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Radioactivity of fertilizers used in Serbia and dose assessments for workers in the industry

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Abstract
Fertilizers contain a certain level of radioactivity and thus can affect the exposure of workers to radiation during production. The activity concentrations of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K were determined using the gamma spectrometry method for 36 samples of chemical fertilizers used in Serbia. Average values of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K are 213 ± 37 Bq kg^{-1}, 51 ± 10 Bq kg^{-1}, 12 ± 2 Bq kg^{-1}, 3671 ± 436 Bq kg^{-1}, respectively. The values of radium equivalent index (Ra_{eq}), absorbed gamma dose rate (D_R), annual effective dose (*AED*) and excess lifetime cancer risk (*ELCR*), alpha dose equivalents for radon exposures (H_E), and radon mass exhalation rates (E_M) were estimated. The obtained values were compared with the results of similar research.

Keywords Fertilizers · Radioactivity · Gamma spectrometry · Worker exposures · Radon · Doses

Introduction

In the light of enhancing crop yield in agriculture, the use of different types of fertilizers has become ubiquitous since it is mandatory to provide the natural nutrients for plants depleted from the soil due to over-cultivation of crops, weathering, and erosion of land–[1, 2]. In Serbia, fertilizer industries achieve production of about 165,000 tones of phosphoric acid and 600,000 tones of fertilizers, and some are imported from other countries. It was estimated that in 2009, the consumption of fertilizers in Serbia was 946,451 tones, while an amount of 224.3 kg ha^{-1} was used for arable lands and 286.9 kg ha^{-1} for fields and gardens [3].

Phosphate rocks, together with potassium ores and nitrogenous compounds, are the main raw materials used for fertilizers in industrial production since phosphorus, potassium and nitrogen are essential elements for plants growth [1, 4].

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The mineralogical composition of phosphate ore is dominated by fluor-apatite [$Ca_5(PO_4)_3F$], goethite, and quartz, with minor amounts of Al-phosphates, anatase, magnetite, monazite, and barite [5, 6]. The typical phosphate (P_2O_5) concentration of the rock is of the order of 15–30% [6]. Phosphoric acid is produced by the reaction of the mineral fluor-apatite and sulfuric acid in the presence of water. On that occasion, a large amount of waste phosphogypsum is created [6, 7]. About 70%, 86%, and 20% of the total activity concentration of ^{238}U, ^{232}Th, and ^{226}Ra from fluor-apatite is distributed in phosphoric acid, respectively [6]. Sedimentary origin phosphate rocks may contain elevated concentrations of ^{238}U and ^{232}Th and its decay products, while during the production of phosphate fertilizers most of them remain in the final fertilizer product, making fertilizers a potential source of radioactivity [1, 4, 8, 9]. Uranium content in fertilizers depends on phosphate content in fertilizers and several studies show a direct relationship between uranium and P_2O_5 [10, 11].

The risk from the use of fertilizers in the agricultural industry comes in two parts. The first one is the use of fertilizers in the agricultural soil, where radionuclides from fertilizers may migrate to soil and finally to human beings through ingestion of plants grown on fertilized land, representing a potential risk due to increased internal exposure to emitted gamma rays [1]. Another path, related to the workers in the fertilizer industry and resulting in external exposure, occurs during handling, packing, and transporting fertilizers. An additional source of exposure for workers is the inhalation of radon, a radioactive gas produced in the alpha decay of ^{226}Ra, recognized as the second leading cause of lung cancer [9, 12]. Stored phosphate fertilizers are a potential source of radon, which requires that warehouses have adequate ventilation [13, 14]. The measured concentration of radon activity in the Pakistani and Nigerian warehouses is about 90 Bq m^{-3} [9, 15], while in the Greek warehouse it is up to 3300 Bq m^{-3} [14], which can lead to an increased risk from the occurrence of cancer during the worker's life. For these reasons, it is important to perform natural radioactivity measurements of fertilizers, as well as to estimate the potential radiological risks. Furthermore, these measurements should be an integral part of environmental monitoring providing at the same time data on natural radiation which are important for designing rules and regulations for radiation protection purposes [10, 13, 15].

Legislation in Serbia [16] imposes permissible levels of ^{238}U, ^{226}Ra, and ^{40}K for all fertilizers imported into Serbia. The permissible level of ^{238}U is 1600 Bq kg^{-1} for mineral fertilizers containing macroelement phosphorous, and 3200 Bq kg^{-1} of ^{238}U for components used in the production of fertilizers. Permissible levels of ^{226}Ra, and ^{40}K is 1000 and 27,000 Bq kg^{-1}, respectively for mineral fertilizers containing macroelement phosphorous and for components used in the production of fertilizers [16]. The activity concentration of ^{232}Th is not limited to the legislation in Serbia [16].

This study aimed to determine the radioactivity levels in 36 samples of fertilizers and to estimate radiological risk for workers in the fertilizer industry from the aspect of exposure to gamma radiation and radon. The results were discussed and compared with the results from similar studies worldwide.

