Monitoring of ^{226}Ra and ^{137}Cs Radioisotopes on Bistrita Valley and their Translocation in Spontaneous Macromycetes

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A number of five species of macromycetes were collected during 2008 on Bistrita Valley in order to study the transfer of ^{226}Ra and ^{137}Cs radionuclides form substrate in the corresponding macromycetes. The soil pollution with ^{137}Cs was evidenced in the substrate corresponding to the Stropharia coronilla but not its translocation. For the other samples, ^{226}Ra coming from the uranium decay chain (often present in the rocks from the region) was detected by gamma-spectroscopy, all the values being below of the maximum admitted one. The obtained results were confirmed by FT-IR spectroscopy, the band presented at 910 cm^{-1} being assigned to the asymmetric stretching vibration of the dioxouranium ions.

Key words: macromycetes, radioactivity, ^{137}Cs, ^{226}Ra, FT-IR spectroscopy

The mushrooms growing into the forests represent an important nutritional source for the inhabitants of Central European countries. Their dry matter is around 10 % from their total weight, being especially constituted from structural polysaccharides and proteins [1,2].

Based of their extremely fast metabolism, macromycetes strongly interacts with the environment. When the environment is polluted, the capacity of hyperaccumulation of the macromycetes became a disadvantage: besides nutrients, the macromycetes also accumulate the pollutants from the environment [3].

Concerning the radioactive pollution, the long or medium half-living artificial radionuclides are of great interest in this part of Europe. Thus, translocation of ^{137}Cs in macromycetes, following the nuclear accident in Chernobyl, has extensively been studied after 1986 [4-10]. Several monitoring surveys have showed that organic horizon of soils accumulates radioactive caesium in forestry ecosystems [11-13]. Radioactive caesium resulted from the atmospheric explosions is also accumulated by the surface horizons of soils, being present in detectable amounts even after 40 years from release [14]. Compared with green plants, the elemental composition of sporipherous bodies could be characterized by high concentrations of ^{137}Cs, K and Rb, respectively low concentrations of Ca and Sr. The ^{137}Cs, Cs and Rb concentrations are with an order of magnitude higher in fungi than in plant species growing in the same woody area. It has been noticed higher concentrations of Cs and Rb in sporipherous bodies in greenhouse experiments by using tracer studies [14].

It has been assessed that 22 % from ^{137}Cs traced in the first 5 cm of the soil under the coniferous forests could be accumulated by the fungal mycelium [15]. This assessment is based on the measurements of radionuclides concentrations, which is more or less equally distributed in the sporipherous bodies as well as in mycchorizal mycelium. By using restrictive fragments of polymorphism patterns it was evidenced that the ^{137}Cs concentrations in sporipherous bodies and mycelium of *Suillus variegatus* were quite similar [16]. The concentration of radioactive caesium varies in different mycocarp parts of the sporipherous bodies. The biomass corresponding to the fruiting body of fungi could accumulate 0.01-0.1 % from the total amount of radioactive caesium inventoried in various years [17].

The accumulation of transuranianum elements (resulting either from nuclear tests or from activation of nuclear fuel in reactors and their accidental releasing in environment) in macromycetes has been also studied [18]. Even if the accumulation of naturals thorium and uranium as well as their decay products in fungi is well established, only a few aspects concerning the mechanisms involved in their translocation and further retention are elucidated [19,20].

In 2005 we started a monitoring study of radioactive pollution in Crucea mining area (the county of Suceava), concluding that there is no radiological hazard over there [21,22]. The main goal of these studies was monitoring ^{226}Ra (daughter of ^{230}Th along the uranium decay chain) in soils and biologic samples. Surprisingly, the anthropogenic radionuclide ^{137}Cs has also been identified in some substrates and biologic materials, most probably originating from the Chernobyl accident. In the region under study, woody species (such as *Abies alba*), plants belonging to spontaneous vegetation (*Fragaria vesca*) or macromycetes species (*Boletus edulis*, *Cantharellus cibarius*, *Laccaria laccata*, *L. amethystina*, *Lactarius deterrimus*, *L. salmonicolor*, *Russula cyanoxantha*, *R. delica*) evidenced significant gross alpha-beta and ^{226}Ra transfer coefficients (FT= 5÷40) [21,23,24].

For the present study, a number of five macromycetes species were collected during 2008 along Bistrita valley in order to study the transfer of ^{226}Ra and ^{137}Cs radionuclides.

