NATURAL RADIOACTIVITY LEVELS AND ESTIMATION OF RADIATION EXPOSURE IN AGRICULTURAL SOILS FROM SKOPJE CITY REGION

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The aim of this study was to determine the activity concentrations of naturally occurring radioisotopes $^{226}$Ra, $^{232}$Th and $^{40}$K in 14 soil samples collected in the Skopje city surroundings, and to calculate the corresponding absorbed gamma dose rates. The radionuclides were measured applying a high purity Ge detector gamma-ray spectrometer with relative efficiency of 30% at 1.33 MeV. The activity concentrations found in 14 soil samples varied in the range of 24.1–41.9 Bq kg$^{-1}$ for $^{226}$Ra, 38.5–52.2 Bq kg$^{-1}$ for $^{232}$Th and 502–707 Bq kg$^{-1}$ for $^{40}$K. The mean radium equivalent (Raeq), for the area under investigation, was 143 ± 16 Bq kg$^{-1}$, while the outdoor radiation hazard index ($H_{ex}$) was 0.39. The total absorbed dose rate due to the three primordial radionuclides investigated lay in the range of 55.3–79.0 nGy h$^{-1}$ with a mean value of 68.1 ± 7.7 nGy h$^{-1}$, yielding a total annual effective dose of (83.5 ± 9.5) μSv y$^{-1}$. The assessed radiological factors were lower than the recommended values, indicating a low radiological health risk for the population living and working in the investigated area. The activity concentrations of radionuclides in soil samples were compared to the international values reported by United Nations Scientific Committee on the Effects of Atomic Radiation and previous studies on geographically close areas and some worldwide regions.

Keywords: natural radioactivity; soil; gamma spectrometry; activity concentrations; radiological risks

НИВОА НА ПРИРОДНИТА РАДИОАКТИВНОСТ И ПРОЦЕНА НА ИЗЛОЖЕНОСТ НА РАДИЈАЦИЈА ОД ЗЕМЈОДЕЛСКОТО ЗЕМИШТЕ БО РЕГИОНОТ НА ГРАДОТ СКОПЈЕ

Целта на ова истражување беше да се одредат концентрациите на активноста на природно присутните радионуклиди $^{226}$Ra, $^{232}$Th и $^{40}$K во 14 примероци почва од околината на градот Скопје, како и пресметка на соодветните апсорбирани дози. Радионуклидите беа измерени со прилаголна гама-спектрометар со висока чистота, со релативна ефикасност од 30 % на 1,33 MeV. Концентрациите на активноста беа одредени во 14 примероци почва и со движење во опсегот од 24.1 до 41.9 Bq kg$^{-1}$ за $^{226}$Ra, од 38.5 до 52.2 Bq kg$^{-1}$ за $^{232}$Th и од 502 до 707 Bq kg$^{-1}$ за $^{40}$K. Просечната вредност за радиумскиот еквивалент (Raex) во истражуваната област беше 143 ± 16 Bq kg$^{-1}$, додека пак вредноста на индексот на радијациона опасност ($H_{ex}$) за опстрена средина беше 0,39. Вкупната апсорбирана доза која потекнува од истражените три приморадијални радионуклиди се движеше во опсегот од 55.3 до 79.0 nGy h$^{-1}$, со просечна вредност од 68.1 ± 7.7 nGy h$^{-1}$, која учествува во вкупната годишна ефективна доза со 83.5 ± 9.5 μSv y$^{-1}$. Проценетите радиолошки фактори беа пониски од препорачаните вредности, што укажува на низок радиолошки ризик по здравјето на населението кој живее и работи во истражуваното подрачје. Определените концентрации на активноста беа споредени со објавените вредности на меѓународно ниво од страна на Научниот комитет на Обединитите Нации за ефектите од атомското зрачење, како и со претходно спроведените истражувања за географски близки региони и некои региони низ светот.
1. INTRODUCTION

Human beings have always been exposed to radiation, arising from different sources such as cosmic rays, natural radioactivity of the environment and plants, and artificially generated radioactivity from fallout, nuclear activities, and medical applications [1]. The soil is a first element in the environmental chain soil–food–humans; therefore, it plays a significant role in the radionuclide transfer and distribution. There are around 40 natural radioactive substances in the soil, with various contributions, but predominantly, the natural environmental radioactivity mainly arises from three primordial radionuclides such as ⁴⁰K, and the nuclides from the ²³⁸U and ²³²Th decay series [2, 3]. These radionuclides are from the nucleo-synthesis process in the stars and are characterized by half-lives comparable to the Earth’s age [3].

