate sunt ușor crescute față de cele raportate în literatură.

**Abstract.** Using the Atomic Absorption Spectrometry (AAS) and Energy Dispersive X-ray spectrometry (EDXRF) techniques we analyzed the contents of heavy metals (Cd, Cr, Ni, Pb, Ti, Sr, Co, Bi) from eight wild mushrooms and soil substrate samples (48 samples of eight fungal species and 32 underlying soil samples), collected from ten forest sites of Dambovița County Romania. It was determined that the elements, especially heavy metals, in soil were characteristic of the acidic soils of the Romanian forest lands and are influenced by industrial pollution. Analytical possibilities of AAS and EDXRF analytical techniques have been compared and the heavy metal transfer from substrate to mushrooms has been studied. The coefficient of accumulation of essential and heavy metals has been calculated as well. Heavy metal contents of all analyzed mushrooms were generally higher than previously reported in literature.

**Keywords:** EDXRF, FAAS, essential element, heavy metal, wild mushroom, soil pollution

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## 1. Introduction

For the assessment of heavy metals pollution levels and identification of their sources, which are a prerequisite for studying effects of contaminants on the environment and human health, a multivariate data base containing as many pollutant elements should be generated. Therefore, multielement methods are usually used for such studies. The analysis of environmental samples for their elemental content is governed by the sample type, the element of interest, the sensitivity, precision and accuracy needed and the availability of the technique. The choice of multielement methods available includes inductively coupled plasma atomic emission spectrometry (ICPAES), inductively coupled plasma mass spectrometry (ICPMS), X-ray fluorescence spectrometry (XRF), ion beam analysis (IBA) [i.e. particle-induced X-ray emission (PIXE) and proton-induced gamma-ray emission (PIGE)], nuclear activation analysis [neutron activation analysis (NAA), prompt gamma neutron activation analysis (PGNAA), charged particle activation analysis (CPAA)], and several other methods, which are seldom used on a routine basis. Some of these methods can be complemented by the use of monoelement techniques such as anodic stripping voltammetry (ASV) or atomic absorption spectrometry (AAS).

Heavy metal pollution is a problem associated with areas of intensive industrial activity. The biomonitoring technique (using the biomonitors: mushrooms) was employed in this work to study the heavy metals from atmospheric deposition in Dambovița County, Romania together with complementary atomic analytical techniques: Atomic Absorption Spectrometry (AAS) and Energy Dispersive X-Ray Fluorescence (EDXRF). These high sensitivity analysis methods were used to determine the elemental composition of some samples of mushrooms used as bioindicators, collected from areas with different pollution industrial sources. We have studied the presence of elements such as Cd, Cr, Cu, Co, K, Fe, Mn, Ni, Pb, Zn, Mg, Se, etc.

Major sources of heavy metals pollutants in soils, in Dambovița County, include atmospheric pollution from metallurgical industries, the combustion of fossil fuels, motor vehicles, urban and industrial wastes, chemicals, textile, paints and many more. Most of the metals in soil are mainly the result of contamination by industrial emissions.

Many studies [1-10] revealed a high ability of mushrooms to accumulate common pollutants present in the biosphere at trace levels, mainly heavy metals and radionuclides.

Mushrooms are saprophytes and include members of Basidiomycota and some members of *Ascomycota* [1]. Mushrooms have been a food supplement in various cultures and they are cultivated and eaten for their edibility and delicacy [2, 3].

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They fall between the best vegetables and animal protein source. Mushrooms are considered as source of proteins, vitamins, fats, carbohydrates, amino acids, and minerals [4]. The energy value varies according to species, which is about equal to that of an apple. Many studies have been demonstrated the fact that some mushrooms species (*Pleurotus* species for examples) are useful in some combination to cure headache, stomach ailments, colds, fever, asthma and high blood pressure [4]; other species are recommended to diabetic and anemic persons, owing to their low carbohydrate and high folic acid content. Some mushrooms are reputed to possess anti-allergic, anti-cholesterol, anti-tumour and anti-cancer properties [5, 6].

Compared to green plants, mushrooms can build up large concentrations of some heavy metals, particularly cadmium, mercury, copper and lead [7]. This suggests that mushrooms possess a very effective mechanism that enables them readily to take up heavy metals from soil [8]. In many studies [7-10] the concentrations of heavy metals have been observed in the fruiting bodies of different mushrooms collected adjacent to heavy metal smelters, landfills of sewage sludge, emission area. *Basidiomycetes* are generally capable of accumulating heavy metals and then become their source in food chain [11]. Moreover, a lot of mushrooms species accumulate radioactive isotopes of cesium [1].

