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RADIOACTIVITY LEVELS IN SOME MUSHROOM SPECIES COLLECTED FROM MACEDONIA AND CONSEQUENT DOSES

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ABSTRACT

Mushrooms are bioindicators in the environment that accumulate radionuclides, therefore they can pose a radiological threat. In the Republic of Macedonia, mushrooms are widely consumed as a part of the diet, for this reason their radiological control is required. In this research, the activity concentrations in different types of mushrooms (Boletus edulis, Marasmius oreades, Morchela conica, Lactarius deliciosus) were determined. The mushrooms were collected from six different locations in the Republic of Macedonia, and information on the radiation dose for the general population were obtained with this measurement. The analyses were performed by means of HPGe gamma spectrometry, i.e. an instrument - gamma spectrometer (Canbera Packard) with a high purity germanium detector. The obtained spectra from the measurement were analyzed by using the GENIE 2000 program. On the basis of the performed tests, the mean values for the activity concentrations in the mushrooms were as follows 41.9±1.2 Bq kg − 1 for 226Ra, 40.3±1.8 Bq kg − 1 for 232Th, 83.75±6.2 Bq kg − 1 for 40K, and 2.34±0.24 Bq kg − 1 for 137Cs. The mean value of the radiation risk index H_{eks} is lower than the maximum allowed value which is <1 for H_{eks}. The value of the radium equivalent activity Ra_{eq} is below the maximum recommended limit, i.e. 370 Bq kg-1. Significant variations were not observed in regard to the activity concentrations of 137Cs and 40K in the same mushroom species from different sampling points. High activity concentrations of 137Cs activity were not detected in any of the mushrooms. The researches in this study show that all mushroom samples pose no biological threat, i.e. it was found that the analyzed radionuclides do not pose a health risk and the levels are below the international standards.

Key words: *mushrooms, gamma-ray spectrometry, natural radioactivity, food safety.*

INTRODUCTION

It is essential to know the concentration of radioactivity in our environment when estimating the dose that accumulates in the population and also in forming the basis for assessing the degree of radioactive contamination or environmental pollution in the future. Radioactive contamination of plant organisms is formed by dynamic continuous common interaction of the atmosphere, the pedosphere and the hydrosphere. From the above-mentioned spheres of life, the influence of the pedosphere is dominant, given that the main part of the mineral matter, which makes up the plant body, originates from the soil. Considering that radionuclides can cause undesired effects on the human organism, it is necessary to control their content in the environment, and on the basis of the obtained results, to calculate the dose that the human receives. Mushrooms as one of the most important components of the forest ecosystem, are considered excellent bioindicators of environmental pollution, because they have the ability to accumulate radionuclides from the soil and the atmosphere (Kalač, 2010). In the Republic of Macedonia, mushrooms are widely consumed in the diet because they contain a large amount of protein and minerals, and for that reason their radiological control is required (Agrahar-Murugkar and Subbulakshmi, 2005). Many researches and studies have been conducted, in order to assess the possible threat to human health from consuming wild mushrooms that contain higher levels of radionuclides (Gast et al., 1988). Most studies have shown that the content of radionuclides in wild mushrooms depends on several parameters, such as the type of mushroom, the soil type, the depth of the mycelium, the climate and the bioavailability of the radionuclide. It was also found that mushrooms collected in coniferous forests are characterized by higher content of radionuclides compared to samples of mushrooms collected in deciduous forests (Čipáková, 2004). In Macedonia, large quantities of wild mushrooms are collected which are consumed in the diet and at the same time large quantities are exported from the country to European countries such as France, Switzerland, Germany, Belgium, the Netherlands, Spain, Sweden. In order to export these products abroad from the country it is necessary to submit a certificate of analysis for the presence of radionuclides in mushrooms. The aim of the research itself was to determine the level of concentration of ^{226}R, ^{232}Th, ^{40}K and ^{137}Cs in different species of wild mushrooms collected from several different locations, in order to determine the behavior of mushrooms as indicators of radioactive contamination in the environment and to calculate radiation doses for the general population on the basis of the obtained results.

MATERIALS AND METHODS

Sampling

The samples of wild mushrooms were collected in 2020 from different locations in the Republic of Macedonia (Table 1). All samples were homogenized, and after removing the inedible parts, they were placed in Marinelli beakers that had the same geometry as the one for the reference materials by which the measuring equipment was calibrated. The capacity of the Marinelli beaker was 0.5 L for gamma spectrometry analysis.