Once present in the environment, these radioisotopes are available for uptake by the plants and animals, thus entering in the food chain. Therefore, the information on the soil radio-contamination is a basis for further establishment of criteria and norms for radiation safety. Natural soil radioactivity and the associated exposure due to gamma radiation are primarily dependent on the geological and geographical properties, even though at different levels, they appear in the soils throughout the whole world [4–6]. The assessment of gamma radiation doses originating from natural sources is of particular significance, as natural radiation predominantly, via soil, water, local vegetation, and the air of a region, contributes to the external dose of the population within a specific region [1]. Furthermore, this data is a valuable input in forming the basis for evaluation of the degree of the possible future radioactive pollution [7]. The growing worldwide interest in natural radioactivity has resulted in extensive surveys in many countries [3, 8–16]. External gamma dose estimation from the terrestrial sources is essential because not only does it present a considerable contribution to the collective dose, estimated at 0.46 mS y⁻¹, but also is important for the implementation of precautionary measures whenever the findings reveal doses above the recommended limits [1, 11]. These doses are variable depending upon the concentrations of the natural radionuclides, ²³⁸U, ²³²Th, and their decay series, and ⁴⁰K, present in soils and rocks [11]. The average abundance in the upper Earth crust of potassium, uranium and thorium is 2.7 %, 2.5 ppm, and 10.5 ppm, respectively. As an alkali metal with an ionic radius of 0.16 nm, potassium is one of the so-called large ion lithophile elements and tends to be depleted in evolved crustal rocks. Uranium with an ionic radius of 0.1 nm and thorium with an ionic radius of 0.11 nm are also considered as large lithophile elements. However, their lower abundances mean that minerals that contain uranium and thorium as essential constituents are present as trace minerals in common rocks. The natural radioactivity is usually determined measuring the activities of ²²⁶Ra, ²³²Th and ⁴⁰K. It is considered that radium and its decay products cause 98.5 % of the radiological effects of the uranium series [11].

Republic of Macedonia is located in the central part of the Balkan Peninsula with an area of 25 713 km² [17]. The average altitude is 832 m, with a north latitude between 40º50′ and 42º20′, and an east longitude between 20º27′30″ and 23º05′ [17]. The vicinity of the city of Skopje is located in the northern part of the state, spread over the Skopje Valley in a northwest southeast direction, being 47 km long. The studied area is surrounded by hills from the north, west and south. The total area is 2100 km² with an altitude between 173 and 340 m, at 41º53′42″ north latitude and 21º18′30″ east longitude. The average annual air temperature in 2012 was 13.7 °C, with average annual rainfalls of 412.7 mm [17]. The city of Skopje, besides being the capital of Macedonia, is known for its steel, cement, and pharmaceutical production industries. The surrounding area is predominantly agricultural with a variety of cultures grown on it, mainly crops and vegetables.

So far, there has been only limited data on natural radioactivity in raw products for building materials applied in Republic of Macedonia [18], as well as the vertical distribution of natural radionuclides ²²⁶Ra, ²³²Th, ⁴⁰K [19] and the natural radioactivity in non-cultivated soils [20]. However, regarding the assessment of doses occurring from the natural radioactivity and absorbed by the population from the Republic of Macedonia, there is data available for other investigated regions [21, 22].

The objective of our study was focused on determining the natural radioactivity levels in collected soil samples from 14 locations in the surroundings of the capital city of Skopje, Republic of Macedonia, where the highest population density (370 km⁻²) is present [17]. For this purpose, the ac-
Natural radioactivity levels and estimation of radiation exposure in agricultural soils from Skopje city region

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2. EXPERIMENTAL

2.1. Sampling

Fourteen soil samples were collected from the locations in the surroundings of the city of Skopje (Fig. 1), during 2012. The sampling was performed at three soil depths: 0–5 cm, 5–10 cm, and 10–15 cm, employing a suitable sampling device with 700 mm length, enabling sampling only at the desired depths. According to International Atomic Energy Agency (IAEA) recommendations [23], sampling was performed in duplicate. Thus, in total, from every location, six soil samples were collected. During the sampling, special care was taken about the micro-location flatness, excluding the consequences of possible horizontal radionuclide translocation.

After removing the stones and organic impurities, the samples were dried in an oven at 110°C for 24 hours, to remove the moisture. Then, the samples were crushed and passed through 150 µm sieve. The homogenized samples were weighed, and a mass from 480 to 490 g of each sample was packed in polyethylene Marinelli beakers with an active volume of 480 cm³. After tightening, the containers were sealed with adhesive tape and left for 21 day before measuring with gamma spectrometry. This was in order to ensure that the daughter products of 226Ra and 228Th had achieved equilibrium with the respective parent radionuclides [11].

Fig. 1. Sampling locations for samples from the surroundings of the city of Skopje
2.2. Gamma spectrometry measurements

The gamma ray spectrometry technique was used for radioactivity determination of the samples tested. The spectrometer consisted of a high purity (HP) Ge detector, model 3020 (Canberra Packard, Meriden, CT, USA), with relative efficiency of 30 % at 1.33 MeV. The detector was enclosed in massive 12 cm thick lead shielding and an internal lining of 2 mm high purity copper. Data acquisition and analysis were performed with an 8192 channel digital analyzer; the duration of acquisition interval for each sample was 65 ks. The activity of $^{226}$Ra was determined from the gamma lines associated with low half-life time daughters of $^{214}$Bi (609.31, 1120.29 and 1794.49 keV) and $^{214}$Pb (351.93 keV). The $^{226}$Th activity was determined by 338.4, 911.2 and 969.1 keV gamma lines from $^{226}$Ac and its decay products. The gamma line at 1460.8 keV was used to determine the activity of $^{40}$K.

