Investigation of natural and anthropogenic radionuclides distribution in arable land soil of southeastern European countries

Amin Shahrokhi, Gábor Szeiler, Hasan Rahimi, Tibor Kovács

Abstract— An investigation of the naturally occurring and anthropogenic radionuclides concentration in fifteen cropland soil samples due to their migration from soil to crops was carried out to ascertain the distribution of ^{235}U, ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in farmland soils of three southeastern European countries as Romania, Bulgaria and Greece. A High-purity Germanium detector by reason of low background and high resolution was used to detect gamma ray emission from radionuclides presented in samples. The concentration of natural radioactive materials were measured in range of 0.5 ± 0.1 to 0.8 ± 0.1 Bq.kg^{-1} by the average of 0.6 ± 0.1 Bq.kg^{-1} for ^{235}U, from 25 ± 4.6 to 37.9 ± 5.7 Bq.kg^{-1} with mean of 28.5 ± 4.8 Bq.kg^{-1} for ^{238}U, 26.8 ± 2.5 to 40.6 ± 3.5 Bq.kg^{-1} by mean of 31.1 ± 2.9 Bq.kg^{-1} as ^{226}Ra, for ^{232}Th ranging from 30.6 ± 5.5 to 41.3 ± 4.2 Bq.kg^{-1} by median of 37.4 ± 5.9 Bq.kg^{-1}, 270.4 ± 13 to 618.1 ± 23.5 Bq.kg^{-1} with an average of 438.5 ± 20.3 Bq.kg^{-1} for ^{40}K and the concentration of ^{137}Cs as anthropogenic nuclide was measured by 3.8 ± 0.7 to 9.8 ± 0.9 Bq.kg^{-1} with average of 5.6 ± 0.7 Bq.kg^{-1}, respectively. In light of results, Bulgarian soils contain the highest average concentration of ^{232}Th, ^{40}K and ^{137}Cs by 39.9, 467.2 and 7.1 Bq.kg^{-1}, whereas Romanian soils have the highest average values of ^{238}U and ^{226}Ra by 29.5 and 33.2 Bq.kg^{-1}, respectively; however, the average concentration of ^{235}U was measured same range in all countries soil. Although in natural ^{238}U is not in equilibrium with its daughters, the higher concentration of ^{226}Ra in some soil samples could be caused by irrigation water source or fertilizers.

Index Terms— Anthropogenic, Cropland, Europe3, Gamma, HPGe, Naturally occurring, Radionuclide, Soil

1 Introduction

THESE days, agro products are the life force and play an important role in life of world population as a source of survival. In near future, next to the quality, health of product could be a main parameter in marketing and agriculture industry. Soil as a mixture of mineral particles, organic matters and live organisms that support plants life contents both naturally and man-made radioactive materials what can be harmful for health after migration from soil to crops in significant quantity. Uranium, Radium, Thorium, and Potassium can be named as main natural radionuclides, while Cesium-137 is a main anthropogenic radioactive element in environment released from nuclear fission and activation processes. All mentioned radionuclides has a long half-life and can have health risk potential for a long time in some cases for our three next generations.

Plants are the primary recipients of radioactive contamination to the food chain following atmospheric releases of radionuclides. Vegetation may be subject to direct and indirect contamination. One of the main depositions of radioactive material in to plants and crops is uptakeing of radionuclides by plant's root from the soil depends on plants type, soil mixture, PH, and weather condition; however, irrigation source and as well as fertilizers type can change the rate of absorption of presented radionuclides in soil. The ratio of absorbed concentration of radionuclide and concentration in soil is described as a Transfer Factor (B_v) for specific radio-matter [1], [2].

Concentration of radionuclides in soils is variable from one location to another one depends on natural condition and human activity. The worldwide average concentration values of ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs nuclides are expressed as 40, 33, 45, 420 and 14.8 Bq.kg^{-1} [3], [4], [5].

The present study has determined concentration levels of the main naturally occurring radionuclides included ^{235}U, ^{238}U, ^{266}Ra, ^{232}Th, ^{40}K and man-made nuclide ^{137}Cs in cropland soil samples from three European countries of Romania, Bulgaria and Greece. The results will show a distribution map of measured radionuclides in farmland soils of selected southeastern European countries.