Table 1. Mushroom species examined in the study

Mushroom Species	Family	Local Name	Growing	Edilebility
Boletus edulis	Boletaceae	Vrganj	Wild	Edible
Lactarius deliciosus	Russulaceae	Rujnica	Wild	Edible
Morchella conica	Morchellaceae	Smrcka	Wild	Edible
Marasmius oreades	Marasmiaceae	Livadarka	Wild	Edible

Instrument

The samples were measured with an instrument - gamma spectrometer (Canbera Packard) with a high purity germanium detector. The measurement was carried out in beakers that were hermetically sealed so that ^{222}Rn produced by the decomposition of ^{226}Ra would not result in gas leakage. After ensuring a time balance between the successors of the ^{238}U and the ^{232}Th series, these sealed samples were prepared for analysis. GENIE 2000 software was used for data acquisition and analysis. The specific activity of ^{226}Ra is calculated for the energy line of 186.1 (keV) and ^{232}Th through its decay descendant ^{228}Ac (second in the decay chain), that is, through its three gamma decay energy lines which occur at 338.4; 911.07 and 968.9 (keV).

The activities of ^{40}K were determined from its γ-line of 1460 keV, while the activities of ^{137}Cs were determined by means of an estimation of the γ-line at 661.66 (keV). The time interval for calculation (counting) was 108000 seconds.

Specific activity

The specific activity (A) is determined according the equation

$$A = \frac{\frac{N}{t} - \frac{N_0}{t_0}}{\varepsilon \cdot \gamma \cdot m} \quad (Bq \cdot kg^{-1})$$

Where, N is clean surface of peak accumulated from a specific radionuclide in analysis of a specific sample (number of readings), N_0 is clean surface of peak accumulated from the spot of a specific radionuclide without an analysis of sample (number of readings), t is live time of accumulation of the sample spectrum (s), t_0 is live time of accumulation of the phone spectrum (s), ε is detector efficiency for a given energy (for a specific peak), γ is intensity of gamma transition in radioactive decay for a respective radionuclide (%), and m is sample mass (kg).

Absorbed dose rate in air (D)

The natural decay of radionuclides is one of the major sources of human radiation exposure. The rate of absorbed dose in the air for radionuclides at a height of 1 m above the Earth's surface was calculated on the basis of data provided by (UNSCEAR, 2000)

D (nGy / h) = 0,462 A_{Ra} + 0,604 A_{Th} +0,0417 A_k +0,030 A_{Cs}

where; D is the dose rate at 1 meter above ground, ARa, ATh, AK and ACs are activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs in the samples, respectively. Conversion factors of ^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs are 0,462, 0,604, 0,0417 and 0,030 nGy/h per Bq/kg, respectively (Kurnaz et al., 2007).

Radium equivalent activity (Raeq)

The calculation of the radium equivalent activity (Raeq) is a quantity for comparing the specific activities of the samples with different contents of ^{226} Ra, ^{232}Th and ^{40}K. The uniformity with respect to radiation exposure was defined in terms of the radium equivalent activity (Raeq) in Bq/kg in order to compare the specific activity of the materials containing different amounts of ^{226}Ra, ^{232}Th and ^{40}K. It is assumed that 370 Bq/kg of ^{226}Ra, 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma-ray dose rate. It is calculated by using the following ratio Ra_{eq}(Bq/kg)= A_{Ra}+1.43A_{Th}+0.07A_k (Beretka and Methew, 1985) A_{Ra}, $A_{Th,}$ A_k – specific activiites (Bq/kg) of ^{226}Ra, ^{232}Th and ^{40}K, respectively. The value of the radium equivalent activity of 370 Bq/kg corresponds to the maximum allowed dose for a population of 1 mSv.

External and internal hazard index

In order to assess the equivalent average of the annual effective dose imposed to the residents of each area, the external hazard index for the soil samples was calculated.