The energy and efficiency calibration of the gamma spectrometer were performed with a standard calibration source MBSS2 with Marinelli beaker geometry and an active volume of 480 cm$^3$. The source was supplied from the Czech Metrological Institute and emitted gamma rays with the energy between 53 and 1836 keV. It contained 11 radionuclides in silicone resin ($^{241}$Am, $^{109}$Cd, $^{133}$Ce, $^{57}$Co, $^{60}$Co, $^{137}$Cs, $^{113}$Sn, $^{85}$Sr, $^{88}$Y, $^{133}$Ba, and $^{54}$Mn), and the total activity was 39.98 kBq, with an expressed measurement uncertainty of 2 %. In order to determine the background radioactivity in the detector environment, an empty sealed Marinelli beaker with the same geometry was measured at equal counts as the soil samples. The analysis procedure included the subtraction of the background spectrum.

Genie 2000 Gamma Analysis Software (Mirion Technologies-Canberra, Meriden, CT, USA) was used to process the obtained spectra. Statistical evaluation of the obtained data was performed using the statistical package OriginPro 8 SR4 v8.0951 software package (OriginLab Corporation, Northampton, MA, USA).

2.3. Calculation of radium equivalent activity

As the distribution for $^{226}$Ra, $^{232}$Th and $^{40}$K in soil samples is not uniform, exposure to radiation can be defined in terms of radium equivalent (Ra$_{eq}$), with the aim to compare the specific activity of the radionuclides of interest [14]. The radium equivalent activity may be defined as:

$$\text{Ra}_{eq} = A_{Ra} + 1.43 \times A_{Th} + 0.077 \times A_{K}$$

(1)

where $A_{Ra}$, $A_{Th}$ and $A_{K}$ are the specific activities (Bq kg$^{-1}$) of $^{226}$Ra, $^{232}$Th and $^{40}$K, respectively. The Ra$_{eq}$ index expresses the specific activities of the investigated radioisotopes assuming that 370 Bq kg$^{-1}$ of $^{226}$Ra, or 259 Bq kg$^{-1}$ of $^{232}$Th, or 4810 Bq kg$^{-1}$ of $^{40}$K produce an equal gamma dose rate [14].

2.4. Calculation of air-absorbed dose rates ($D$)

It is considered that for calculation of the outdoor air-absorbed dose rate due to the terrestrial gamma rays at 1 m above the ground, only $^{226}$Ra, $^{232}$Th and $^{40}$K concentration values in soils should be taken into account, assuming that other radionuclides, such as $^{137}$Cs, $^{90}$Sr and the $^{235}$U decay series reveal a negligible contribution to the total dose [14]. The conversion factors used to calculate the absorbed dose rates are the ones proposed by UNSCEAR [24]:

$$D = 0.462 \times C_{Ra} + 0.604 \times C_{Th} + 0.0417 \times C_{K}$$

(2)

where $D$ is the dose rate in nGy/h, and $C_{Ra}$, $C_{Th}$ and $C_{K}$ are the concentrations, expressed in Bq kg$^{-1}$, of $^{226}$Ra, $^{232}$Th and $^{40}$K, respectively. The equation above is given assuming that all decay products of $^{226}$Ra and $^{232}$Th are in equilibrium with their precursors.

2.5. Calculation of the external hazard index ($H_{ex}$)

The external hazard index is calculated by equation proposed by Beretka and Matthew [14]:

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_{K}/4810 \leq 1$$

(3)

where $H_{ex}$ is external hazard value, and $C_{Ra}$, $C_{Th}$ and $C_{K}$ are the mean activity concentrations (Bq kg$^{-1}$) of $^{226}$Ra, $^{232}$Th and $^{40}$K, respectively. The value of this index must be less than unity, thus keeping the radiation hazard insignificant. The maximum value of $H_{ex}$, equal to unity, corresponds to the upper limit of Ra$_{eq}$ (370 Bq kg$^{-1}$).

2.6. Calculation of annual effective dose

When estimating the annual effective dose received by a human individual, one has to take into consideration the conversion coefficient from the absorbed dose in air to the human effective dose, and the outdoor occupancy factor of 20 %. The annual effective dose rate ($D_{A,eff}$) is calculated by the equation [4]:

$$D_{A,eff} = D \times Nh \times 0.7 \times 0.2$$

(4)

where $D_{A,eff}$ is the annual effective dose in $\mu$Sv y$^{-1}$, $D$ is the air absorbed dose rate, and $Nh$ is the annual number of hours (8760). Within Eq. (4) the dose...
rate data obtained from the concentration values of natural radionuclides in soil (D), conversion factor of 0.7 µSv Gy⁻¹ from the absorbed dose in air to effective dose received by adults [4], and approximation of 20 % outdoor time, are included.

2.7. Calculation of annual gonadal equivalent dose

According to UNCEAR [24], human organs of interest for measurable biological effects of radiation are the gonads, the active bone narrow, and the bone surface cells. Therefore, the annual gonadal equivalent dose (AGDE) for the studied population, due to the concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K, was calculated using Eq. (5) [9]:

\[
AGDE = 3.09 \times C_{Ra} + 4.18 \times C_{Th} + 0.314 \times C_K, \tag{5}
\]

where AGDE is annual gonadal equivalent dose in µS y⁻¹, and \(C_{Ra}\), \(C_{Th}\) and \(C_K\) are the specific activities (Bq kg⁻¹) of ²²⁶Ra, ²³²Th and ⁴⁰K, respectively.