2 Study Area, Sampling and Sample Preparation

2.1 Study Area Geology

Southeastern Europe is a geographical and political region located primarily in the Balkan Peninsula and is inhabited by 13 European countries. The Balkan region popularly referred to as The Balkans that takes its name from the Balkan Mountains. Fig. 1 shows map of Southeastern region of Europe and existed countries in this region.

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Fig. 1. The Balkan Peninsula region and covered countries.

Three countries of The Balkans region as Romania, Bulgaria and Greece were selected for this study to cover this region from the north up to the south.

2.2 Sampling

From each selected country, five croplands from difference parts were chosen in order to cover all area. The soil samples were taken after plowing of land and when it's ready for implant. One kilogram mixed soil of each site from surface within 15 centimeter was collected, sealed and named. PH of soil was measured at time of collecting. Fig. 2 presents soil collection point in three selected countries.

Fig. 2. Samples collection location on the map

2.3 Sample Preparation

After transferring samples to laboratory, samples were air-dried in a ventilated cabinet with constant room temperature for 2 days. Samples were crushed and pulverized to less than 3 mm to be analogous to the standard reference geometry, and then it was dried in an oven at 90 °C for 6 h to remove moisture and reached to a constant weight. Then 500 grams of the homogenized prepared samples were filled into a leak-proof, air-tight Marinelli beaker in same as reference sample beaker geometric, weighed and sealed approximately for 29 days in order to reach secular equilibrium between ^{226}Ra and ^{222}Rn prior to counting [6].

3 Methods and Measurements

3.1 Measurements And Calculations

To determine the concentration of presented radionuclides in samples, a low background and high resolution HPGe gamma ray detector with a relative efficiency of 45% was used to evaluate all gamma emitting components both by quality and quantity through the detection of the amplitude, and energy level of the emitted gamma photons from isotopes. HPGe detector is the most reliable instrument for detection of all emitted gamma and X-ray from nuclides. The detector is covered with a 20 centimeter thickness of lead shield and a layer of nickel all around to decrease the natural background rate. Data and detected gamma rays were analyzed by Aptec MCA Multichannel Analyzer software.

The activity of each radionuclide (Bq.kg^{-1}) presents in sample with same geometric of standard is calculated by (1):

$$A_x = (1000\ N/t_c\ P_\gamma\ \varepsilon\ M)\ e^{-\lambda t} \quad (1)$$

where A_x is activity concentration of specific radionuclide in time of sampling (Bq.kg^{-1}), N is net count rate of photo-peak, t_c is expressed as counting live time (second), P_γ is probability of gamma ray transition via the specific energy, ε is the counting efficiency at specific photo-peak energy, M is the mass of sample (Kg), t is time interval between sampling and measuring (day), T is half-life of radionuclide calculated and λ is decay constants of specific nuclide and by (2):

$$\lambda = \ln 2/T \quad (2)$$

To determine the activity concentration of ^{235}U, ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs the following energy peaks regards to their sufficient discrimination of gamma ray energy were used [6], [7], [8], [9]:

- Measuring activity concentration of ^{235}U via its gamma ray energy ^{235}U: 185.7 keV with a gamma ray emission probability of 0.572 and by using (3).

$$^{235}U = ((C/\varepsilon_{peak})/\ M)\ -\ Ra\ I_{\gamma Ra})/I_{\gamma U} \quad (3)$$

where ^{235}U is activity concentration of ^{235}U (Bq.kg^{-1}), C is net count rates under ROI (cps), ε_{peak} is the efficiency of detector at ROI, M is expressed as mass of sample (kg), Ra is the activity concentration of ^{226}Ra (Bq.kg^{-1}) and $I_{\gamma Ra}$ and $I_{\gamma U}$ are

defined as probability of gamma ray transition of ^{226}Ra and ^{235}U at 186.2 and 185.7 keV peak energy.

- Determination of ^{226}Ra activity concentration by mean of gamma energy peaks of ^{214}pb: 351.9 keV with 0.3534 emission probability and ^{214}Bi: 609.3 keV with gamma emission probability of 0.451 and calculated via (4).