Materials and methods

Gamma spectrometry measurements of radioactivity

In order to measure radioactivity of 36 samples of fertilizers, imported or produced in Serbia, were selected, so it can be said that the analyzed samples well represent artificial fertilizers used by farmers in Serbia. The samples produced in Serbia were taken from the largest producer of fertilizers.

Before measurements, samples were homogenized and dried at the temperature of 105 ºC for 6–8 h to minimize the moisture content in the samples. After preparation, samples were packed in cylindrical containers (dimensions of 6.7 cm in diameter and 6.2 cm in height). Sample containers are warmed with wax to prevent the release of radon. The typical mass of the sample was 250 g. All samples were sealed and left for a minimum of 30 days in order to achieve secular radioactive equilibrium between ^{226}Ra and its progenies.

Samples were prepared and analyzed using the IAEA TRS 295 method [17]. Samples were measured with the standard gamma spectrometry method using low-level high purity germanium (HPGe) detector, model GMX-20,190 (relative efficiency of 33.5% and energy resolution of 1.92 keV for gamma line of ^{60}Co at 1332 keV), with passive lead shielding thickness of 12 cm. The front window of the detector is made of beryllium glass thickness of 0.5 mm, suited for the detection of low-energy gamma photons. The detector was in the Laboratory for Radioactivity and Dose Measurements, located on the ground floor of the Department of Physics, Faculty of Sciences, University of Novi Sad. The laboratory is accredited for gamma spectrometric measurements by the Accreditation Body of Serbia.

The radon activity concentration in the Laboratory is low (average value is 30(5) Bq m^{-3}), provided together with a passive shielding condition in which the background of the HPGe detector is significantly reduced. The acquisition and analysis of spectra were done using Canberra Genie 2000 software. The typical measurement time was 72,000 s.

The calibration of the used HPGe detector was performed using a cylindrical reference radioactive standard embedded in silicone resin, volume 250 cm^3 produced by the Czech Metrological Institute (Cert. No. 1035-SE-40001-17). Correction of the effect of self-absorption due to the different matrix densities of the analyzed material was performed using the ANGLE software [18], while correction due to the true coincidence summing effect was performed using EFFTRAN software. This precise calibration is required to ensure the small measurement uncertainty $<$ 10% necessary when radioisotope activity is determined in the low-energy region (below 100 keV) (e.g. for ^{234}Th, progeny ^{238}U) [19].

Radionuclides of interest, in this case, were naturally occurring radionuclides: ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K. The activity concentration of these radionuclides was measured based on gamma lines listed in Table 1 [20]. The interference of the ^{232}Th gamma line (at 63.8 keV, quantum probability of 0.259(15)%) with the gamma line of ^{234}Th (Table 2) was taken into account to avoid overestimation of ^{238}U activity concentration.

Typical minimum detectable activities (MDA) determined using the equation given in ref. [7] for ^{238}U, ^{226}Ra, ^{232}Ra and ^{40}K were: 1.1 Bq kg^{-1}, 0.3 Bq kg^{-1}, 0.4 Bq kg^{-1} and 4.2 Bq kg^{-1}, respectively.

Assessment of radiological risk for workers

The radiological risk for workers was assessed in terms of two separate sources; one from exposure to gamma radiation originating from the presence of radionuclides in fertilizers

Table 1 List of samples, country of origin, and activity concentration of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K in fertilizers used in Serbia

