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Activity concentrations of Cs-137, Cs-134, Th-234 and K-40 in wild edible mushrooms gathered 32 years after the Chernobyl power plant accident in Batak Mountain, Bulgaria

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The aim of this study was to evaluate Cs-137, Cs-134, Th-234 and K-40 activity concentrations and effective doses in *Hydnum repandum, Suillus luteus* and *Morchella esculenta* mushrooms gathered in Batak Mountain, between April 2018 and November 2018. The time interval is chosen purposely as 2016 marks 30.17 years elapsing from the Chernobyl nuclear disaster, equal to the half-life of Cs-137. Thus, the difference between laboratory and real conditions will be evaluated. The *Hydnum repandum* mushroom was chosen as it is present in the Rapid Alert System for Food and Feed database for excessive radioactive contamination and substantial accumulation of Cs-137, Cs-134, Th-234 and K-40. Mushrooms *Suillus luteus* and *Morchella esculenta* are characterized by low and medium levels of Cs-137, Cs-134, Th-234 and K-40. The present study showed that the concentration of Cs-137 in the selected mushroom species *Hydnum repandum, Suillus luteus* and *Morchella esculenta* in 2018, e.g. 32 years after Chernobyl, were 110 Bq kg^{-1} DM, 50 Bq kg^{-1} DM and 6 Bq kg^{-1} DM. The effective annual doses of Cs-137 in the selected mushroom species *Hydnum repandum, Suillus luteus* and *Morchella esculenta* were 7.46E-06, 3.39E-06 and 4.07E-07 Bq kg^{-1} DM, while for K-40 were 5.69E-05, 5.62E-05 and 6.79E-05 Bq kg^{-1} DM, i.e. < 0.1% of the natural background radiation.

Keywords: Cs-137, Cs-134, Th-234 and K-40, Effective dose, Wild edible mushrooms, Bulgaria

INTRODUCTION

Mushrooms are often considered as excellent bioindicators for evaluation of environmental pollution, since they are known to accumulate metals and other elements [1-3]. Cs-137 in wild mushroom species can be detected consistently, due to atmospheric radioactive fallout in aerosol particle and precipitation form, initially as a result of the explosion of nuclear devices in the atmosphere, and after the Chernobyl nuclear accident in 1986 [4-9]. Cs-137 values in mushrooms can be used to trace and evaluate fallout of radioactive material from past and future nuclear accidents. Furthermore, mushrooms are consumed by man and directly eaten by animals. The European mushrooms in 1986-2015 may have given humans a greater amount of Cs-137 compared to any other kind of food [10]. Regular consumption of some types of mushroom species or animals that eat them may pose a human health concern [1]. The Rapid Alert System for Food and Feed (RASFF) database contains 24 overdose radioactivity signals in wild mushrooms originating from Bulgaria for the period from 1998 to 2011 [11]. Therefore, it is important to have information on radioactivity concentration of mushrooms originated from Bulgaria.

The aim of this study was to evaluate Cs-137, Cs-134, Th-234 and K-40 activity concentrations and effective doses in *Hydnum repandum, Suillus luteus and Morchella esculenta* mushrooms gathered in Batak Mountain, between April 2018 and November 2018. The time interval is chosen purposely as 2016 marks 30.17 years elapsing from the Chernobyl nuclear disaster, equal to the half-life of Cs-137. Thus, the difference between laboratory and real conditions will be evaluated. The *Hydnum repandum* mushroom was chosen as it is present in the RASFF database for excessive radioactive contamination and substantial accumulation of Cs-137, Cs-134, Th-234 and K-40. Mushrooms *Suillus luteus* and *Morchella esculenta* are characterized by low and medium levels of Cs-137, Cs-134, Th-234 and K-40.