- Measuring of the activity concentration of ^{232}Th by median of ^{228}Th and ^{228}Ra activity that ^{228}Th is calculated from energy peaks ^{212}Pb: 238.6 keV and 0.436 probability of gamma emission and ^{208}Tl: 583.2 keV by emission probability of 0.3055; and ^{228}Ra is determined from energy peaks ^{228}Ac: 911.1 and 969.1 keV with emission probability of 0.277 and 0.166, respectively and calculated via (4).

$$A_{\text{parent}} = (A_{d1} + A_{d2})/2 \quad (4)$$

where A_{parent} is activity of a specific radionuclide with a long half-life time (Bq.kg^{-1}) And A_{d1}, A_{d2} are activity of daughters of A_{Parent} in equilibrium with parent (Bq.kg^{-1}).

- Calculation of the activity concentration of 40K directly via its gamma ray energy ^{40}K: 1460.82 keV with a gamma ray emission probability of 0.107.

- Determination of the ^{137}Cs activity concentration by its gamma ray energy ^{137}Cs: 661.6 keV with a gamma ray emission probability of 0.8499.

Background contribution was measured for an empty marinelli container with the same geometry of standard and sample container for 200000 seconds and each sample was counted for 100000 seconds.

Equation (5) and (6) show the calculation of uncertainty and Minimum Detectable Limit of measurement in accordance with given data by Aptec analyzer software.

$$MDL = \left(\sigma^2 + 2\,\sigma\left(\sqrt{2\,B}\right)\right)/t \quad (5)$$

where MDL is minimum detectable for photo-peak energy, σ is uncertainty, B is background rate under photo-peak ROI and t live counting time.

$$\sigma = \left(\left(2\sqrt{C+B}\right)/C\right) \quad (6)$$

where σ is uncertainty, C is net sample count rate under photo-peak ROI (cps) and B is net background rate under photo-peak ROI (cps).

3.2 Calibration and Characterization

The HPGe gamma ray detector of this study was calibrated in laboratory of institute of Radiochemistry and Radioecology of University of Pannonia. Three closed standard sources as ^{137}Cs by two peaks energy 32.19 and 661.9 keV, ^{60}Co with two peaks energy of 1173.2 and 1332.5 keV and ^{241}Am with 59.5 peak energy were used for energy calibration[7],[9]. Fig. 3 shows an example of full energy peak efficiency in function of gamma ray energies as a typical efficiency for High-purity Germanium detectors [9].

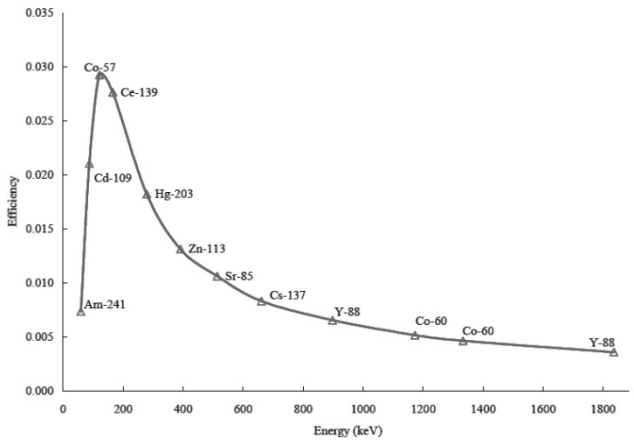

Fig. 3. Typical energy efficiency graph for HPGe detectors

IAEA-327 soil standard with known isotopes and activity concentration as same as geometry of the sample was used to determine gamma ray count detection efficiency via (7):

$$\varepsilon = (N/A\,P_\gamma\,T)\,S \quad (7)$$

where ε is efficiency for specific energy, N is neat counts rate under the full energy peak , S is decay correction factor and A is reference specific radionuclide (Bq.kg^{-1}).

4 Results and Discussion

The specific detection efficiency and MDA were measured by using IAEA reference standard in same geometry with the sample for ^{235}U, ^{226}Ra, ^{40}K, ^{232}Th and ^{137}Cs by 4.9%, 2.4%, 1.2%, 3.7% and 2.2% as specific efficiency of each photo-peak and 0.5, 1.3, 46, 2.3 and 0.31 Bq.kg^{-1} as minimum detectable activity, respectively.