Sample No.	Sample name	Country of origin	Activity concentration (Bq kg^{-1})			
			^{238}U	^{226}Ra	^{232}Th	^{40}K
1	EURONATURE P 26 B	Austria	162 ± 23	218 ± 10	21 ± 2	40 ± 4
2	EUROFERTIL TOP 34 NPK	Austria	280 ± 30	77 ± 8	23 ± 3	2610 ± 220
3	EUROFERTIL TOP 51 NPK	Austria	420 ± 41	111 ± 9	9.2 ± 0.7	4050 ± 300
4	EUROFERTIL TOP 51 NPK	Austria	78 ± 7	69 ± 6	6.2 ± 0.6	5760 ± 400
5	EUROFERTIL TOP 34 NPK	Austria	86 ± 9	81 ± 7	12 ± 2	2540 ± 110
6	EUROFERTIL PLUS 37 HORTI	Austria	35 ± 4	20 ± 2	7.6 ± 0.7	4170 ± 220
7	DUOFERTIL NPK 46	Austria	233 ± 30	85 ± 6	27 ± 2	6800 ± 400
8	DUOFERTIL NPK 46	Austria	139 ± 20	50 ± 5	12 ± 2	5480 ± 400
9	EURONATURE P 26 B	Austria	184 ± 25	205 ± 8	21 ± 2	143 ± 20
10	EUROFERTIL PLUS 37 HORTI	Austria	34 ± 4	29 ± 3	14 ± 2	5340 ± 300
11	DUOFERTIL 30 PK	Austria	446 ± 27	268 ± 15	9.3 ± 0.8	4710 ± 260
12	EUROFERTIL TOP 35 NP	Austria	95 ± 8	72 ± 6	20 ± 2	338 ± 17
13	YARA TERA KRISTA MKP	China	90 ± 8	10 ± 1	22 ± 2	10,500 ± 500
14	NP 20:20	Croatia	670 ± 40	80 ± 6	16 ± 2	117 ± 18
15	NPK 15:15:15	Croatia	470 ± 30	93 ± 8	42 ± 4	4740 ± 300
16	YARA MILA COMPLEX 12:11:18 S + MGO + TE(SOP)	Finland	160 ± 18	220 ± 8	9.2 ± 0.7	5830 ± 190
17	YARA MILA 16:27:7	Finland	30 ± 2	15 ± 2	8 ± 2	2100 ± 120
18	YARAMILA ACTYVA 18-11-13	Finland	110 ± 12	10 ± 1	9.2 ± 0.8	4320 ± 290
19	YARA MILA CROPCARE 11-11-21	Finland	35 ± 3	7.2 ± 0.5	2.2 ± 0.3	5920 ± 320
20	ACTISTART	France	990 ± 85	44 ± 5	16 ± 2	1640 ± 100
21	ACTISTART	France	13 ± 2	9 ± 2	20 ± 2	1360 ± 40
22	ACTISTART	France	920 ± 40	30 ± 1	2.9 ± 0.3	1710 ± 30
23	KAN	Hungary	4.7 ± 0.5	8.0 ± 0.4	7.4 ± 0.6	98 ± 5
24	EUROFERTIL 67 NPK N-PROCESS	Italy	203 ± 25	18 ± 2	12 ± 2	3450 ± 180
25	EUROFERTIL 67 NPK N-PROCESS	Italy	135 ± 15	10 ± 2	5.2 ± 0.4	4000 ± 250
26	FERTICARE 14-11-25 KOMBI	Netherlands	320 ± 35	55 ± 6	3.2 ± 0.3	7420 ± 220
27	FERTICARE 14-11-25 KOMBI I	Netherlands	50 ± 5	6.2 ± 0.6	5.2 ± 0.4	6840 ± 300
28	YARA MILA COMPLEX 12 11 18 S + MGO + TE	Norway	42 ± 5	106 ± 8	35 ± 3	5270 ± 260
29	NPK 15:15:15	Russia	6 ± 3	1.70 ± 0.20	7.6 ± 0.8	3550 ± 150
30	NPK 16:16:16	Serbia	530 ± 40	13 ± 2	8.2 ± 0.7	5000 ± 300
31	NPK 7:20:30	Serbia	500 ± 40	11 ± 2	7.4 ± 0.6	8800 ± 300
32	NPK 12:11:18	Serbia	269 ± 20	22 ± 2	3.4 ± 0.4	4900 ± 180
33	KAN	Serbia	4.7 ± 0.5	8.0 ± 0.4	0.70 ± 0.10	98 ± 5
34	KSC III PHYTACTYL 15:5:35 + ME	Spain	560 ± 52	38 ± 4	6.2 ± 0.5	9600 ± 600
35	KSC PHYTACTYL V	Spain	250 ± 20	23 ± 3	52 ± 5	11,000 ± 300
36	NPK 14:14:17	Taiwan	395 ± 15	3.1 ± 0.4	7.2 ± 0.5	3950 ± 170
Range			**4.7–990**	**1.7–268**	**0.7–52**	**40-11000**
Average ± SD			**213 ± 37**	**51 ± 10**	**12 ± 2**	**3671 ± 436**
Permissible value			**1600[a]**	**1000[a]**	**–**	**27,000[a]**

[a]given in ref. [16]; SD = standard deviation

(^{226}Ra, ^{232}Th, and ^{40}K) and the other one from exposure to radon. In both cases, annual effective doses are calculated for workers in the fertilizers industry, having in mind they are dominantly exposed to radiation.

The risk from exposure to gamma radiation was estimated through several quantities:

(1) Radium equivalent index, representing the total exposure to radiation from naturally occurring radionuclides and defined as [21]:

$$Ra_{eq} = C_{Ra} + 1.43 \cdot C_{Th} + 0.077 \cdot C_K \left(\mathrm{Bqkg}^{-1}\right) \quad (1)$$

Table 2 List of naturally occurring radionuclides analyzed in fertilizer samples by gamma spectrometry method, together with its progenies and used gamma lines (with quantum probabilities)

Radionuclide	Progenies	Gamma line (keV)	Quantum probability (%)
^{238}U	^{234}Th	63.3(2)	3.75(8)
	^{234m}Pa	1 001.026(18)	0.847(8)
^{232}Th	^{228}Ac	911.196(6)	26.2(8)
	^{224}Ra	685.48(15)	94.73(5)
	^{212}Pb	238.632(2)	43.6(5)
	^{212}Bi	727.330(9)	6.65(4)
^{226}Ra	^{214}Pb	351.932(2)	35.60(7)
	^{214}Bi	609.312(7)	45.49(19)
^{40}K	–	1 460.822(6)	10.55 (11)

where C_{Ra}, C_{Th}, C_K are activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K, respectively, in Bq kg^{-1}. The maximal permissible Ra_{eq} is 370 Bq kg^{-1} [22].