2.8. Excess lifetime cancer risk

Excess lifetime cancer risk (ELCR) is a radiological parameter which describes the additional risk of developing cancer resulting from exposure to gamma irradiation during a lifetime. It was calculated using the following equation [9]:

\[
ELCR = AEDE \times DL \times RF \tag{6}
\]

where AEDE, DL and RF are the annual effective dose equivalent, average duration of lifetime (70 years) and fatal risk factor (Sv⁻¹), respectively. For stochastic effects, the International Commission on Radiological Protection (ICRP) as a fatal risk factor recommends the value of 0.05 per Sievert for the public [25].

3. RESULTS AND DISCUSSION

3.1. The activity concentrations

The results for vertical distribution of the radionuclides throughout the soil at 0–5, 5–10 and 10–15 cm depth have been previously published and discussed [19]. Therefore, in Table 1, the average values of the activity concentrations for ²²⁶Ra, ²³²Th and ⁴⁰K obtained from six measurements (three different depths in duplicate), associated with the respective standard deviations (SD) that occur due to sampling and counting errors, are presented.

From the table we found that the standard deviation values for the three radioisotopes are less than their corresponding average, showing a high degree of uniformity of their distribution in the studied samples, as other authors have also concluded [26]. The negative values of the skewness for ²²⁶Ra (Table 1), shows that the frequency distribution is slightly asymmetric, i.e. slightly skewed to the left, while the frequency distribution for ²³²Th is slightly positively skewed. On the other hand, the skewness value for ⁴⁰K is very close to zero, indicating that the frequency distribution curve is normal. Besides that, the kurtosis for the activity concentrations of the investigated radionuclides have negative values, showing that the frequency distribution curve is less peaked than the normal curve for each of the radioisotopes ²²⁶Ra, ²³²Th, ⁴⁰K. This may be attributed to the unequal distribution of the investigated natural radioisotopes in the soil samples from the agricultural area in Skopje city surroundings.

As expected, and in accordance with the worldwide data [4], the activities for ²³²Th are higher than the ones for ²²⁶Ra, while the values for ⁴⁰K are one magnitude higher. The activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K ranged from 24.1 ± 0.6 Bq kg⁻¹ to 41.9 ± 5.6 Bq kg⁻¹, from 38.5 ± 2.5 Bq kg⁻¹ to 52.2 ± 1.6 Bq kg⁻¹ and from 502 ± 55 Bq kg⁻¹ to 707 ± 14 Bq kg⁻¹, respectively. In comparison to the worldwide median values for ²²⁶Ra 35 Bq kg⁻¹ [4], the measured activities for locations 3, 4, 6, 7, 8, 9, 12 and 13 revealed higher ²²⁶Ra values. However, the average ²²⁶Ra value for all 14 locations (34.1 Bq kg⁻¹ ± 6.0 Bq kg⁻¹) is practically equal to the worldwide median value (35 Bq kg⁻¹). On the other hand, all values measured for ²³²Th were higher than the world average (30 Bq kg⁻¹) [4]. Regarding the ⁴⁰K activities, similarly to ²³²Th, all values revealed are higher than the worldwide average value, reported to be 400 Bq kg⁻¹ [4]. The data ranges for ²²⁶Ra, ²³²Th and ⁴⁰K determined within this study are lower than the ones determined by other authors [7, 10, 11, 15] and the ranges reported by UNCEAR for findings in different countries worldwide [4].

This is probably due to the fact that the studied area is smaller (around 2100 km²) in comparison to other studies [10, 11, 16]. For this reason, the factors mainly affecting the radionuclide distribution in soils (geographical, geological and hydrological) have a low variability (less than 20 % relative standard deviation), resulting in a relatively higher uniformity in the ²²⁶Ra, ²³²Th and ⁴⁰K distribution on...
the territory of Skopje city surroundings. Even though the worldwide average concentrations of radionuclides in soils are low, there is a large variability of the data reported, with revealed levels up to 1000 Bq kg\(^{-1}\) for \(^{238}\)U, 360 Bq kg\(^{-1}\) for \(^{232}\)Th and 3200 Bq kg\(^{-1}\) for \(^{40}\)K (UNSCAR, 2008) [27]. Therefore, for the purposes of global dose assessment, the data presented needs to be linked with the respective population distributions.

### Table 1

**Measurement data and descriptive statistics for specific activities of \(^{226}\)Ra, \(^{232}\)Th, and \(^{40}\)K in soil samples**