Consumption of wild growing mushrooms has been preferred to eating of cultivated fungus in Romania (e.g. *Armillariella mellea*, *Amanita vaginata*, *Amanita rubescens*). But, the knowledge of the nutritional value of wild growing mushrooms has been limited when compared with other vegetables. It seems that mushrooms are still much more to offer, but is necessary to concentrate all studies for establishing a real metabolic features for one species in the view to promote it as hyperaccumulator or bioindicators for one metal species.

Different heavy metals such as As, Cd, Ni, Hg, accumulated in high concentration in mushrooms are toxic for the peoples; on the other hand many elements are essential for the human metabolism, such as Fe, Zn, Mn, Cu, Cr, Se, but in low concentrations, because they are enzyme activators. These essential elements become toxic in the measure of increasing their concentrations too much. It is well know that the content of heavy metals are related to species of mushrooms, collecting area of the sample, age of fruiting bodies and distance from any source of pollution.

The aim of this work was to determine the heavy metal content of the fruiting bodies of four species eight wild mushrooms (*Amanita vaginata*, *Amanita rubescens*, *Amanita phalloides*, *Armillariella mellea*, *Armillariella tabescens*, *Agaricus campestris*, *Hypholoma fasciculare*, *Hypholoma pudorinus*) and soil samples, collected from ten forest sites of Dambovița county, Romania.

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The elements Zn, Cu, Fe, K, Mn, Mg, P, Se, Cd, Cr, Ni, Pb, Ti, Sr, Co and Bi were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry and Atomic Absorption (AA) Spectrometry.

From the same collecting point were taken  $n = 6$  samples from the young fruiting bodies of wild young mushrooms species and their substrate at different times of the day: morning, afternoon and mid-day. The pH between 4.5 and 6.2 of forest sites of studied mushrooms species have been determined according to ISO 10390:2005.

## 2. Materials and Methods

### 2.1. Materials

The young mushrooms species, *Amanita vaginata*, *Amanita rubescens*, *Amanita phalloides*, *Armillariella mellea*, *Armillariella tabescens*, *Agaricus campestris*, *Hypholoma fasciculare*, *Hypholoma pudorinus* (Table 1) were collected from ten forest sites of Dambovița county, Romania, in the same direction of wind. Usually, the mushrooms represent the fruiting body (carpophore, mycocarp), mostly above ground, of higher fungi.

Collections of species were made at different times of the day: morning, afternoon and mid-day by uprooting its substratum with aid of the scalpel.

A fruiting body of mushroom species is formed from spacious underground mycelia (*hyphae*) by the process of fructification.

Mycelia of ectomycorrhizal species live in symbiosis with roots of a plant, mostly a tree.

The fruiting body samples have been washed with deionised water, from dirt, then, with a plastic knife, have been chopped up in 1 mm portions; the samples have been dried at 60 ° between 10 and 24 hours (depends of the species), then grinded until to fine powder and finally weighed (*CEN Standard 'Foodstuffs — Determination of trace elements — Performance criteria, general considerations and sample preparation*).

Substrate and soil samples have been dried at 70<sup>0</sup>C in 24 hours. After drying the solid samples have been grinded until to fine powder and weighed. Chemicals used included nitric acid (65% Aldrich), hydrochloric acid (37% Fluka), hydrogen peroxide (30% Fluka), and potassium chloride (Aldrich). Distilled deionised water had a resistivity better than 17.5 MΩ cm.

The solutions used for calibration of FAAS were prepared from standard solution (Merck) of elements studied.

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## 2.2. Methods

### 2.2.1. Energy Dispersive X-ray Fluorescence

Two grams of sample ( $n = 6$ ) for each species collected and soil collected from forest area, Dambovița County, Romania were pressed manually, without any chemical treatment, in a plastic vial with Mylar in the bottom and then were analyzed.

The elemental content of samples was determined by Energy Dispersive X-Ray Fluorescence (EDXRF) [12-14] technique, using the ElvaX spectrometer having a X-ray tube with Rh anode, operated at 50 kV and 100 $\mu$ A. Samples were excited for 300 s and the characteristic X-rays were detected by a multichannel spectrometer based on a solid state Si-pin-diode X-ray detector with a 140  $\mu$ m Be window and a energy resolution of 200eV at 5.9 KeV. ElvaX software was used to interpret the EDXRF spectra. The accuracy and precision of the results was evaluated by measuring a certified reference sample (NIST SRM 1571- *Orchard leaves*). Good agreements were achieved between certified values and data obtained, with recoveries ranging from 98 to 104%.