Experimental part

Crucea uranium mining area (Suceava County) has been thoroughly described from various geographical, climatological, geochemical and radiological perspectives [23]. Due to the presence of uranium in this region, radioactive translocation from soil to living bodies became of interest. Thus, five species of macromycetes (*Stropharia coronilla*, *Tremiscus helvelloides*, *Tremiscus helvelloides*, *Russula fragilis*, and *Cantharellus cibarius*) have been collected in June 2008, from the waste dumps accumulated in Tarnita (Crucea) and from a forest

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Table 1
SPECIFIC ACTIVITIES OF ^{226}Ra AND ^{137}Cs IN MACROMYCETES AND CORRESPONDING SUBSTRATES

Sample	Weight, g	Activity, Bq	Specific activity, Bq/g
Substrate *Stropharia coronilla*	104.8	20.96 ^{226}Ra, 5.25 ^{137}Cs	0.20 ^{226}Ra, 0.05 ^{137}Cs
Stropharia coronilla	3.0	0.33 ^{226}Ra	0.11 ^{226}Ra
Substrate *Tremiscus helvelloides* (Crucea)	13.0	0.91 ^{226}Ra	0.07 ^{226}Ra
Tremiscus helvelloides (Crucea)	4.2	n.d.*	n.d.
Tremiscus helvelloides (Farcasa)	7.3	n.d.	n.d.
Substrate *Russula fragilis*	15.0	n.d.	n.d.
Russula fragilis	0.5	n.d.	n.d.
Cantharellus cibarius + substrate (Farcasa)	5.1	0.30 ^{226}Ra	0.06 ^{226}Ra

* n.d. - not detected

ecosystem located at about 30 km away from Crucea, *i.e.* on Farcasa brook.

In order to measure the radioactivity in macromycetes and the corresponding substrates, the collected materials were transported in plastic bags till the measurement place, in order to avoid any contamination. Subsequently, substrates were dried for 3-4 h in autoclave at about 110°C and introduced in 1 L Marinelli beakers (if necessary, traces of soil were carefully mechanically removed from mycocarp and mycelium before treatment). The macromycetes were dried in air for about 10 days and subsequently placed into Marinelli beakers after weighting. The filled beakers were sealed with silicon. The activity measurements were performed after at least 30 days, to reach the radioactive equilibrium.

^{226}Ra and ^{137}Cs in the sample was determined by means of a 10 cm lead shielded γ-spectrometer (Canberra InSpector™ 1000 high-performance hand-held NaI spectrometer). The channel width was set at 4.986 keV and the energy resolution was determined to be 9 % at 662 keV (peak of ^{137}Cs). Data evaluation was performed using the PC Genie 2000 software (Canberra-Packard). The ^{214}Bi peak (609 keV, abundance 46.3 %) was used for the evaluation of the ^{226}Ra activity. The measurement time was selected to obtain a final SD less than ± 20% for each measured value.

The IR spectra were recorder over the 4000-400 cm^{-1} domains, on KBr pellets by using a Jasco 660 Plus device.

Results and discussions

The radioactivity measurement results are presented in table 1.

Specific activities of 0.06-0.20 Bq/g ^{226}Ra have been measured in the corresponding substrate of *Stropharia coronilla*, *Tremiscus helvelloides*, and *Cantharellus cibarius.* Besides, a value of 0.05 Bq/g ^{137}Cs in the corresponding substrate of *Stropharia coronilla* has been detected. While ^{226}Ra is produced along the uranium decay chain naturally appearing in biosphere as a result of biogeochemical processes, ^{137}Cs most likely originates from the Chernobyl accident.

Translocation of ^{226}Ra and ^{137}Cs was evidenced in *Stropharia coronilla* and *Cantharellus cibarius,* but not in *Tremiscus helvelloides*. Besides, the absence of the analysed radionuclides (or their presence below the detection limits) in the corresponding substrate of *Russula fragilis* does not allow any conclusion in respect with the accumulation capacity of this species, when is collect outside of the controlled area. *Tremiscus helvelloides* is a ligneous species, fact which can explain the presence of ^{226}Ra exclusively in substrate but not its accumulation.

The present data confirms that it is no radiological hazard concerning the investigated area, contrarily to other studies on similar systems. Thus, it was mentioned that species of *Stropharia* genus are responsive to ^{134}Cs and ^{137}Cs uptake [2]; it was also recommended moderate consumption of *Cantharellus*, since this species accumulate up to 1100 Bq ^{137}Cs/ kg [25]. Such species are in the so-called "red area" of macromycetes which accumulate radionuclides over the CEE standards (600 Bq/ kg) [25, 26].