Table 1 shows the concentration and uncertainty of ^{235}U, ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in all soil samples with their location.

TABLE 1
Concentration of Radionuclides in Soil Samples (Bq.kg^{-1})

	Location	^{235}U	+-	^{238}U	+-	^{226}Ra	+-	^{232}Th	+-	^{40}K	+-	^{137}Cs	+-
BG	Near Montana	0.7	0.1	30.9	4.7	30.9	3.1	38.4	4.5	380	15	6.2	0.5
BG	Near Boboshevb	0.7	0.1	27.6	5.5	34.5	3.3	38.8	7.1	618	23	5.0	0.9
BG	Near Petrich	0.5	0.1	28.8	6.1	26.8	2.5	41.3	4.2	585	18	9.8	0.9
BG	Near Smolyanovtsi	0.8	0.1	27.1	5.0	37.8	3.0	40.1	7.7	270	13	8.3	0.9
BG	Near Plovdiv	0.6	0.1	28,4	6.1	28.4	3.5	40.7	6.7	483	16	6.4	0.8
RO	Near Maqlavit	0.7	0.1	27.5	4.4	28.8	2.7	31.6	5.1	369	15	4.7	0.6
RO	Near Pitesti	0.8	0.1	26.0	4.5	34.3	3.2	39.9	6.7	430	16	3.8	0.7
RO	Near Deva	0.6	0.1	37.9	5.7	40.6	3.5	41.2	7.3	457	20	4.3	1.0
RO	Near Arad	0.5	0.1	27.6	4.6	29.9	2.5	35.5	5.5	360	15	5.9	0.7
RO	Near Floresti	0.6	0.1	28.5	5.1	32.3	3.7	37.2	6.7	405	17	4.1	0.5
GR	Near Sidirokastro	0.7	0.1	31.2	4.6	28.8	2.8	33.3	6.6	433	16	4.8	0.6
GR	Near Vasilika	0.6	0.1	26.2	4.2	27.5	2.5	30.6	5.5	372	15	4.9	0.6
GR	Near Lagyna	0.6	0.1	25.0	4.6	27.9	2.6	39.0	5.9	505	15	5.4	0.7
GR	Near Kitros	0.6	0.1	27.6	4.9	29.0	2.5	38.3	4.9	424	73	5.1	0.5
GR	Near Sarantaporo	0.5	0.1	27.3	4.9	28.4	2.7	35.6	3.8	487	18	4.9	0.5
	Mean	0.6	0.1	28.5	4.8	31.1	2.9	37.4	5.9	438.5	20	5.6	0.7

In light of results, the average concentrations of all samples are below than worldwide average values expect ^{40}K that is exceeded by around 47 $Bq.kg^{-1}$.

The highest concentration of ^{137}Cs and ^{232}Th were found in sample from near Petrich city and ^{40}K in sample near Boboshevb city in Bolgaria, however sample from near Deva city in Romania shows the highest value concentration of ^{238}U and ^{226}Ra whilst highest concentration of ^{235}U was found in soil sample from near Pitesti in Romania.

Fig. 4 shows the concentration of measured radionuclides in each country samples on a graph.