### 2.2.2. Atomic Absorption Spectrometry

The Atomic Absorption Spectrometry (AAS)[16], is the most widely utilized method today for rapid and quantitative elemental analysis. The detection limit in AAS analysis method is up to 0.1  $\mu$ g/kg under optimum test conditions. A material sample, in a liquid solution, is atomized through rapid heat application and placed in the radiation path of several element-specific light source. The sample atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of light absorption. The atomic density determine the absorption rate and the Lambert-Beer's law give the value of absorbance from each element of the sample which is proportional with the concentration of that element. The Lambert-Beer law is difficult to applying directly in AAS due to variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AA). The high sensitivity by AAS is obtained using the relative analysis method.

Mushroom is a very specific sample for destruction. It contains plant oils and chitin in the cell membrane which is difficult to destroy. In this study dried samples was digested in an acid solution using a Berghof MWS-2 microwave digestion system. The Teflon digestion vessels used in this procedure was reusable and the clean-up step was relatively easy and less time consuming. Dried fungus samples (500 mg) were introduced into the digestion vessels; then 3 mL nitric acid and 5 mL hydrogen peroxide were added. After digestion time (40 min) the vessels were cooled to room temperature (about 30 min.). The clear solution

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volume was made up to 50 mL for each sample using deionised water. Certified Standard Reference Material SRM 1577c (Bovine Liver) from the National Institute of Standards and Technologies was used to verify the methods.

Dried solid substrates (500 mg) were introduced into the digestion vessels and then 3 mL nitric acid and 9 mL hydrochloric acid (aqua regia) were added. For soil, EPA 3051A program was chosen. After digestion time (30 min) the vessels were cooled to room temperature and then the each solution volume was made up to 50 mL for each sample using deionised water. Certified Standard Reference Material SRM for soil GBW 07406 and IAEA-375 was used, too.

The elemental content of samples of mushrooms and their substrate was determined by Atomic Absorption Spectrometry, by using an AVANTA GBC flame spectrometer and hollow cathode lamps. Prepared samples are analyzed by an AAS, an instrument of choice for metals analysis that provides a good sensitivity and requires less sample volume.

Due to the specificity of this spectrometer, the results obtained are accurate and seldom require confirmation. In atomic absorption spectroscopy a liquid sample is aspirated and mixed as an aerosol with combustible gasses [15, 16].

All samples concentrations were reported as mg/kg dry weight of material. The measured levels for mushrooms were compared with the admitted levels according to the (EC) No 1881/2006 - *setting maximum levels for certain contaminants in foodstuffs* [17], (EC) No 333/2007 - *laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs* [18] and for soil, according to the Romanian legislation (MAPPM Ord. 756/Nov.1997).

### **3. Results and Discussion**

The determination of heavy metal concentration in the fruiting bodies of mushrooms is essential in dietary intake studies, because mushrooms form a non-negligible part of the diet in many countries, especially for certain population groups.

The minerals can be accumulated in mushrooms, and this accumulation is generally species metabolism-dependent and also strongly affected by the chemical composition of the substrate from which mushrooms get their nutrients.

Mushrooms are regarded as healthy foods, when are young especially, with higher content of protein and carbohydrate than vegetables. They are also rich in minerals, dietary fibers and vitamins.

The level of metals of the fruiting body of wild mushrooms and their substrate has been presented in Table1 and 2 and Figure 1 and 2. The concentration of essential

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elements, K and Mg has been determined on a dry weight basis only by EDXRF spectrometry.

The elements Zn, Cu, Fe, Mn and Se were determined by FAA spectrometry. Fe and Zn are determined by both analytical methods. Some metals were concentrated in considerably higher levels in the fruiting body than the soil.