(2) Absorbed gamma dose rate (D_R), representing a dose rate in the air at 1 m above the ground surface for the uniform distribution of naturally occurring radioactive nuclides, calculated as [23, 24]:

$$D_R = 0.462 \cdot C_{Ra} + 0.604 \cdot C_{Th} + 0.0417 \cdot C_K \left(\mathrm{nGyh^{-1}}\right) \quad (2)$$

The average value of the absorbed gamma dose rate in the world is 59 nGy h^{-1} [23].

(3) Annual effective dose (*AED*), estimated for workers in the fertilizer industry and calculated as [24]:

$$AED = D_R \cdot T \cdot CF \cdot 10^{-6}\left(\mathrm{mSvy^{-1}}\right)) \quad (3)$$

where *T* is the exposure time for workers in the fertilizer industry (assuming 1600 working hours in a year) and *CF* is the conversion factor with a value of 0.7 Sv Gy^{-1}. The recommended value of the annual effective dose, without taking into account radon exposure, is 1 mSv y^{-1} [16, 25].

(4) Excess lifetime cancer risk (*ELCR*) is a risk of a person developing cancer if exposed to carcinogen materials for a long time. It is calculated assuming that there is a linear relation between dose and the stochastic effects. UNSCEAR reported that the worldwide average limit value was 0.29×10^{-3} [23]. The ELCR factor can be estimated using the following Eq. (4) [24, 26]:

$$ELCR = AED \cdot DL \cdot RF \quad (4)$$

where *AED* is the annual effective dose, *DL* is the duration of life (70 years) and *RF* is a fatal cancer risk, this risk factor is appreciated by 0.05 Sv^{-1}.

The risk from exposure to radon was estimated through two following quantities:

(1) The criterion was established that an annual effective dose of 0.05 mSv corresponds to an indoor radon concentration of 1 Bq m^{-3} [27]. The recommended indoor concentration of radon activity is in the range of 100–300 Bq m^{-3} [12], which according to the previous criterion corresponds to a dose range of 5–15 mSv y^{-1}. Article 54 of the European Union directive from 2014 states that it is necessary to ensure radon exposure of less than 300 Bq m^{-3} at workplaces [25]. Effective alpha dose equivalent (H_E) in mSv y^{-1}, attributable to the presence of radon and its short-lived daughters of radon (^{222}Rn) in air and calculated as [19]:

$$H_E = 0.18 \cdot C_{Ra} \cdot \epsilon + 0.45\left(\mathrm{mSvy^{-1}}\right) \quad (5)$$

where ε is the radon emanation coefficient and C_{Ra} is radium activity concentration in Bq kg^{-1}.

(2) Radon mass exhalation rate (E_m), defined as [19]:

$$E_M = C_{Ra} \cdot \lambda \cdot \epsilon\left(\mathrm{Bqkg^{-1}h^{-1}}\right) \quad (6)$$

where C_{Ra} is the activity concentration of ^{226}Ra, λ is the radioactive decay constant of radon (7.6 10^{-3} h^{-1}) and ε is the radon emanation coefficient.

Results and discussion

The list of 36 analyzed samples of fertilizers used in Serbia with measured activity concentrations of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K is shown in Tabe 2. It can be seen that the highest percentage of analyzed phosphate fertilizers is compared to nitrogen fertilizers. The measured values of ^{238}U activity concentrations range from 4.7 ± 0.5 Bq kg^{-1} (sample No. 23 from Hungary) to 990 ± 85 Bq kg^{-1} (sample No. 20 from France). The measured values of activity concentrations of ^{226}Ra range from 1.70 ± 0.20 Bq kg^{-1} (sample No. 29 from Russia) to 268 ± 15 Bq kg^{-1} (sample No. 11 from Austria). The measured values of ^{232}Th activity concentrations range from 0.70 ± 0.10 Bq kg^{-1} (sample No. 33 from Serbia) to 52 ± 5 Bq kg^{-1} (sample No. 35 from Spain). The measured values of ^{40}K activity concentrations range from 40 ± 4 Bq kg^{-1} (sample No. 1 from Austria) to $11{,}000 \pm 300$ Bq kg^{-1} (sample No. 35 from Spain), Table 1. Average activity concentrations, measured in 36 analyzed fertilizer samples, are 213 ± 37 Bq kg^{-1}, 51 ± 10 Bq kg^{-1}, 12 ± 2 Bq kg^{-1}, and 3671 ± 436 Bq kg^{-1} for ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K respectively, (mean value ± standard deviation), Table 1. All measured activity concentration values are below the permitted values in Serbia of 1600 Bq kg^{-1}, 1000 Bg kg^{-1}, and 27,000 Bq kg^{-1} for ^{238}U, ^{226}Ra, and ^{40}K, respectively [16]. No significant correlations were observed between the measured values of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K activity concentrations. This may be a consequence of the uneven distribution of radionuclides in the technological procedures through the fertilizer passes during process production.