EXPERIMENTAL

Mushroom samples

The Batak Mountain is located in the western Rhodopes, Bulgaria. Its western border is defined by the Chepinska river, the southern border – by Dospatska river and Dospat dam, the eastern border – by Vacha river and the northern border – by the

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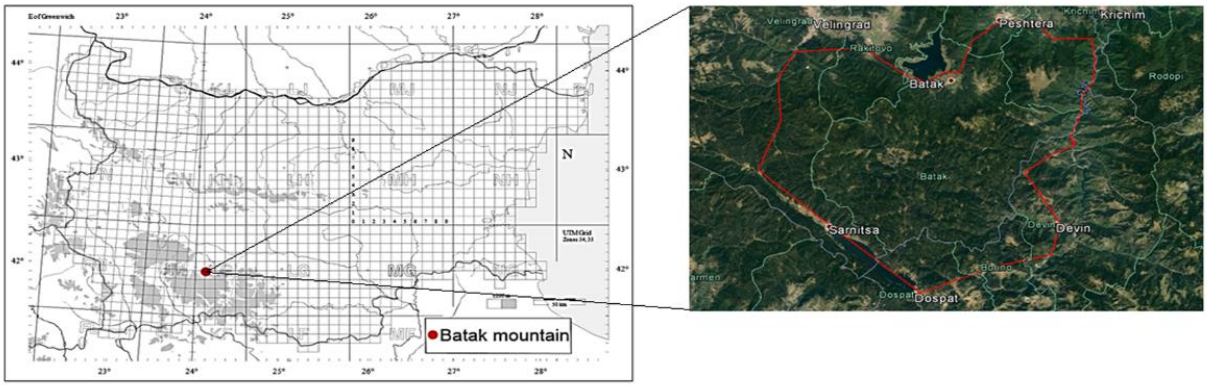

Fig. 1. Location of the sampling sites

Thracian Plane (GPS41°46'02.6"N 24°08'48.4"E) (Fig. 1). The region is industry-free and is characterised with forests, land and low buildings. The mushroom species discovered and collected for research in this article are as follows:

Mushroom samples from the species *Hydnum repandum, Suillus luteus* and *Morchella esculenta* were collected in 2018 from the Batak Mountain by the authors themselves. The Batak Mountain territory was conditionally divided into 15 regions. From each region, we collected 5 kg of fresh mushrooms. After sampling, the fungal specimens, were immediately transferred to the laboratory; they were cleaned from soil and other impurities first by hand and then washed with tap water and finally rinsed with bidistilled water in order to be perfectly free from residuals. After that, they were dried and finally fresh weight (FW) was appropriately obtained. Then, they were ashed at 360 °C (> 90% recovery of radionuclides according to ERL treatment protocols, IAEATRS No 118 of 1970 and IAEATRS No 295 of 1989) until constant weight which was measured and the percentage ratio (ashing factor) was estimated. Finally, they were homogenized up to fine powder and enclosed in white cups for immediate gamma measurement.

Reagents

All chemicals were at least of analytical-reagent grade. Water was deionized in a Milli-Q system (Millipore, Bedford, MA, USA) to a resistivity of 18.2 MΩ cm. All plastic and glassware were cleaned by soaking in diluted HNO_3 (1/9, v/v) and were rinsed with bidistilled water prior to use.

Gamma spectrometry

The Laboratory of Radioecology and Radioisotopes Research at IC FT is accredited by EA 'BAS' for determination the radioactive elements in soils, plants, foods, food products and waters.

The procedures for low background determination of natural and technogenic gamma-emitters in agricultural objects, developed and validated in the Laboratory of Radioecology and Radioisotopes Research, allow for the simultaneous determination of a large number of radionuclides with energies ranging from 50 to 2000 keV, by means of a spectrum, produced by semi-conductive Ge detector with high resolution. The used gamma-spectrometric system, produced by Canberra USA, includes the following modules:

– coaxial detector of extremely pure Ge with diameter of the drill 76 mm and relative efficiency 20% and resolution at 661, 4 keV of Cs-137 – 1.3 keV.

– multi-channel analyser (MCA) 'Canberra 85' with low-background protective camera of old steel. The working volume is suitable for installing containers, type 'Marinelli' with capacity of 0.5 and 1L dry matter (DM).

In that way, the coupled low-background system strongly reduces the natural background and allows direct spectrometry of samples of environmental origin.

Uranium-238 activity concentrations were calculated *via* Th-234 peaks, namely, the one at 63.3 keV and the double peak at 92.4 and 92.8 keV. In basidiomata, which are short-lived, Th-234 is not in secular equilibrium with its parent radionuclide U-238. In order to determine if fungi accumulate U-238 or Th-234, a second measurement was carried out about 1 month after the first one.

