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HEAVY METALS CONCENTRATION LEVEL IN SOME WILD GROWING SPECIES OF *CORTINARIUS GENUS*

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Abstract
The analyzed species of Cortinarius genus – C. armillatus, C. largus, C. callisteus and C. subfulgens – were sampled from many wooded areas of Dambovita County, in Bucegi Mountain, Paduchiosu pass. The heavy metals content (Sn, Cu, Bi and Ba) of mushrooms' fruiting body was established by Inductively Coupled Plasma - Atomic Emission Spectrometry method (ICP-AES), from the dry matter, detached the cap and the stipe of each mushroom.
Dry weight content of mushrooms, from the analyzed species range of 8.53% to 39.77%, with significant variation from one to another species of Cortinarius genus.
The results of heavy metals concentration appreciation are given in mg of metal per kg of dry matter and demonstrate important variation between the level of concentration in cap and in stipe. The tin concentration in the cap of mushrooms range of 105.25 - 137.93 mg/kg, respectively 147.15 - 828.20 mg/kg dry matter in the stipe of fungus; the cooper was founded in values that excel the device detection limit only in the cap and range of 59.13 to 83.62 mg/kg dry matter; the bismuth shows values of concentration higher in cap of mushrooms, range of 524.26 - 917.67 mg/kg, than in the stipe (473.84 - 560.83 mg/kg dry matter); and barium shows for the majority of analyzed species values of concentration few times higher in the stipe (1.45 - 9.86 mg/kg) comparing with the values in the cap of mushrooms which range from 0.80 to 3.33 mg/kg dry matter.
Based on the values of heavy metals concentration in the analyzed mushrooms may be distinguished the similarity of the species from the Cortinarius genus according the accumulation level and the translocation of heavy metals in the fruiting body of these macrofungus.

Keywords: mushrooms, heavy metals concentration, dry weight, soil

1. INTRODUCTION

Mushrooms represent responsible agents for the breaking down of the organic matter and play an important role in the continual changes of the nature. Heavy metals concentrations in mushrooms are, frequently higher than those in the agricultural crop plants, vegetable and fruits. This is possible because of them very effective mechanism to accumulate heavy metals from the environment. The mushrooms can be used to evaluate the level of environmental pollution [11]. On the other hand, many studies carried out to evaluate the possible danger to human health from the ingestion of mushrooms containing heavy metals [6, 10, 3].
Numerous data on metals contents in fungal fruiting bodies were published [1, 4, 5, 7, 8, 12, 13]. The reported metal concentrations vary over a wide range within the mushrooms species, because of many factors affecting the accumulation rate.
Density and depth of the mycelium living in the soil for several months or even years influence the metals contents in the fruiting bodies. Also, the soil properties, such as pH, redox potential, organic matter content, clay mineralogy, cation exchange capacity of the soil phase, competition with other metal ions and composition of the soil solution concentrations influence metals absorption of the mushrooms [2]. Because macrofungi are integral part of the forest ecosystems, sometimes the soil-to mycelium transfer of metals depends on relationship between mycelium and symbiotic plants species affecting element absorption and translocation [9].
In the present study were analyzed wild-growing mushrooms species from the forest area, edible and non-edible, to establish some heavy metals contents in them fruiting bodies. The aim is the identification of the best species from the *Cortinarius* Genus which accumulate the higher quantities of Sn, Cu, Ba and Bi, in

order to use it in a mycoremediation technology of the polluted soils.

2. MATERIAL AND METHODS

The species from the *Cortinarius* genus has, for the young specimens, a cortina (veil) between the cap and stem [15]. The grow exemplars are characterized by the specific radish smell and they are founded in summer – autumn in coniferous and deciduous forests from hill and mountain [14].

Figure 1. *Cortinarius largus*

In the past, mushrooms from the *Cortinarius* genus were a very popular delicacy in many countries, species like *C. armillatus* and *C. largus* were consummated very often, but in the last time, many cases of decease were founded. Several mushrooms in the genus are poisonous and some are even lethal. A common rule when it comes to mushrooms from this genus is that none of them should be eaten or even tasted [15].

In this study were analyzed 4 species of mushrooms from *Cortinarius* genus: *C. callisteus, C. armillatus, C. largus* and *C. subfulgens*. For each species were sampled 6 specimens, 3 for the analyses of the all fruiting body and 3 for the analyses separately, for cap and stipe. The results represent the mean value of three measurements.