| Location No. | Sampling site        | \(^{226}\)Ra Activity concentrations ± SD (Bq kg\(^{-1}\)\)* | \(^{232}\)Th Activity concentrations ± SD (Bq kg\(^{-1}\)\)* | \(^{40}\)K Activity concentrations ± SD (Bq kg\(^{-1}\)\)* |
|--------------|----------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 1            | Petrovec             | 34.4 ± 4.2                                               | 42.4 ± 4.2                                               | 588 ± 11                                                  |
| 2            | Belimbegovo          | 32.4 ± 3.3                                               | 42.5 ± 1.2                                               | 574 ± 16                                                  |
| 3            | Aračinovo            | 41.2 ± 1.8                                               | 48.1 ± 1.2                                               | 677 ± 18                                                  |
| 4            | Radašani             | 31.4 ± 1.2                                               | 51.5 ± 2.7                                               | 623 ± 9                                                   |
| 5            | Čučer-Sandevo         | 24.1 ± 0.6                                               | 38.5 ± 2.5                                               | 502 ± 55                                                  |
| 6            | Vizbegovo            | 40.8 ± 1.0                                               | 49.6 ± 1.7                                               | 705 ± 17                                                  |
| 7            | Bardovci             | 41.9 ± 5.6                                               | 49.8 ± 2.2                                               | 707 ± 14                                                  |
| 8            | Saraj                | 36.0 ± 0.5                                               | 41.0 ± 1.9                                               | 629 ± 19                                                  |
| 9            | Nerezi               | 36.3 ± 1.3                                               | 52.2 ± 1.6                                               | 624 ± 16                                                  |
| 10           | Lisiče               | 26.3 ± 1.4                                               | 40.8 ± 2.1                                               | 527 ± 39                                                  |
| 11           | Dračevo              | 25.7 ± 1.6                                               | 39.9 ± 1.5                                               | 549 ± 24                                                  |
| 12           | Pintija              | 40.9 ± 1.2                                               | 46.0 ± 3.3                                               | 656 ± 26                                                  |
| 13           | Batinci              | 36.0 ± 4.2                                               | 42.4 ± 1.2                                               | 630 ± 32                                                  |
| 14           | Volkovo              | 29.3 ± 5.1                                               | 41.9 ± 3.6                                               | 526 ± 72                                                  |

| Location No. | Sampling site        | Average±SD** | Median | Minimum | Maximum | Range (max-min) | Skewness | Kurtosis |
|--------------|----------------------|---------------|---------|----------|----------|----------------|----------|----------|
| 1            | Petrovec             | 34.0 ± 6.1 | 35.2 | 24.1 | 41.9 | 17.8 | -0.27 | -1.17 |
| 2            | Belimbegovo          | 44.7 ± 4.6 | 42.4 | 38.5 | 52.2 | 13.5 | 0.42 | 1.17 |
| 3            | Aračinovo            | 608 ± 66 | 623 | 502 | 707 | 205 | -0.07 | -1.05 |

*Average values of 6 measurements ± SD

**SD – standard deviation

Nevertheless, when comparing our results with the published values for the surrounding countries on the Balkan Peninsula, one may conclude that they are more or less similar. Thus, the published data for Serbia ranged between 26.77 ± 1.4 Bq kg\(^{-1}\) and 38 ± 2.3 Bq kg\(^{-1}\) for \(^{226}\)Ra, 2.97 ± 9.4 Bq kg\(^{-1}\) and 53 ± 8 Bq kg\(^{-1}\) for \(^{232}\)Th, and 457 ± 192 Bq kg\(^{-1}\) and 554 ± 92 Bq kg\(^{-1}\) for \(^{40}\)K [28–31]. The data reported for Bulgaria are similar for \(^{226}\)Ra and \(^{232}\)Th (45 and 30 Bq kg\(^{-1}\)), but are lower for \(^{40}\)K (400 Bq kg\(^{-1}\)) [4]. The available data for Greece revealed significantly lower levels of activity concentrations, being 25 Bq kg\(^{-1}\), 21 Bq kg\(^{-1}\) and 360 Bq kg\(^{-1}\) for \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K, respectively [4]. The same conclusion is true for the natural radioactivity in soils from Albania; the concentrations determined were 19 ± 5 Bq kg\(^{-1}\) for \(^{226}\)Ra, 20 ± 5 Bq kg\(^{-1}\) for \(^{232}\)Th and 297 ± 5 Bq kg\(^{-1}\) for \(^{40}\)K [32]. As reported, the activity concentration results for Croatia were higher for \(^{226}\)Ra and \(^{232}\)Th (73.3 ± 15.8 Bq kg\(^{-1}\) and 61.8 ± 13.4 Bq kg\(^{-1}\), respectively), but were close for \(^{40}\)K (645 Bq kg\(^{-1}\) and 61.4 Bq kg\(^{-1}\)) [33]. According to the UNSCEAR data base [4], the levels of \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K in Romania were 32, 38 and 490 Bq kg\(^{-1}\), respectively, being very close to our results for \(^{226}\)Ra and \(^{232}\)Th, but lower for \(^{40}\)K. In comparison to the previously published average data for the Kavadarc region from Macedonia (35.5, 39.2 and 516 Bq kg\(^{-1}\) for \(^{226}\)Ra, \(^{232}\)Th and \(^{40}\)K, respectively) [21, 22], the results from this study seem to be quite similar.