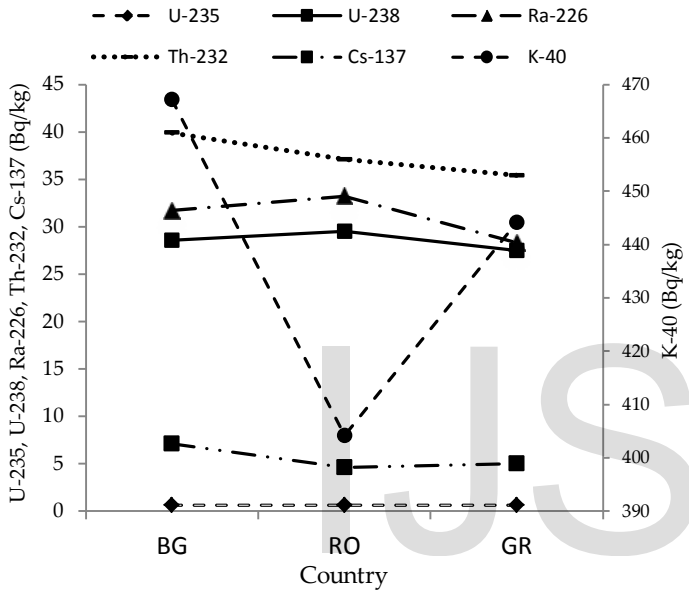

Fig. 4. Average concentration of radionuclides in each country soils

The average concentration of ^{235}U, ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs for each country were measured and are shown in table 2 in order to show distribution of each radioactive material in cropland soil in studied countries.

TABLE 2
THE AVERAGE CONCENTRATION OF RADIONUCLIDES IN SOIL OF EACH COUNTRY ($Bq.kg^{-1}$)

	Bulgaria		Romania		Greece	
U-235	0.6	± 0.1	0.6	± 0.1	0.6	± 0.1
U-238	28.6	± 5	29.5	± 4.9	27.5	± 4.6
Ra-226	31.7	± 3.1	33.2	± 3.1	28.3	± 2.6
Th-232	39.9	± 6	37.1	± 6.3	35.4	± 5.3
K-40	467.2	± 17	404.2	± 16.6	444.2	± 27.4
Cs-137	7.1	± 0.8	4.6	± 0.7	5	± 0.6

The Bulgarian soils show the highest value of Thorium, Potassium and Cesium concentration whilst Radium is in highest value in Romanian soils. Greece soils show the lowest concentrations of all radionuclides expect Potassium that after Bulgaria is second. In Fig. 5, 6 and 7, column charts are used to compare the concentration of each radionuclide in soil of each country and the worldwide average concentration value.