For each mushroom we sample the soil closer with the mycelium, down to the depth of 5 cm. Both the sampling of mushrooms and soil, and them processing were done with plastic, glass and pottery instruments to avoid any metal contacts which can influence the final results. To establish the heavy metals concentration in the analyzed fungal species and in the soil, the samples were dry out into an oven until the complete process and then grinding to a fine powder (conform SR ISO 11464). The estimation of metallic charge range of analyzed plants and them soil with heavy metals was done by the Inductively Coupled Plasma - Atomic Emission Spectrometry method (ICP-AES). For the analyzes with ICP-AES method, the biological samples (plants) were mineralized, in Berghof microwave digestor, by mixture with 10 ml of nitric acid concentrated 65% and 2 ml of hydrogen peroxide, and for the soil samples were done hot extractions with nitric acid 1:1.

In present paper, the metals contents of mushrooms were established with a 110 Liberty Spectrometer type of Varian brand. To disintegrate the sample in constituents atoms or ions is used a plasma source, which will stir up them on superior energetic layer. They will revert to the initial form by the emission of characteristic energy photon, emission recorded by an optical spectrometer. The radiation intensity is proportional with each element concentration in the sample and is intern calculated by a couple of calibration curves to obtain directly the measured concentration.

The concentration resulted are given in mg of metal related with kg of dry soil or plants. The minimal detection limits of device range according the analyzed element and is 0.4 mg/kg for Cu and 0,6 mg/kg for Sn, Bi and Ba.

3. RESULTS AND DISCUSSIONS

The level of concentration in the mushrooms depends on many factors like species and ecology and soil characteristics. In the present study is analyzed the content of some heavy metals in the fruiting body, the ratio of metals compared between the cap/stipe, and the influence of metals concentration in the soil.

Table 1. The mean metal ratio Cap/Stipe of mushrooms from *Cortinarius* genus

Species Metals	*Cortinarius calisteus*	*Cortinarius largus*	*Cortinarius armilatus*	*Cortinarius subfulgens*
Ba	0.15	0.25	0.28	2.3
Bi	1.11	1.18	1.28	1.64
Cu	*	*	*	*
Sn	0.16	0.94	0.29	0.32
* The copper content in stipe is under the detection limit of the method				

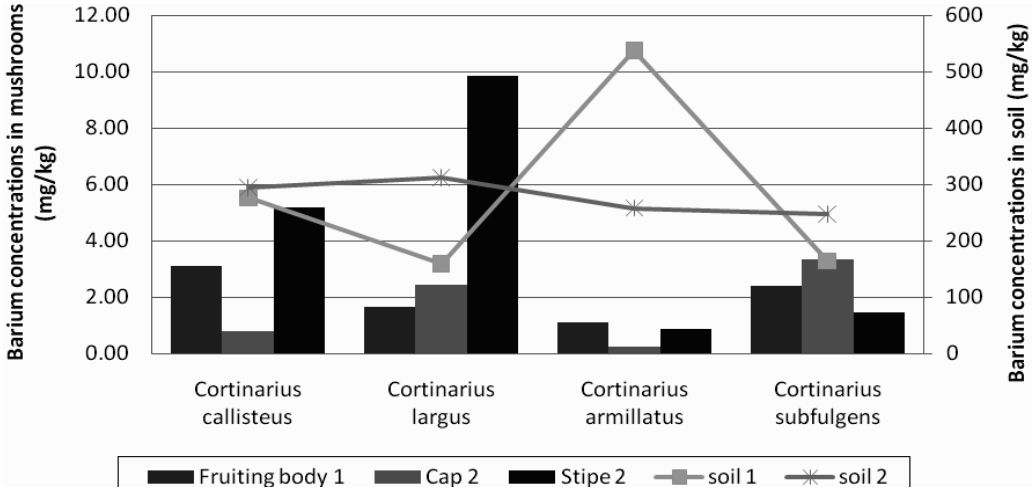

Figure 2. The correlation between the barium concentration in mushrooms of *Cortinarius* genus and metal concentration in the substrate