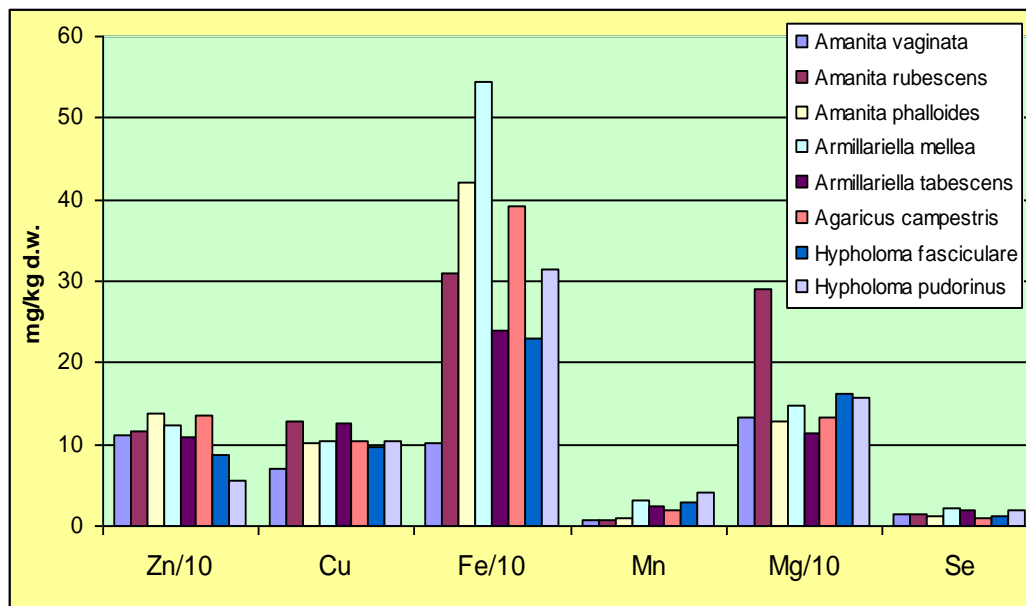
**Table 1:** Mean concentration of essential elements in fruiting body of mushrooms and their substrate (mg/kg d.w)

Mushroom species and substrate	Zn*	Cu*	Fe*	K**	Mn*	Mg**	Se*
<i>Amanita vaginata</i> (n = 6)	112.1	7.11	101.6	53087	0.7	133.6	1.53
Soil (n = 6)	74.9	11.4	789.2	3736.9	1.37	109.0	2.95
<i>Amanita rubescens</i> (n = 6)	115.2	12.9	308.9	16654	0.82	289.3	1.48
Soil (n=6)	79.5	15.7	856.8	2310.0	2.57	147.8	2.93
<i>Amanita phalloides</i> (n = 6)	137.4	10.2	421.9	40892.7	0.89	128.2	1.12
Soil (n = 6)	83.2	20.7	746.4	2380.4	2.71	95.4	2.34
<i>Armillariella mellea</i> (n = 6)	124.0	10.43	543.8	35294.6	3.06	148.2	2.08
Soil (n = 6)	93.5	32.8	1092.1	4301.3	8.67	102.3	6.34
<i>Armillariella tabescens</i> (n = 6)	108.7	12.5	240	48248	2.52	113.6	1.89
Soil (n = 6)	76.8	24.7	772.1	4789.3	8.02	101.7	4.02
<i>Agaricus campestris</i> (n = 6)	135.7	10.3	391.9	49983	1.90	134.1	1.03
Soil (n = 6)	98.7	22.7	832.1	5305.6	5.67	102.0	2.06
<i>Hypholoma fasciculare</i> (n = 6)	86.4	9.67	229.5	59406	2.98	162.2	1.16
Soil (n = 6)	110.6	20.2	761.3	3421.0	6.07	160.6	4.56
<i>Hypholoma pudorinus</i> (n = 6)	55.8	10.51	313.7	43253	4.21	157.8	1.98
Soil (n = 6)	101.2	14.3	621.3	6430.2	8.92	134.5	3.24
RDS %	2.5-6.4	4.8-11.2	1.1-3.7	2.8-7.5	1.3-4.5	1.8-5.3	3.2-4.6

**Table 2.** Mean concentration of heavy metals in fruiting body of mushrooms and their substrate (mg/kg d.w)

Mushroom species and substrate	Cd*	Cr*	Ni*	Sr*	Pb*	Co*	Ti*	Bi*
<i>Amanita vaginata</i> (n = 6)	0.03	0.18	1.12	0.03	1.93	0.02	nd	nd
Soil (n = 6)	0.28	1.19	2.48	0.64	8.03	0.16	0.07	0.02
<i>Amanita rubescens</i> (n = 6)	0.08	0.55	0.97	0.2	0.68	0.01	nd	nd