A comparison of the activity concentrations of the measured radionuclides with the values obtained for fertilizers in other countries is shown in Table 3. Most of the studies analyzed phosphate fertilizers. It can be observed that the measured values of radionuclide activity concentrations vary with country origin of fertilizers, which can be attributed to different initial radioactivity in the mineral fluor-apatite. It is also necessary to take into account the different technologies used in different countries, which may affect the different distribution of radionuclides in primary and secondary products in the production process. It can be seen that the measured values of ^{238}U, ^{226}Ra, and ^{232}Th activity concentrations are comparable to the results reported in other research. The measured ^{238}U values are comparable to the results reported in research [11, 28] for fertilizers from Finland and Greece, Table 3. The measured values of ^{226}Ra are comparable to the results reported in research [4, 11, 24, 26, 28–30] for fertilizers from Serbia, Iraq, Egypt, Saudi Arabia, Vietnam, Finland and Greece, Table 3. The measured concentrations of ^{232}Th activity are comparable to the results reported in research [2, 4, 11, 24, 26, 31, 32] for fertilizers from Iraq, Egypt, Saudi Arabia, India, Vietnam, USA, Pakistan and Greece, Table 3. The measured values of ^{40}K are higher than most of the results reported in previous studies, Table 3, and are comparable to the results given in the previous study [29].

The frequency distribution of analyzed radionuclides in fertilizers is shown in Fig. 1. Based on the frequency distribution, it is observed that the largest number of samples have the activity concentration of ^{238}U, ^{226}Ra, and ^{232}Th in the lowest ranges: 0–200 Bq kg^{-1}, 0–50 Bq kg^{-1} and 0–10 Bq kg^{-1}. The highest concentration of ^{40}K activity in samples is between 4000 and 6000 Bq kg^{-1}. The average abundance of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K in the samples is 5.4%, 1.3%, 0.3%, and 93%, respectively, given in Fig. 2.

Obtained values used to assess the risk

Obtained values used to assess the risk from gamma radiation: radium equivalent index (Ra_{eq}), absorbed gamma dose rate (D_R), annual effective dose (*AED*), and excess lifetime cancer risk (*ELCR*) for 36 samples of fertilizers are given in Fig. 3.

The radium equivalent index (Ra_{eq}) ranges from 16.5 ± 0.6 Bq kg^{-1} (sample No. 33 from Serbia) to 944 ± 24 Bq kg^{-1} (sample No. 35 from Spain). The average value of the radium equivalent index is 350 ± 34 Bq kg^{-1} (mean value ± standard deviation), which is below the recommended value of 370 Bq kg^{-1} [22]. In the individual consideration of the samples, it can be seen that this value is exceeded in 50% of the samples, Fig. 3a.

Table 3 Activity concentrations of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K reported in earlier research and in this work

Country	No. samples	Activity concentration (Bq kg^{-1})				References
		^{238}U	^{226}Ra	^{232}Th	^{40}K	
Serbia	33	31–2640 (35 ± 8)	4–452 (43 ± 11)	8–226 (42 ± 20)	43–40800 (569 ± 134)	[29]
Egypt	15	–	349–384 (366 ± 10.5)	59–81 (66.7 ± 7.3)	2.9–6.1 (4.0 ± 2.6)	[10]
Iraq	50	–	0.1–134	0.1–74	1–12000	[24]
Egypt	43	–	12–244	3–99	109–670	[4]
Saudi Arabia	20	–	51.5–106.3	5.1–9.9	472–661	[30]
India	5	2.03–396.3	–	4.7–39.3	32.9–92.8	[31]
Egypt	3	788–1063	302–554	29.4-193.9	737–979	[8]
Egypt	5	–	312–782	ND-67.2	88–251	[5]
Egypt	12	–	0.6–1312	<MDA-14.5	<MDA-5313	[33]
UAE	1	1.32	–	0.3	188.16	[1]
Greece	30	–	0–4584	–	4–5254	[14]
Vietnam	21	1.2–62.2	0.6–111.3	2.3–17.6	80-6390	[26]
Finland	10	< 55–610	1.5–110	–	3700–4100	[28]
USA	–	–	5.10–13.4 (7.45 ± 2.76)	0.5–8.6 (2.63 ± 0.29)	3024–4092 (3581 ± 601)	[32]
Pakistan	–	–	232–511 (386 ± 92)	21–58 (38 ± 14)	556–1302 (885 ± 220)	[2]
Greece	10	< 38–703	< 1–529	< 1–95	238–4483	[11]
Serbia	**42**	**4.7–990 (213 ± 37)**	**1.7–268 (51 ± 10)**	**0.7–52 (12 ± 2)**	**40-11000 (3671 ± 436)**	**Present study**