FT-IR studies (fig. 1) conducted on the macromycetes' corresponding substrates present vibration bands characteristics to carbonates, mineralized clays and organic compounds [27]. The substrates originating in Crucea area also contain blendes included in bitumen, which are usually present in minerals associated with uranium deposits.

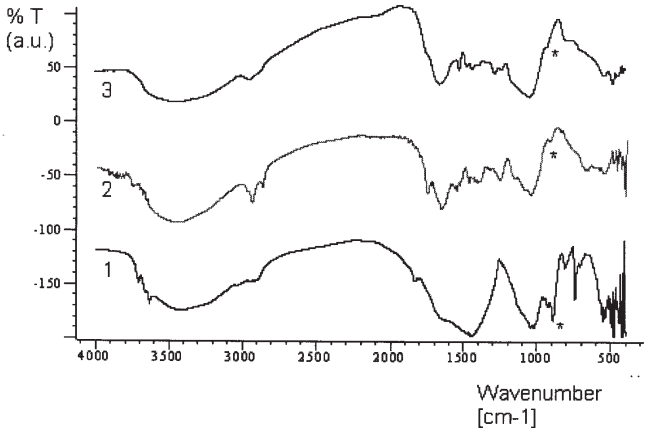

Fig. 1. FT IR spectra of the substrate *Stropharia coronilla* (Crucea) -1, *Tremiscus helvelloides* (Crucea) - 2, *Tremiscus helvelloides* (Farcasa) - 3

Thus, in the IR spectra of the substrates collected in the Crucea exclusion area, it is noted the presence of a characteristic band $\nu_{O=U=O}$ (dioxouranium ions) situated at 910 cm^{-1} (*), well structured and intensive in the case of the substrate corresponding to *Stropharia coronilla* and of a lower intensity in the case of the substrate corresponding to *Tremiscus helvelloides*. Besides, in the substrate collected around *Tremiscus helvelloides* (originating from Farcasa zone), this band is also present, but with a very low intensity. In the FT-IR spectra of certain sample, small inflexion corresponding to the IR bands of dioxouranium ions may be observed, confirmed or not by the radioactivity measurements. For example, this band is absent or very low for the macromycetes species which are originated in Farcasa.

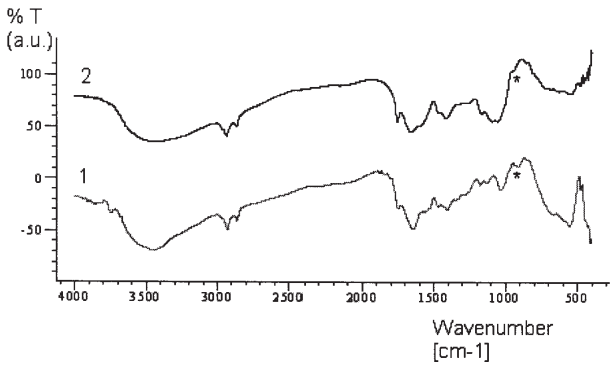

Fig. 2. FT IR spectra of the macromycetes species (taken from their sporipherous bodies): *Stropharia coronilla* - 1, *Cantharellus cibarius* - 2

The macromycetes contain in their structure especially cellulose-like compounds, proteins, aminoacids and, in lower amounts, mineral salt absorbed from the substrate. Thus, in the FT IR spectra of macromycetes, besides of the bands characteristic to the organics substances, bands characteristic to some inorganic salts coming from substrate could also appear. In the case of the investigated macromycetes originating from the Crucea area (*Stropharia coronilla*, *Cantharellus cibarius*), one could also remark the presence of the band situated a round 910 cm^{-1} (fig. 2). Apart of the asymmetric stretching vibration of the dioxouranium unit, in the present case this band is also attributed to the interactions between the UO_2^{2+} ions and the groups belonging to various cellular components (such as peptides, phospholipids, peptidoglycans, etc).

Conclusions

The presence of ^{226}Ra (daughter of ^{230}Th along the uranium decay chain) has been emphasized in Crucea uranium mining area and its proximity along the Bistrita river valley. Casually, it also has been identified the anthropogenic radioisotope ^{137}Cs. Translocation of ^{226}Ra and ^{137}Cs (when it is present) has been evidenced for *Stropharia coronilla* and *Cantharellus cibarius* macromycetes.

FT-IR spectroscopy experiments support the presence of ^{226}Ra in macromycetes (genetically related with the parent uranium), by the occurrence of some additional vibration bands - comparatively with the references.

Acknowledgement: This work was supported by the project ANCS-CNCSIS-175/2006.

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Manuscript received: 4.02.2010