Consequently, the radionuclide present in the fungal samples follows the decay of Th-234 and, thus, Th-234 is accumulated by fungi and not U-238.

Potassium-40 activity concentrations were calculated *via* its only peak at 1460.8 keV, Cs-137 activity concentrations *via* its only peak at 661.7 keV, and Cs-134 activity concentrations *via* its two peaks at 604.7 and 795.8 keV. In cases where more

than two peaks were used, calculation of the mean value was performed.

Radioactivity units and legislation

One Bq (becquerel) has been the unit for the activity of a radioactive source in which one atom decays per second on average. Activity concentration, that is activity per dry matter unit, was used in this review. The usual statutory limit for foods was 600 Bq per kg of fresh weight, i.e. 6 kBq per kg of dry matter for mushrooms. However, in response to the Chernobyl disaster, the European Communities published a Council Regulation defining values for the maximum permitted levels of foodstuff radioactive contamination [12]. The regulation was established with a view to responding to accidents of a similar magnitude to the Chernobyl disaster. Under this regulation, the maximum permitted level of Cs-137 for foodstuffs such as mushrooms, was 1.25 kBq kg^{-1} fresh weight (i.e. 12.5 kBq kg^{-1} DM for mushrooms). A similar limit of 1.0 kBq kg^{-1} fresh weight (i.e. 10 kBq kg^{-1} DM for mushrooms) was recommended by the International Atomic Energy Agency [13].

Effective dose

A possible risk of radioactivity for human health is expressed by the effective dose (E) given in mSv (millisievert) per year. The acceptable yearly burden for an adult of the public, recommended by the International Commission for Radiation Protection, has been 5 mSv. A contribution to the yearly effective dose to an adult from mushroom consumption may be calculated as follows [14]:

$$E = Y \times Z \times d_k$$

where Y - annual intake of mushrooms (kg DM per person), Z - activity concentration (kBq kg^{-1} DM), d_k - dose coefficient (conversion factor) defined as the dose received by an adult per unit intake of radioactivity. Their values are 1.3×10^{-8} and 6.2×10^{-9} Sv Bq^{-1} for Cs-137 and K-40, respectively. During an explosive fission reaction many radionuclides are produced, among them Cs-137 with long half-lives of 30.17 years.

Statistical analysis

All analyses were carried out in triplicate and the data were reported as means ± standard deviation (SD). All statistical computing, test and graphics were performed within the statistical software R version 3.5.1 (2018-07-02). The results were analyzed for normality through Shapiro-Wilks test (chosen alpha level was 0.05) and quantile-quantile plots. The null-hypothesis of Shapiro-Wilks test is that the population is normally distributed. If p-value>0.05, then the null hypothesis that the data came from a normally distributed population can not be rejected [15].

RESULTS AND DISCUSSION

The activity concentrations for Cs-137, Cs-134, Th-234 and K-40 in the samples were checked for normality using the Shapiro–Wilks test and density plot (Tables 1, 2, 3 and Fig. 2). For the radionuclides K-40 and Cs-137, the hypothesis that they are normally distributed cannot be rejected based on their p-values (Tables 1, 2, 3).

The present study showed that the concentration of Cs-137 in the selected mushroom species *Hydnum repandum*, *Suillus luteus* and *Morchella esculenta* in 2018, i.e. 32 years after Chernobyl, were 110 Bq kg^{-1} DM, 50 Bq kg^{-1} DM and 6 Bq kg^{-1} DM.

In 2018 (32 years after the Chernobyl disaster) Cs-137 activity concentration was 110 (Bq kg^{-1} DM), while literature data show a half-life of radiocesium of 30.17 years. The results demonstrated that the relief, climate, mechanical soil composition, mushroom species had a crucial role for Cs-137 decay.