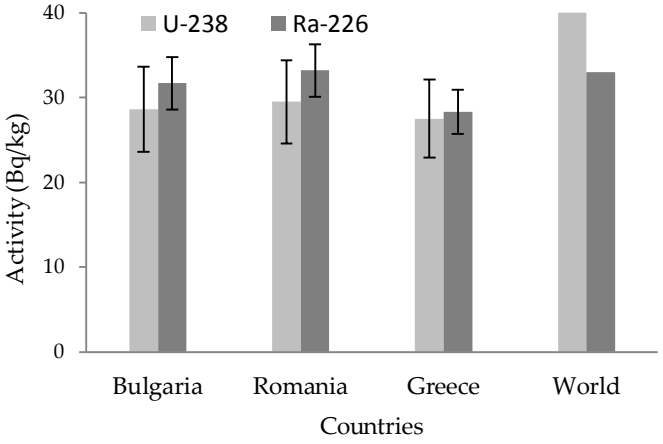

Fig. 5. Samples collection location on the map

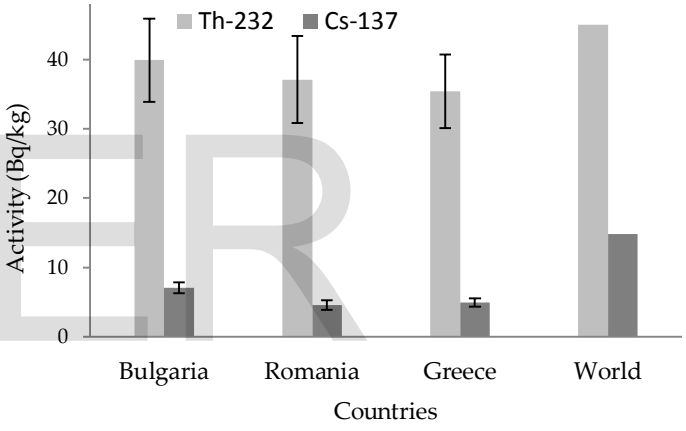

Fig. 6. Samples collection location on the map

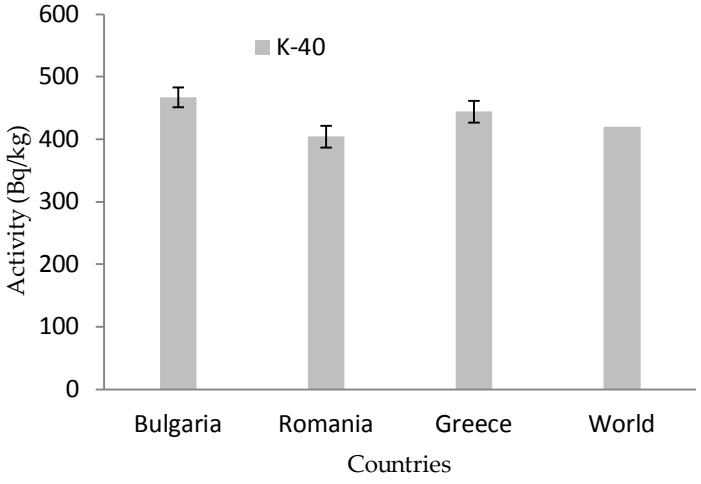

Fig. 7. Samples collection location on the map

In general the concentrations of all measured radioactive materials in all countries are lower than world average value

except ^{40}K and ^{226}Ra that it may caused by irrigation water or fertilizers.

4 CONCLUSION

In this study an investigation on distribution of natural and anthropogenic radionuclides present in cropland soil samples of three southeastern European countries were carried out. In light of results, distribution of ^{235}U was same in selected countries; however, Bulgarian soils show higher man-made radionuclide of ^{137}Cs by minimum 5 and maximum 9.8 with average of 7.1 Bq.kg^{-1}, respectively. All radionuclides average concentration in soils from Romania and Greece are lower than worldwide average value whilst in Bulgarian soils the concentration of ^{40}K is more than world average by about 17 Bq.kg^{-1}. Higher concentration of ^{40}K and ^{226}Ra in some soil samples may caused by used irrigation water or fertilizers for cropland. The PH of soil samples were measured at time of sampling between 5.4 and 6.8 which are in typical PH range for cropland depends on farmed plants.

7.2 Acknowledgments

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REFERENCES

[1] United Nations Scientific Committee on the Effects of Atomic Radiation, "UNSCEAR 2000 Report to the General Assembly," *Annex A: Dose assessment methodologies*, UNSCEAR, Volume I, pp. 37-40, 2000.

[2] J. D. Sartor, W. B. Lane, J. J. Allen," Uptake of radionuclides by plants," California: U.S.N.R.D.l, pp. 1-43, 1993.

[3] H. Vanmarcke, "UNSCEAR 2000: SOURCES OF IONIZING RADIATION – La radioactivité," Departement Stralingsbeschermings Onderzoek, belgium, pp. 1-10, 2003.

[4] O. A. Haija, "Determination of natural radionuclides concentrations in surface soil in Tafila/Jordan," Modern Applied Science, vol. 6, no. 3, pp. 87-90, March 2012, doi: 10.5539/mas.v6n3p87.

[5] Argonne National Laboratory, "Human Health Fact Sheet – Cesium HPS Chapter," Argonne: U.S. Department of energy, pp. 1-3, October 2001.

[6] F. J. Maringer, A. Baumgartner, F. Rechberger, C. Seidel, M. Stietka, "Activity measurement and effective dose modelling of natural radionuclides in building material," Applied Radiation Isotopes, vol. 81, pp. 279-283, 2013.

[7] International Atomic Energy Agency, "Gamma Ray Decay Data Standards for Detector Calibration and Other Applications," Vienna: IAEA, vol. 2, pp. 2-34, May 2007, STI/PUB/1287.

[8] I. H. Saleh, "Radioactivity of ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs and assessment of depleted uranium in soil of the Musandam Peninsula, Sultanate of Oman," Turkish J. Eng. Env. Sci, vol. 36, pp. 236-248, 2012, doi:10.3906/muh-1110-1.

[9] S. Harb, A. H. El-Kamel, A. I. Abd El-Mageed, A. Abbady, Wafaa Rashed, "Concentration of U-238, U-235, Ra-226, Th-232, K-40 for some granite samples in eastern desert of Egypt," *Proc. Third Environmental Physics Conf*, Egyept, pp. 109-117, Feb 2008.