– range; (average ± standard deviation); *ND* none detected value, *MDA* minimum detectable activity

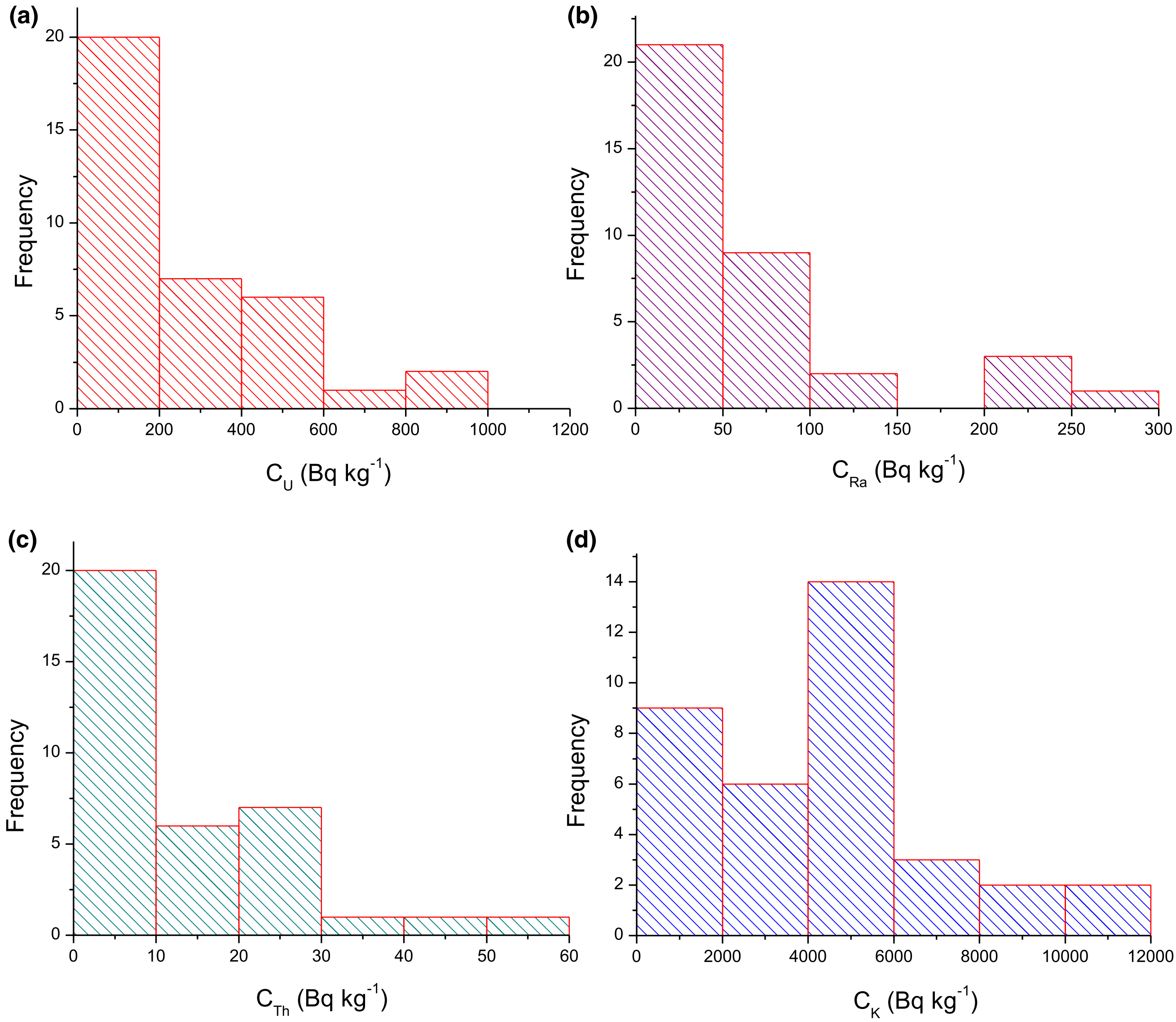

Fig. 1 Frequency distributions of ^{238}U-(a), ^{226}Ra-(b), ^{232}Th-(c) and ^{40}K-(d) activity concentrations in 36 fertilizer samples from Table 1

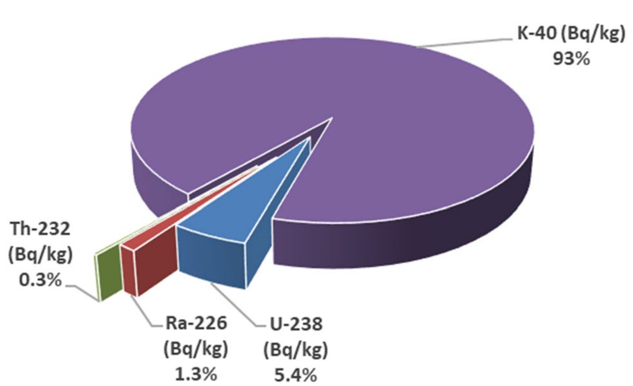

Fig. 2 Average abundance of ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K in 36 analyzed fertilizer samples from Table 1

Figure 4 shows the correlation between the radium equivalent index (Ra_{eq}) and the activity concentration of ^{40}K, where a strong correlation was observed ($R^2 = 0.90$). No significant correlations were observed between the radium equivalent index (Ra_{eq}) and other analyzed radionuclides.