The latest UNSCEAR data for the worldwide natural radionuclides concentrations in soil samples [27], as well as some data published from other authors [9, 15, 16, 34–40] are presented in Table 2.
Table 2
Comparison of natural radioactivity levels in soil and air-absorbed doses at different world locations and our study

| Country (Region) [Ref.] | Activity concentrations range (Bq kg⁻¹) | Absorbed dose rate (nGy h⁻¹) |
|------------------------|----------------------------------------|-----------------------------|
|                        | ²²⁶Ra                                  | ²³²Th                       | ⁴⁰K                        |
| Indonesia [27]         | 2.4–422                                | 0.5–66                      | 48–252                     | 33–224 (97)* |
| Islamic Republic of Iran (Ram-sar) [27] | 80–50 000                        | 15–47                      | 300–945                    | 80–100 000 (765)* |
| Islamic Republic of Iran (Mashallat) [27] | 500–7300                          | 15–41                      | 364–873                    | 300–3800     |
| Azerbaijan [27]        | 500–2500                               | 100–1000                    | 800–1000                   | 877–8770     |
| Indonesia (Bankog Island) [27] | –                                  | –                          | –                          | 90–540 (330)* |
| Indonesia (Karim Island) [27] | –                                  | –                          | –                          | 200–410 (310)* |
| Phillipines [27]       | –                                      | –                          | –                          | 75–1558 (300)* |
| Russian Federation [27] | 100–150                              | 10–160                      | –                          | up to 300    |
| Spain [27]             | 60–250                                 | 42–71                       | 810–1240                   | 136–260      |
| Switzerland [27]       | –                                      | –                          | –                          | 100–200      |
| Saudi Arabia [34]      | 17–28 (23)*                            | 1.1–81 (20)*                | 218–255 (233)*             | 17–72 (33)*  |
| Palestine (Tulkarem) [16] | –                                  | 5.3–44.8 (23.8)*           | 10.2–404 (120)*            | 11.5–82.7 (35.5)* |
| Oman (Musandam) [35]   | 5–26 (14)*                             | 1–20 (10)*                  | 10–283 (158)               | 4–35 (19)*   |
| Egypt (Dakahlia) [9]   | 5.7–140 (43)*                          | 9–139 (54)*                 | 22–319 (183.8)             | 51–166 (62)* |
| Iran (Teheran) [36]    | 30.5–45.4 (38.8)*                      | 27.3–57.1 (43.4)*           | 328.0–768.5                | 48.1–88.7    |
| Pakistan (Sind) [37]   | 18–47                                  | 24–69                       | 254–769                    | 33–87        |
| Kenya (Mount Homa) [38] | 17–1447 (195)*                        | 23–1369 (409)*              | 64–3017 (915)*             | 154.8–2280.6 |
| Thailand (Hat Yai) [15] | 25.73–156.06                         | 6.77–91.28                  | 62.40–949.44               | 35.36–160.19 (68.4)* |
| (67.66)*               |                                         |                             |                            |              |
| Turkey (Anatolia) [39] | 27–100 (27.2)*                        | 255–1273 (524)*             | 21.8–81.3 (47.0)*          |              |
| Turkey (Marmara region) [40] | 4.2–86.95 (22.45)*       | 4.6–88.85                   | 69.2–1085.6                | 54.86        |
| (26.63)*               |                                         |                             |                            |              |
| Belgrade (Serbia) [31] | 33.6*                                  | 39.3*                       | 508*                       | 60.5*        |
| Egypt (Mueilha area) [26] | 121.28*                             | 82.19*                      | 839.97*                    | 34.12*       |
| Present study          | 24.1–41.9 (34.1)*                      | 38.5–52.2 (44.9)*           | 502–707                    | 55.5–79.1 (68.5)* |
|                        | (614)*                                 |                             |                            |              |

*Average values

3.2. Estimation of radiological effects

The air-absorbed dose rates, calculated from the activity concentrations data for ²²⁶Ra, ²³²Th and ⁴⁰K (Table 1), applying the corresponsive equation (Eq. 2), are presented in Table 2. The ranges calculated varied between 11.1 nGy h⁻¹ and 19.4 nGy h⁻¹, 23.3 nGy h⁻¹ and 30.1 nGy h⁻¹, and 55.5 nGy h⁻¹ and 79.1 nGy h⁻¹, for ²²⁶Ra, ²³²Th and ⁴⁰K, respectively. The calculated average air-absorbed dose was 68.5±8.1 nGy h⁻¹, being higher than the world average value for terrestrial radiation, which is estimated at 60 nGy h⁻¹ [4]. The average estimated absorbed dose within this study was compared with the worldwide published data (Table 2). However, this value remains under 1000 μSv y⁻¹, which is the recommended maximal dose criterion by ICRP [25].

On the basis of equations 1 and 3–6, the values for radium equivalent activity, external hazard index, annual effective dose, annual gonadal dose and excess lifetime cancer risk for the different sampling locations in the Skopje city region were calculated. As can be seen from the presented data (Table 4), the radium equivalent activity values for the soil samples varied from 114 Bq kg⁻¹ in Čučer-Sandevo to 163 Bq kg⁻¹ in Bardoci, with an average value of 143 ± 16 Bq kg⁻¹. These values are lower than 370 Bq kg⁻¹ which is considered as the safe radium equivalent level for the population [11]. The variation of the Raeq values is attributed to the mineralogical alteration processes affecting the studied soils [26], and additional contamination with naturally occurring radionuclides from soil fertilizers [41].
**Table 3**