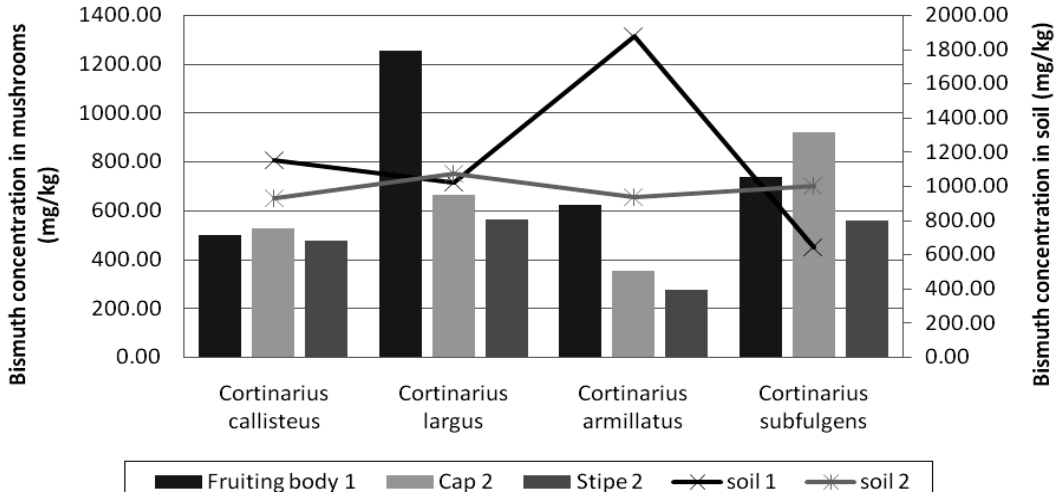

Figure 3. The correlation between the bismuth concentration in mushrooms of *Cortinarius* genus and metal concentration in the substrate

The values of metal ratio cap/stipe are given in table 1. For barium we can observe that the ratio is lower than 1, range of 0.15 – 0.28, which means that the barium concentration is bigger in stipe than in cap for the majority of these species, apart of *C. subfulgens* which accumulate more barium in cap than in stipe (the barium ratio is 2.3). The tin is also accumulating in higher quantities in stipes than in caps for all the analyzed species with a Sn ratio cap/stipe range of 0.16 – 0.94. The bismuth concentration in the fruiting body of mushrooms is different than Ba and Sn, the cap concentrating a higher quantity of Bi than the stipe, the Bi ratio cap/stipe ranging between 1.11 – 1.64. The copper is accumulated only in caps, the concentration in stipe showing values under the detection limit.

Barium concentration in mushrooms is influenced as by species, as by the barium concentration in the soil (fig. 2). The lowest concentration of this metal is *C. armillatus* which accumulate a small quantity of barium, 1.09 mg/kg, even in his substrate this metal has higher concentration 537.95 mg/kg. For the other three species, *C. calisteus, C. largus* and *C. subfulgens* the values of concentration are comparable, 3.10 mg/kg of dry weight, 1.66

mg/kg of dry weight and 2.39 mg/kg of dry weight respectively, the accumulation of barium in the fruiting body depending on the metal concentration in the soil and on the age physiological parameters of the specimens. In the same figure can be observed the difference of accumulation between the barium in cap and barium in stipe; meaning that the concentration of this metal is higher in the stipe, between 0.85 – 9.86 mg/kg, than in cap (0.24 – 2.44 mg/kg), excepting the *C. subfulgens* species. This species concentrate 1.45 mg/kg in stipe and 3.33 in cap.

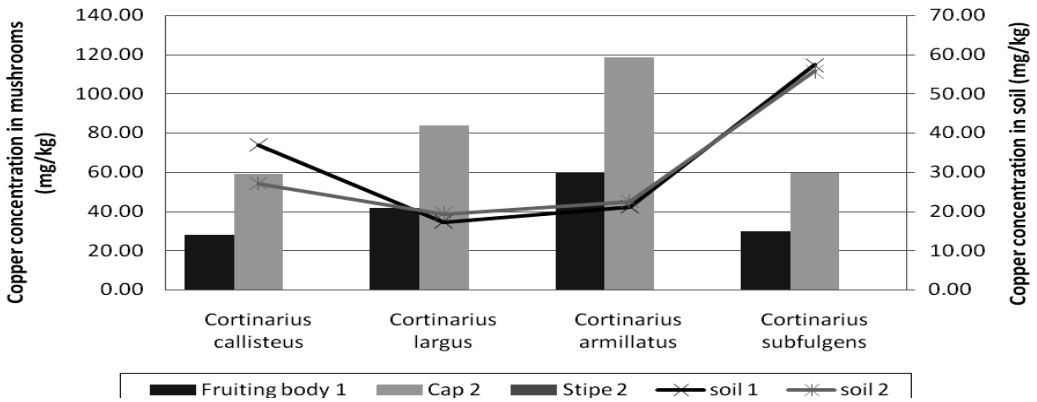

Figure 4. The correlation between the copper concentration in mushrooms of *Cortinarius* genus and metal concentration in the substrate