Soil (n = 6)	0.42	1.32	2.09	0.83	4.96	0.52	0.03	0.03
<i>Amanita phalloides</i> (n = 6)	0.3	0.52	0.64	0.04	3.03	0.01	0.07	nd
Soil (n = 6)	0.65	1.83	1.94	0.34	5.73	0.21	0.4	nd
<i>Armillariella mellea</i> (n = 6)	0.11	1.1	1.02	nd	2.36	nd	nd	nd
Soil (n=6)	0.24	3.4	7.45	0.04	4.43	0.76	0.16	nd
<i>Armillariella tabescens</i> (n = 6)	0.05	0.07	1.19	nd	1.78	nd	nd	nd
Soil (n = 6)	0.73	1.62	3.02	nd	3.61	0.11	nd	nd
<i>Agaricus campestris</i> (n = 6)	0.06	0.03	1.06	nd	1.32	0.04	0.06	nd
Soil (n = 6)	0.91	0.93	2.69	nd	4.02	0.63	0.53	nd
<i>Hypholoma fasciculare</i> (n = 6)	0.35	0.06	1.12	nd	0.95	0.04	0.03	nd
Soil (n = 6)	1.04	0.82	3.06	nd	2.47	0.4	0.29	nd
<i>Hypholoma pudorinus</i> (n = 6)	0.04	0.08	1.54	0.01	0.09	0.02	0.05	nd
Soil (n = 6)	0.10	0.57	3.23	0.48	1.03	0.13	0.53	nd
RDS %	1.5-7.1	2.2-8.4	1.3-10.1	1.1-5.1	1.9-11.2	2.1-6.3	1.4-4.3	1.7-10.3
<ul style="list-style-type: none"> <li>• *AA spectrometry concentrations</li> <li>• ** EDXRF technique</li> </ul>								



**Fig 1.** Mean concentration of essential elements in fruiting body of wild mushrooms.



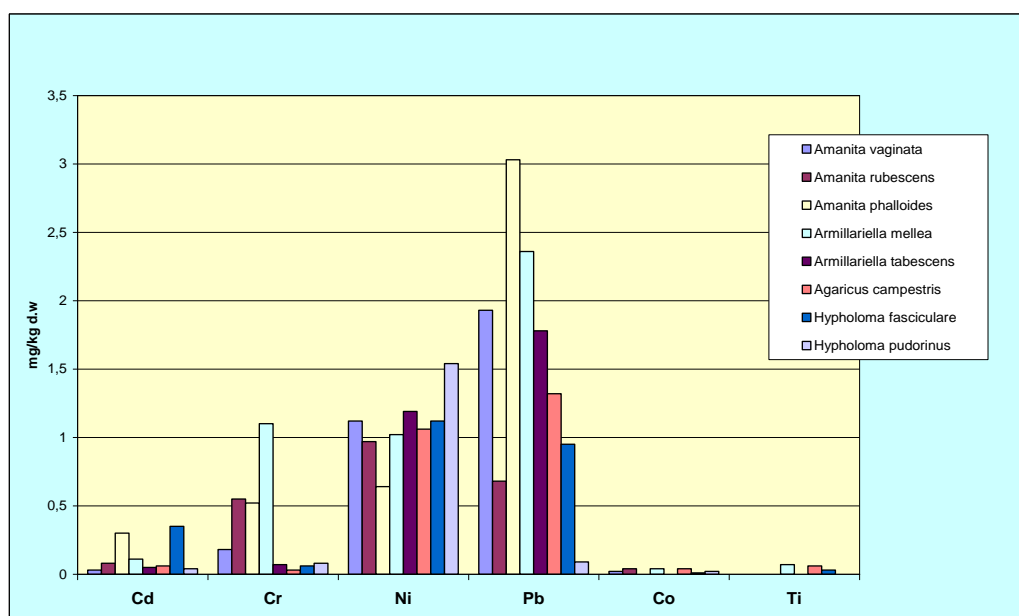


Fig. 2. Mean concentration of heavy metals in fruiting body of wild mushrooms.

These toxic and non-toxic young mushroom species accumulated in higher quantities calcium magnesium and zinc, only in two cases (*Hypholoma fasciculare* and *Hypholoma pudorinus*) absorbed zinc in smaller concentration comparatively with substrate samples level (Table 1 and Figure 1). Concerning copper and iron these mushrooms species have been absorbed in appreciable quantities. The level of the iron is very high in toxic mushrooms species as *Amanita phalloides*, *Hypholoma pudorinus*, *Agaricus campestris* and *Armillariella mellea* comparative with the similar content from soil and this high level depends by pH of the forest soil (pH 4.98, 5.20, 5.62 and 5.25) and the location of the sites (altitude, type of soil, nature of vegetation). These values of pH lead to a significant adsorption of zinc by the six mushrooms species, according with the results presented in Table 2.