The obtained absorbed gamma dose rate (D_R) values range from 8.2 ± 0.3 nGy h^{-1} (sample No. 33 from Serbia) to 501 ± 13 nGy h^{-1} (sample No. 35 from Spain). The average value of the absorbed gamma dose rate (D_R) for all analyzed samples is 184 ± 18 nGy h^{-1} (mean value ± standard deviation), which is about 3 times higher than the world average of 59 nGy h^{-1} [23]. In individual considerations, only 4 samples do not exceed this value, Fig. 3b.

Based on the obtained absorbed gamma dose rate (D_R) values, annual effective doses (AED) (Eq. 3) for external

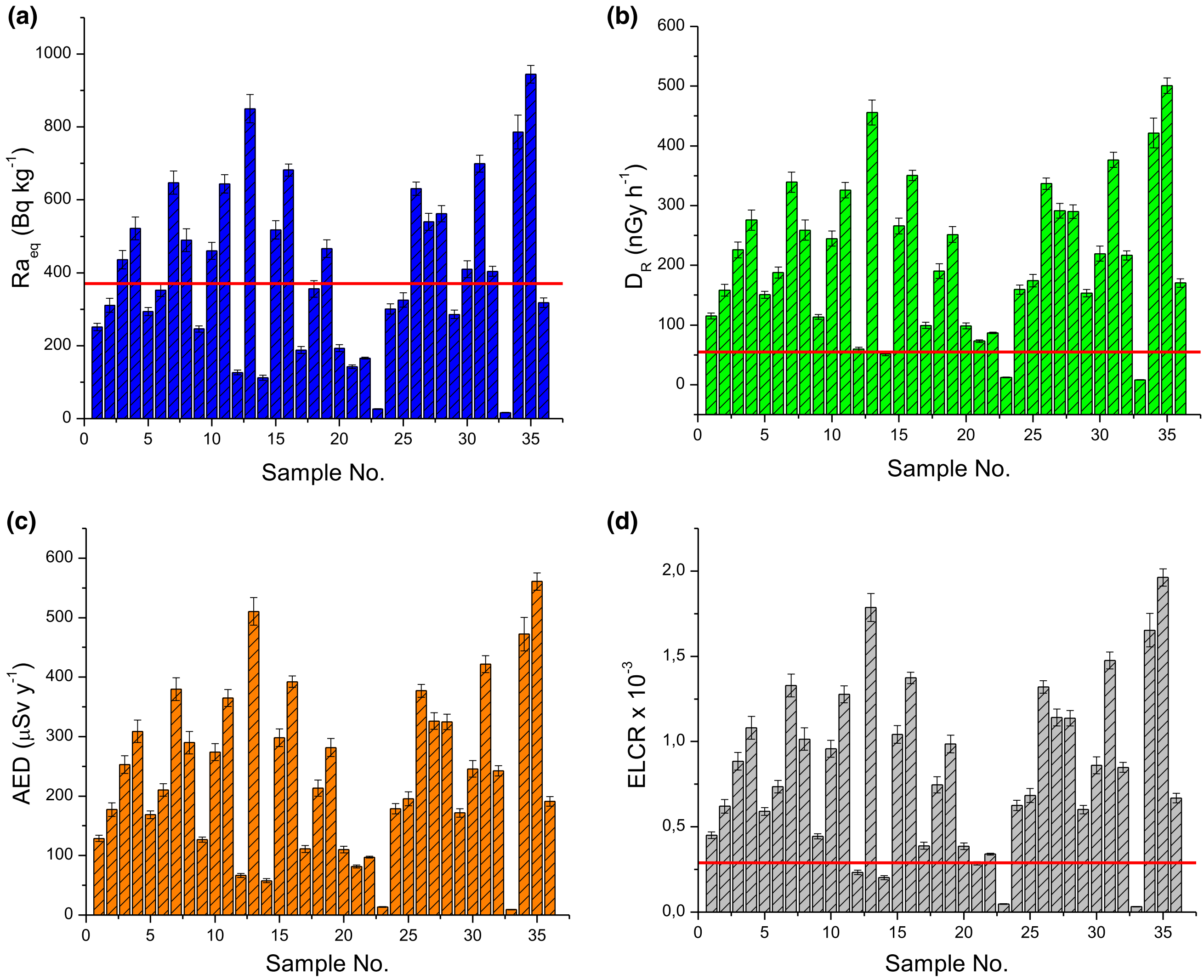

Fig. 3 Obtained values: **a** radium equivalent index (Ra_{eq}), **b** absorbed gamma dose rate (D_R), **c** annual effective dose (*AED*) and **d** excess lifetime cancer risk (*ELCR*) for 36 samples of fertilizers from Table 1. The red line indicates the mean or recommended values