H_{eks} = A_{Ra}/370+ A_{Th}/259+ A_k/4810≤ 1

A_{Ra}, $A_{Th,}$ A_{k-}specific activites (Bq/kg) ,^{226}Ra^{232} Th and ^{40}K, respectively (Kurnaz et al., 2007)

Annual gonadal dose equivalent (AGDE)

The activity bone marrow and the bone surface cells are considered the organs of interest by UNSCEAR (1988). Therefore, the AGDE due to the specific activities of 226Ra, 232Th and 40K was calculated using the following formula (MamontCiesla et al., 1982),

AGDE (μSv/year) = 3.09 ARa + 4.18 ATh + 0.314 AK (Kurnaz et al., 2007)

Annual effective dose equivalent (AEDE)

In order to estimate the annual effective doses, one has to take into consideration the conversion coefficient from the absorbed dose in the air to effective and the outdoor occupancy factor. In the UNSCEAR from 2000 reports, a value of 0.7 Sv/Gy was used for the conversion coefficient from absorbed dose in air to

effective dose received by adults, and 0.2 for the outdoor occupancy factor. The annual effective dose equivalent was calculated from following equation:
AEDE (μSv/year) = D(nGy/h) × 8760(h/year) × 0.2 ×0.7(Sv/Gy) ×10-3 (Kurnaz et al., 2007).

RESULTS AND DISCUSSION

The concentration of activity of **^{40}K** in all types of mushrooms is greater than the one of ^{232}Th and ^{26}Ra which is in accordance with the literature data. In the radioisotope ^{40}K, the highest level of activity is determined, with an average value of 83.7±6.2 Bq/kg. Since potassium is a basic nutrient, its range of variation is limited. Also no correlation was observed between ^{40}K and ^{137}Cs, although cesium is a chemical analogue of potassium, which suggests different uptake mechanisms for these two elements (Mietelski et al., 1994).

Table 2. ^{232}Th, ^{26} Ra , ^{40}K and ^{137}Cs activity concentrations of mushroom samples

	Specific activity* (Bq/kg – 1)			
	^{26} Ra	^{232}Th	^{40}K	^{137}Cs
S1	19.4±0.5	17.2±0.9	140.6 ± 6.8	<4.8
S2	33.5±3.9	28,6±0,3	46.9 ± 10.7	<1.0
S3	21.7±0.9	16.2±0.5	124.8± 10.4	0.5 ± 0.1
S4	44.3±0.5	31.5±0.5	52.1 ± 5.2	0.4 ± 0.1
S5	31.2±0.4	26.5±0.5	49.7 ± 3.0	<0.5
S6	28.7±0.3	19.8±0.2	68.3 ± 5.0	<1.0
M1	11.7±0.9	27.1±5.0	47.4±6.8	<1.0
M2	10.2±0.5	21.7±5.2	41.6±6.8	<1.0
M3	9.2±0.2	16.3±3.0	44.2±6.0	<0.5
M4	11.5±0.9	21.8±2.0	39.1±6.0	<0.5
M5	10.7±0.5	17.0±2.5	40.3±5.0	<0.5
M6	17.6±0.8	31.3±2.0	47.7±6.2	<0.5
D1	74.3±2.0	75.3±1.0	98.1 ± 5.0	3.6 ± 0.1
D2	71.5±3.0	66.2±0.5	124.7 ± 5.8	2.4 ± 0.3
D3	82.7±2.0	71.5±0.5	96.1 ± 3.8	5.1 ± 0.3
D4	66.3±0.5	59.2±0.1	115.3 ± 5.0	0.4 ± 0.1
D5	79.1±0.5	77.1±1.0	100.6 ± 6.8	2.8 ± 0.2
D6	72.0±0.5	71.7±0.9	142.3 ± 2.2	3.4 ± 0.1
E1	55.0±2.5	51.2±0.3	124.7 ± 11.5	0.8 ± 0.2
E2	49.0±0.5	46.0±0.5	102.1 ± 5.0	0.5 ± 0.1
E3	49.7±0.5	38.2±0.5	111.76 ± 6.5	2.68 ± 0.5
E4	57.4±2.0	44.3±0.2	89.5 ± 5.0	<1
E5	49.9±2.5	42.7±0.2	68.4 ± 2.5	<1
E6	51.2±2.0	49.0±0.1	92.9 ± 12.1	5.6 ± 0.8

*S1-S6 (Boletus edulis): M1-M2 (Marasmius oreades): D1-D6 (Morchela conica): E1-E6 (Lactarius deliciosus)

The mean specific activity of ^{226}**Ra** is 41.9 ± 1.2 Bq kg-1, while the one of ^{232}Th is 40.3±1.8 Bq kg-1 (Table 3). It can be noticed that these two radionuclides occur with nominal concentrations.