The amount of the manganese and copper was higher in *Hypholoma fasciculare* and *Hypholoma pudorinus*, 2.98 and 4.21 mg/kg d.w., respectively 9.67 and 10.51 mg/kg d.w., comparative with the content of the same metals in other studied mushrooms.

The content of selenium was higher in *Armillariella mellea*, *Armillariella tabescens*, 2.08 mg/kg d.w. and 1.89 mg/kg d.w., respectively.

The content of heavy metals Cd, Cr, Ni, Pb, Co and Ti, in the fruiting body of toxic mushrooms are higher comparative with the similar heavy metals level in non-toxic species (Table 2 and Figure 2).

The mean concentration of heavy metal (Cd, Cr, Ni, Pb, Ti, Sr, Co, Bi) was higher at mushrooms which were collected on forest sites near urban settlements in Dambovița County, as well. The highest cadmium content was observed in toxic species *Hypholoma fasciculare* (0.35 mg/kg d.w.) and *Amanita phalloides* (0.30 mg/kg d.w.); the higher chromium level was obtained in *Armillariella mellea* (1.10 mg/kg d.w.) and nickel was founded in high concentration in *Hypholoma pudorinus* (1.54 mg/kg d.w.).

The amount of lead was higher in *Amanita vaginata*, *Amanita phalloides*, *Armillariella mellea*, *Armillariella tabescens*, *Agricus campestris* and smaller in *Amanita rubescens*, *Hypholoma fasciculare* and *Hypholoma pudorinus*. Lowest level of heavy metals is founded in *Hypholoma pudorinus* because the mountain forest soil, with pH 5.20, was low in heavy metals as well. This forest sites are in an area without industrial and traffic pollution.

All the wild toxic species, *Amanita phalloides*, *Hypholoma pudorinus*, *Hypholoma fasciculare* and *Agricus campestris* accumulated Co and Ti from soil in low concentrations. The Co and Ti level in non-toxic species, as *Amanita vaginata*, *Amanita rubescens*, *Armillariella mellea* and *Armillariella tabescens*, could not determine by FAA spectrometry. In this case, to determine the level of Co and Ti in non-toxic mushrooms the Solid Sampling Graphite Furnace Atomic Absorption Spectrometry (SS-GFAAS) can be applied.

The bismuth amount in some mushrooms species and their substrate can be determined by Solid Sampling Graphite Furnace Atomic Absorption Spectrometry (SS-GFAAS) as well.

The studied mushrooms are very good bioaccumulators of zinc, calcium, magnesium, selenium and copper; the smaller affinity for titanium, strontium and bismuth was observed at all studied wild mushrooms (Table 2).

In the soil samples collected at forest sites near industrial urban (pH weakly acid) it was observable a higher amount in iron, zinc, lead, manganese and chromium.

The results of this study showed the fact those wild toxic mushrooms species are metal bioaccumulators. Heavy metal contents of all analyzed mushrooms were generally higher than previously reported in literature. For example, a highest accumulation of Fe, Cu, Mg and Zn from substrate was observed for all the analyzed mushrooms samples. Furthermore, a high accumulation of Pb, Cd and Cr was observed in mushrooms growing *Amanita* and *Armillariella* species by compared with *Commission Regulation (EC) No 1881/2006 of 19 December 2006 [17] setting maximum levels for certain contaminants in foodstuffs: section 3 – Metals Vegetables, excluding brassica vegetables, leaf vegetables, fresh herbs and fungi*.

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## Conclusions

Generally, the studied mushrooms contained minerals required in the human diet, such as Fe, Zn, Mn, Cu, Cr and Se and also the mainly toxic elements, such as Cd, Ni and Pb. The level of toxic elements was lower than that of minerals.

The weakly acid pH value of soil influenced the accumulation of zinc inside studied mushrooms species.

The concentrations obtained for heavy metals in non-toxic species seems to be acceptable for human consumption and nourishment value.

Analytical possibilities of EDXRF and AAS analytical methods were compared and the heavy metal transfer from substrate to mushrooms was studied.

The results of this study showed the fact those wild toxic mushrooms species are metal bioaccumulators. Heavy metal contents of all analysed mushrooms were generally higher than previously reported in literature.

In Romania is the first study which following to identifier the mushroom species which accumulated heavy metals from forest sites near polluted cities in Dambovița County.

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