Table 1. Descriptive values for Cs-137 and K-40 activity concentrations (Bq kg^{-1} dm) in *Hydnum repandum*

Activity concentration	Cs-137	Cs-134	Th-234	K-40
Mean	110	< 2	< 2	1760
Std. Dev.	10.43			95.49
Median	109			1750
Minimum	98			1650
Maximum	124			1890
Range	26			240
Shapiro-Wilks Test	0.93			0.94
p-value	0.59			0.63
Effective dose	7.46E-06			5.69E-05

Table 2. Descriptive values for Cs-137 and K-40 activity concentrations (Bq kg^{-1} DM) in *Suillus luteus*

Activity concentration	Cs-137	Cs-134	Th-234	K-40
Mean	50	< 2	< 2	1760
Std. Dev.	10.41			79.83
Median	49.50			1735
Minimum	98			1650
Maximum	124			1836
Range	26			186
Shapiro-Wilks Test	0.853			0.87
p-value	0.167			0.25
Effective dose	3.39E-06			5.62E-05

Table 3. Descriptive values for Cs-137 and K-40 activity concentrations (Bq kg^{-1} DM) in *Morchella esculenta*

Activity concentration	Cs-137	Cs-134	Th-234	K-40
Mean	6	< 2	< 2	2100.83
Std. Dev.	1.79			138.72
Median	6			2102.51
Minimum	4			1940
Maximum	8			2260
Range	4			320
Shapiro-Wilks Test	0.97			0.89
p-value	0.86			0.31
Effective dose	4.07E-07			6.79E-05

The content of radioactive cesium varied substantially among the mushroom species. In general, those having gills, pores or teeth, as well as mushrooms with stalk, were more likely to accumulate radioactive cesium. On the basis of the ability to accumulate Cs-137 mushroom species could be divided into two groups: mushrooms with predominantly low cesium concentrations and mushrooms with high and medium levels of accumulated cesium. The following species belong to the group with low Cs-137 levels: *Craterellus cibarius*, *Morchella esculenta*, *Boletus* spp., *Albatrellus ovinus*, *Armillaria* spp., *Gyromitra esculenta*, etc. The Cs-137 levels in this group rarely exceed the reference limit of 600 Bq kg^{-1}. Medium to high Cs-137 contamination was observed in *Russula* spp., *Suillus luteus, Craterellus tubaeformis, Craterellus lutescens, Craterellus cornucopioides, Lactarius* spp., *Hydnum* spp., *Suillus variegatus, Rozites caperatus, Hygrophorus camarophyllus,* etc [13, 14]. Hedgehog mushrooms (*Hydnum repandum*) are among mushrooms, most capable to accumulate Cs-137. They grow in small groups in coniferous or deciduous woodlands and in them, detected Cs-137 concentrations attained several thousand Bq kg^{-1}.

Tables 1, 2 and 3 demonstrate that our results agreed with those reported in the literature. Our results confirmed that *Hydnum repandum* mushrooms were among mushrooms, most capable to accumulate Cs-137. *Suillus luteus* was outlined with a medium capacity for Cs-137 accumulation, while *Morchella esculenta* exhibited low Cs-137 levels.

The effective dose *per capita* in Bulgaria is calculated for average consumption of 50 kg fresh weight or 5 kg dry weight of mushrooms. The effective annual dose of Cs-137 in the selected mushroom species *Hydnum repandum, Suillus luteus* and *Morchella esculenta* were 7.46E-06, 3.39E-06 and 4.07E-07 Bq kg^{-1} DM, while for K-40 were 5.69E-05, 5.62E-05 and 6.79E-05 Bq kg^{-1} DM, i.e. <0.1% of the natural background radiation. This fact suggests that the consumption of mushrooms, even at the background of high levels of radioactive contamination, has a little contribution to the effective dose for Bulgarian population.

Quantile-quantile plots (or QQ plots) were used to visually check the normality of the data (Figs. 2, 3 and 4). QQ plots depict graphically the correlation between the given sample and the normal distribution. A 45-degree reference line was also plotted. As all points falled approximately along this reference line, normality was assumed.