Table 3. ^{232}Th, ^{26}Ra , ^{40}K and ^{137}Cs activity concentrations of mushroom samples mean values

Radionuclides	Bq kg – 1
^{26} Ra	41.9±1.2
^{232}Th	40.3±1.8
^{40}K	83.7±6.2
^{137}Cs	2.35±0.2

The highest content of ^{137}Cs was found in Morchela conica (5.1 ± 0.3) Bq/kg f.m., while Marasmius oreades had the lowest level of ^{137}Cs (Table 2). There are several factors that affect the content of ^{137}Cs in mushrooms. First, the amount deposited on the soil is closely related to the content range, especially the maximum content (UNSCEAR, 2000). The consequences of Chernobyl were inhomogeneous in all affected countries and, therefore, in a specific country there can be areas with different radioactive contamination (Mietelski et al., 1996). The content of ^{137}Cs also varied from one type of mushroom to another, depending on the type of the nutritional mechanism and the habitat of the mycelium (Yoshida and Muramatsu, 1994). The analyzes revealed very low levels of ^{137}Cs if compared to the specific activity limits determined with the international legislation of 600 Bq/kg for ^{137}Cs.

Table 4. D, Raeq, Hex, AGDE, AEDE, Risk of lifetime cancer values of mushroom

Parameters	Family	[1]WAV
D (nGy/h)	47.25	55
Raeq (Bq/kg)	90.07	370
Hex	0.28	/
AGDE (µSv/year)	207.42	2398
AEDE (µSv/year)	57.94	70

[1]WAV: The world average value

From the specific activities, the doses were calculated and compared with other researches. The absorbed dose rate was calculated and it amounted to 47.25nGy/hour (Table 4). This value is lower than the values of the eastern desert in Egypt (488 nGy/h) (Arafa, 2004) and Istanbul, Turkey (49 nGy/h)). (Karahan and Bayulken, 2000) Our score was lower than the international recommended value (55 nGy/h) (UNSCEAR, 1988).

The radium equivalent activity (Raeq) was calculated and amounts to 90.07 Bq/kg respectively. Our results were lower than those surveyed in the Firtina Valley, Turkey (166.3 Bq/kg) (Kurnaz et al., 2007) and the Eastern Desert of Egypt (493.8 Bq/kg) (Arafa, 2004). In addition, our score was lower than the international recommended value (370 Bq/kg), (UNSCEAR, 2000) for Raeq (UNSCEAR.

2000). The external hazard index (Hex) is calculated and it amounts to 0.28, the value of which is lower than other countries Egypt (Eastern Desert) (2.03) (Arafa, 2004) The average value of the Radiation Risk Index H_{eks} shows that there is no significant radiation risk to the population. The values of the external hazard index obtained in this study, regardless of the location, did not exceed the safety limits, noting the negligible radiation hazard arising from naturally occurring terrestrial radionuclides.

The annual gonadal dose equivalent (AGDE) is calculated with a value 207.42 µSv/year, which is lower than other studies (246.4, 214.9 µSv/year, (Yılmaz et al., 2016) and (2398 µSv/year) for the Eastern Desert in Egypt. (Arafa, 2004)

The annual effective dose rate (AEDE) is calculated and amounts to 57.94 mSv/year, respectively. The world average annual effective dose equivalent (AEDE) from outdoor terrestrial gamma-radiation is 70 mSv/year (UNSCEAR, 1988). Hence, our values are lower than the world average value and the Istanbul value (69.8 mSv/year) (Karahan and Bayulken, 2000).

CONCLUSION

It can concluded that even after many years since the Chernobyl nuclear accident, the levels of cesium in mushrooms in the region of the Republic of Macedonia are very low compared to the limit set by international law. The small differences observed between different types of mushrooms may be due to the different contamination at the selected sampling site, the mycelial depth, the climate and the radionuclide bioavailability. However, the data from this research provide useful information about the environmental risk of the studied area and can be further used for radiological imaging.

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