Air-absorbed dose rates for **226**Ra, **232**Th and **40**K at various locations in the Skopje city region

| Location No. | Sampling site     | **226**Ra (nGy h⁻¹) | **232**Th (nGy h⁻¹) | **40**K (nGy h⁻¹) | Total (nGy h⁻¹) |
|--------------|-------------------|----------------------|---------------------|-------------------|-----------------|
| 1            | Petrovec          | 15.9                 | 25.6                | 24.5              | 66.0            |
| 2            | Belimbegovo       | 15.0                 | 25.6                | 23.9              | 64.5            |
| 3            | Aračinovo         | 19.0                 | 29.0                | 28.2              | 76.3            |
| 4            | Radišani          | 14.5                 | 31.1                | 26.0              | 71.6            |
| 5            | Čučer-Sandevo     | 11.1                 | 23.3                | 20.9              | 55.3            |
| 6            | Vizbegovo         | 18.8                 | 29.9                | 29.4              | 78.2            |
| 7            | Bardovci          | 19.4                 | 30.1                | 29.5              | 79.0            |
| 8            | Saraj             | 16.7                 | 24.7                | 26.2              | 67.6            |
| 9            | Nerezi            | 16.9                 | 31.5                | 26.0              | 74.3            |
| 10           | Lisiče            | 12.1                 | 24.6                | 22.0              | 58.7            |
| 11           | Drachevo          | 11.9                 | 24.1                | 22.9              | 58.9            |
| 12           | Pintija           | 18.9                 | 27.8                | 27.4              | 74.0            |
| 13           | Batinci           | 16.6                 | 25.6                | 26.3              | 68.5            |
| 14           | Volkovo           | 13.5                 | 25.3                | 21.9              | 60.8            |

*Average value from all sampling sites ± standard deviation

**Table 4**

Radium equivalent (**Ra_eq**), external hazard index (**H_eks**), annual effective dose (**D_{A,eff}**), annual gonadal dose equivalent (**AGDE**), and excess lifetime cancer risk (**ELCR**)

| Location | Sampling site     | **Ra_eq** (Bq kg⁻¹) | **H_eks** | **D_{A,eff}** (μSv) | **AGDE** (μSv y⁻¹) | **ELCR** × 10⁻³ |
|----------|-------------------|---------------------|-----------|---------------------|--------------------|-----------------|
| 1        | Petrovec          | 136                 | 0.38      | 80.9                | 468                | 0.31            |
| 2        | Belimbegovo       | 133                 | 0.37      | 79.1                | 458                | 0.31            |
| 3        | Aračinovo         | 157                 | 0.44      | 93.6                | 541                | 0.36            |
| 4        | Radišani          | 149                 | 0.41      | 87.7                | 508                | 0.34            |
| 5        | Čučer-Sandevo     | 114                 | 0.32      | 67.8                | 393                | 0.26            |
| 6        | Vizbegovo         | 161                 | 0.45      | 95.9                | 554                | 0.37            |
| 7        | Bardovci          | 163                 | 0.45      | 96.8                | 560                | 0.37            |
| 8        | Saraj             | 139                 | 0.39      | 82.9                | 480                | 0.32            |
| 9        | Nerezi            | 155                 | 0.43      | 91.1                | 526                | 0.35            |
| 10       | Lisiče            | 125                 | 0.34      | 72.0                | 490                | 0.33            |
| 11       | Drachevo          | 125                 | 0.33      | 72.2                | 419                | 0.28            |
| 12       | Pintija           | 157                 | 0.43      | 90.7                | 524                | 0.35            |
| 13       | Batinci           | 141                 | 0.39      | 84.0                | 486                | 0.32            |
| 14       | Volkovo           | 126                 | 0.35      | 74.6                | 431                | 0.29            |

*Average value from all sampling sites ± standard deviation

*Average value from all sampling sites
The ultimate purpose of the radionuclides measurement in the soil samples is to assess the radiation dose delivered externally to the population in the form of gamma dose. The calculated values for the radiation risk index ($H_{eq}$) for the soil samples analyzed within this study were within the range from 0.33 to 0.45, with an average of 0.39 ± 0.05 (Table 4). Since all these calculated values are lower than unity, as desired, they may be considered as safe for exploitation as agricultural soils.

The average annual effective dose was found to be 83.5 ± 9.5 µSv, using the respective conversion factor (0.7 Sv Gy⁻¹) and the outdoor occupancy factor of 0.2 [40]. The lowest annual effective dose was calculated for Lisiče (72.0 µSv) and the highest at the location of Bardovci (96.8 µSv) (Table 4). The calculated average effective dose was higher than the world average (70 µSv) [4]. Accordingly, the effective dose average within this study was higher than the values revealed from most of the investigations conducted in Turkey (49 µSv, 54.86 µSv and 57.7 µSv) [39, 40] and Egypt (76 µSv) [9]. However, the calculated annual effective dose was lower than the values obtained for India (105.9 µS) [11] and Iran (193.15 µSv) [36]. The annual effective dose that we determined for the Skopje city region (Republic of Macedonia) was very close to the one previously determined for the city of Kavadarci (Republic of Macedonia), estimated at 82 ± 26 µSv [21, 22].

The annual gonadal dose equivalent (AGDE, µSv y⁻¹) due to the specific activities of $^{226}$Ra, $^{233}$Ra and $^{40}$K, calculated applying Eq. (5), varied within the values from 419 (location Dračevo) to 560 µSv y⁻¹ (location Bardovci), with an average value of (493 ± 50) µSv y⁻¹ (Table 4). The calculated AGDE was lower than the recommended ICRP equivalent limit of 1000 µSv y⁻¹ for the general public [25]. However, the average value obtained was higher than the reported values for agricultural soils in Egypt (76 µSv y⁻¹) [9] and Palestine (230 µSv y⁻¹) [16].