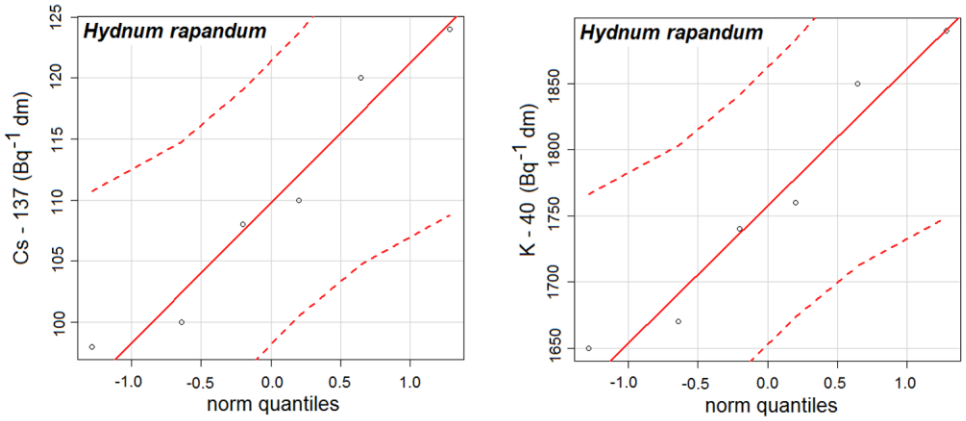

Fig. 2. Quantile-quantile plot showing the distribution of Cs-137 and K-40 in *Hydnum rapandum*

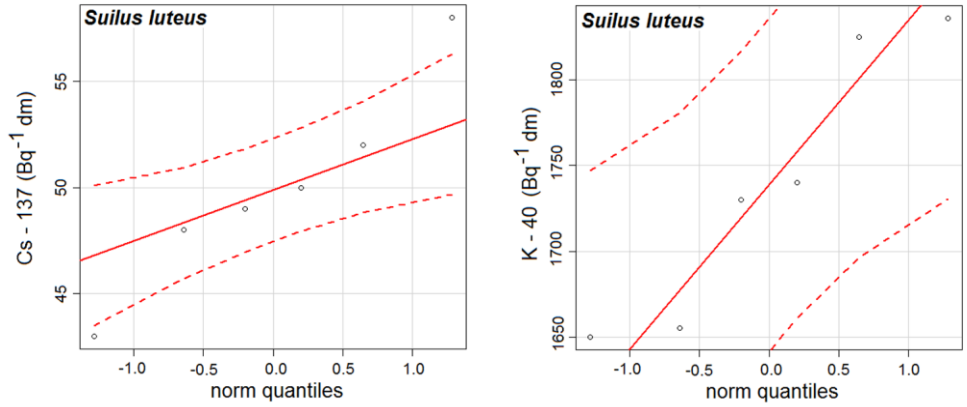

Fig. 3. Quantile-quantile plot showing the distribution of Cs-137 and K-40 in *Suilus luteus*

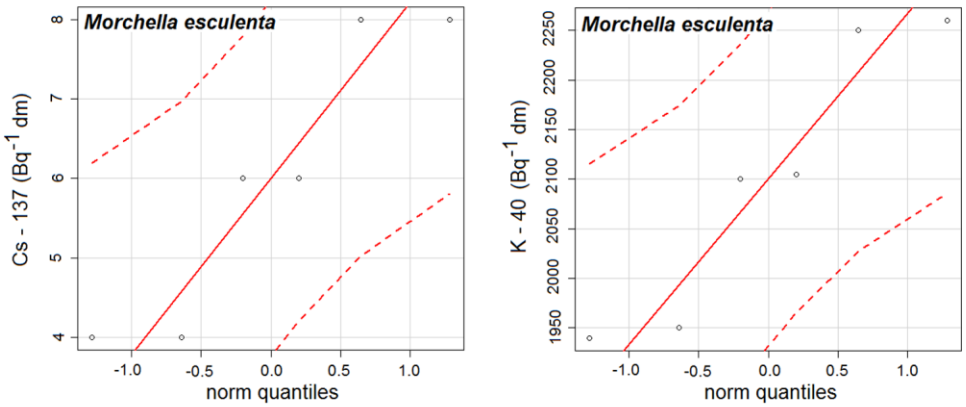

Fig. 4. Quantile-quantile plot showing the distribution of Cs-137 and K-40 in *Morchella esculenta*

CONCLUSIONS

The mushrooms analyzed by us during the year 2018 do not exceed the EU approved standards for Cs-137.

It was calculated that the effective dose for Cs-137 was in the range of 4.07E-07 to 7.46E-06 Bq kg^{-1} DM per year, and for K-40 was in the range of 5.62E-05 to 6.79E-05 Bq kg^{-1} DM, which was below 0.1% of the natural radioactive background.

It was found that cesium half-life is longer than 30.17 years at high altitudes in soils with low clay content and acidic reaction.

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