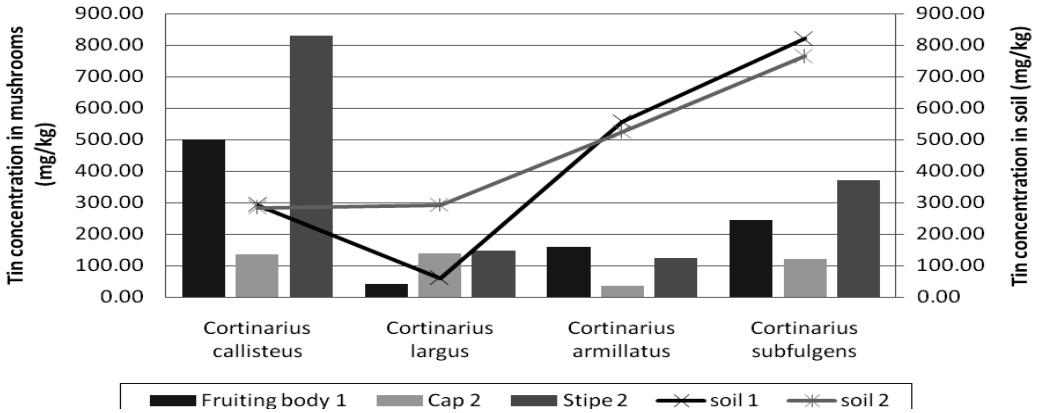

Figure 5. The correlation between the tin concentration in mushrooms of *Cortinarius* genus and metal concentration in the substrate

The bismuth accumulation in the fruiting bodies is different in the morphological parts of the mushrooms, higher concentration showing the cap than the stipe, but the range of these concentrations is not very wide (fig. 3). The concentration in the caps range of 350.24 – 917.67 mg/kg and bismuth concentration in stipe range of 273.20 – 560.83 mg/kg, the higher differences showing *C. subfulgens*. Concerning the bismuth concentration in the fruiting body, the lowest values shows *C. calisteus*, 497.79 mg/kg, was comparing with the highest concentration of bismuth which was founded in the substrate. The highest concentration of bismuth shows *C. largus* which has 1251.66 mg of Bi/kg dry weight. The accumulation of bismuth in the fruiting body doesn't depend too much on the metal concentration in the soil, because even the concentrations in the soil are different, the bismuth concentrations in mushrooms are

comparable, varying only from one species to another.

The copper concentrations vary with the fungal species and the concentration of this metal in soil has not such a great importance. In figure 4 we can observe that, even the concentration of copper in substrate has the highest value, *C. callisteus* and *C. subfulgens* show the lowest values of concentration in the fruiting body, 28.08 mg/kg and 29.65 mg/kg respectively. The highest copper concentration in the fruiting body shows *C. armillatus,* 59.26 mg of copper/kg of dry weight. Also, we can observe than any of the analyzed species doesn't accumulate copper n the stipe, all the concentration was founded in caps.

The tin concentrations in the morphological part of the analyzed species of mushrooms vary in caps and in stipe. Apart of *C. largus*, which has comparable values in bought parts, the other species shows big difference of accumulation on the morphological parts, with highest values of concentrations in the stipe, than in cap. The tin concentration in fruiting body is influence, beside the species, by the tin concentration in the soil. The highest is the concentration in soil the highest is the concentration in the fruiting bodies of mushrooms.

4. CONCLUSIONS

- The tin and barium is accumulated in higher quantities in the stipe than in caps;
- Bismuth concentration has comparable values in bought morphological parts, cap and stipe;
- For all the analyzed macrofungi from *Cortinarius* genus the level of metals concentration in the mushrooms depends on the species;
- Apart of bismuth, the level of metals concentration in the fruiting bodies of mushrooms depends on the metals concentration in the soil.

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