Excess lifetime cancer risks (ELCR), calculated by Eq (6) revealed range values from 0.26–0.36 × 10⁻³. The calculated average value is 0.33 ± 0.03 × 10⁻³, which is somewhat higher than the word average estimated at 0.29 × 10⁻³ [4], but still, the indices for cancer risk are negligible. The lowest ELCR value (0.26 × 10⁻³) was estimated for the location Ćučer-Sandevo, while the highest values were for Vizbegov and Bardovci (0.37 × 10⁻³). As a comparison, some worldwide estimated ELCR values were 0.59 × 10⁻³ for South Eastern Desert, Egypt [26], 0.29 × 10⁻³ for Dakahlia province, Egypt [9], 0.28 × 10⁻³ for Vojvodina province in Serbia [31], and 0.95 × 10⁻³ found for Palestine [16].

3.3. Pearson’s correlation analysis

The statistical analysis of the Pearson correlation coefficient was performed between the activity concentrations of the three radioisotopes of interest in this study, and the radiological variables arising from them (Table 5).

| Variables | $^{226}$Ra | $^{232}$Th | $^{40}$K | AGDR | $R_{eq}$ | $H_{eq}$ | $D_{A,eft}$ | AGDE | ELCR × 10⁻³ |
|-----------|------------|------------|---------|------|---------|---------|------------|------|-------------|
| $^{226}$Ra | 1.000      |            |         |      |         |         |            |      |             |
| $^{232}$Th | 0.659      | 1.000      |         |      |         |         |            |      |             |
| $^{40}$K  | 0.545      | 0.543      | 1.000   |      |         |         |            |      |             |
| AGDR      | 0.939      | 0.866      | 0.569   | 1.000|         |         |            |      |             |
| $R_{eq}$  | 0.927      | 0.873      | 0.558   | 0.994| 1.000   |         |            |      |             |
| $H_{eq}$  | 0.942      | 0.866      | 0.558   | 0.997| 0.992   | 1.000   |            |      |             |
| $D_{A,eft}$ | 0.939     | 0.866      | 0.569   | 1.000| 0.994   | 0.997   | 1.000      |      |             |
| AGDE      | 0.860      | 0.829      | 0.600   | 0.933| 0.945   | 0.938   | 0.933      | 1.000|             |
| ELCR × 10⁻³ | 0.845     | 0.830      | 0.583   | 0.922| 0.937   | 0.928   | 0.923      | 0.997| 1.000       |

The correlation between $^{226}$Ra and $^{232}$Th displayed a good positive value ($r = 0.659$), because $^{226}$Ra as a product of the $^{238}$U decay and $^{232}$Th decay chains, are associated together in nature [26]. A weak correlation noted between $^{40}$K and $^{232}$Ra, and $^{40}$K and $^{232}$Th, with a small positive Pearson’s coefficient (0.545 and 0.543, respectively), is due to the fact that $^{40}$K does not belong to the $^{238}$U and $^{232}$Th chains [26]. The activity concentrations of $^{226}$Ra and $^{232}$Th had a high positive correlation with the radiological variables ($r ≥ 0.829$), but a weak correlation between $^{40}$K and the respective varia-
bles ($r \leq 0.6$). Accordingly, the activity concentrations of $^{238}$U and $^{232}$Th were significantly related and mainly responsible for the radiological risks.

4. CONCLUSION

Gamma ray spectrometry was used to determine the activity concentration due to the naturally occurring $^{226}$Ra, $^{232}$Th and $^{40}$K radioisotopes and the associated radiation hazard levels in 14 soil samples from the surroundings of Skopje City (North Macedonia). The estimated average concentrations for $^{226}$Ra, $^{232}$Th and $^{40}$K were $34.0 \pm 6.1$ Bq kg$^{-1}$, $44.7 \pm 4.6$ Bq kg$^{-1}$ and $608 \pm 66$ Bq kg$^{-1}$, respectively. The average $^{226}$Ra value was practically equal to the worldwide average, while the activities for $^{232}$Th and $^{40}$K were higher than the reported average world values. Similarly, the respective average dose rates and other calculated hazard indices were higher than the average world values, however, they did not pose health risks to the population of the area studied. The total annual effective dose was lower than the value of 1000 $\mu$Sv y$^{-1}$, the dose limit recommended by the ICRP for radiation exposure of the public. This study also revealed that the risk of cancer is negligible in the region under investigation. The results for activity concentrations and the associated radiological risks obtained within this study are comparable with other studies carried out in the regionally close countries. The activity concentrations for $^{238}$U and $^{232}$Th were significantly related and may be considered as the main contributors to the radiological risks. In conclusion, the results from this study are significant for the assessment of naturally occuring radioactivity and the possible radiological risks coming out from the agricultural soils in the Skopje city surroundings. Additionally, the obtained results provide the necessary baseline information on radiation levels in any environment for the implementation of precautionary measures whenever the findings reveal doses above the expected one.

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