exposure to gamma radiation of workers were estimated. It was assumed that a worker spends 1600 h a year in the production of fertilizers. The obtained values range from 9.2 ± 0.3 µSv y^{-1} (sample No. 33 from Serbia) to 561 ± 14 µSv y^{-1} (sample No. 35 from Spain). The average annual effective dose (*AED*) value for 36 analyzed fertilizer samples is 206 ± 20 µSv y^{-1} (mean value ± standard deviation). The average value, as well as all individual values of the annual effective dose (*AED*) for the samples, are below the recommended value of 1 mSv y^{-1} [16, 25], Fig. 3c. Based on the representation of radionuclides shown in Fig. 2, it can be stated that the biggest contribution to the annual effective dose is given by ^{40}K, which is the most represented radionuclide in fertilizers on average.

Based on the estimated annual effective dose (*AED*) values, the excess lifetime cancer risk (*ELCR*) was estimated using Eq. (4). The obtained values range from $(0.0322 \pm 0.0011)\times10^{-3}$ (sample No. 33 from Serbia) to $(1.96 \pm 0.05)\times10^{-3}$ (sample No. 35 from Spain). The mean value of excess lifetime cancer risk (*ELCR*) is $(0.72 \pm 0.07)\times10^{-3}$ (mean value ± standard deviation) and is 2.5 times higher than the average value in the world of 0.29×10^{-3} [23]. In individual considerations, only 4 samples do not exceed this value, Fig. 3d.

Furthermore, the potential exposure of workers to radon was assessed. Using Eq. (5 and 6) alpha dose equivalents (H_E) and radon mass exhalation rates (E_M) were determined for all analyzed fertilizer samples. The value of the radon emanation coefficient (ε) required for the evaluation of these parameters was taken from a previous study [5] where the values of the radon emanation coefficient were obtained in the range of (2.32–11.43)%. For the calculations in this

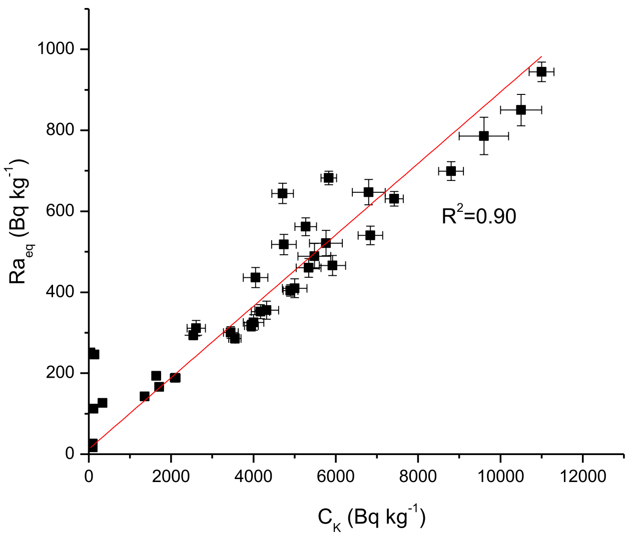

Fig. 4 Correlation between radium equivalent index (Ra_{eq}) and activity concentration of ^{40}K

research, the maximum determined value of the radon emanation coefficient in the previous research of 11.43% was taken, which represents the worst possible scenario. The estimated values of alpha dose equivalents (H_E) and radon mass exhalation rates (E_M) are shown in Fig. 5.

The estimated values of alpha dose equivalents (H_E) range from 0.485 ± 0.005 mSv y^{-1} (sample No. 29 from Russia) to 5.96 ± 0.43 mSv y^{-1} (sample No. 11 from Austria), Fig. 5a. The mean value of alpha dose equivalent (H_E) is 1.43 ± 0.21 mSv y^{-1} (mean value ± standard deviation). The obtained average value is comparable to the average value for exposure to zircon minerals in the ceramic industry as reported in our previous work [19]. Only one sample recorded a value of alpha dose equivalents (H_E) above 5 mSv y^{-1} (sample No. 11 from Austria), so that according to the recommended values of the World Health Organization [12], the worker's exposure to radon is certainly below 100 Bq m^{-3}. This also satisfies the recommendation from Article 54 of the European Commission directive that the concentration of radon in workplaces is less than 300 Bq m^{-3} [25]. In an earlier study of radon concentration in the premises where fertilizer is stored, indoor radon concentration was measured in the range of 37–117 Bq m^{-3}, which gave an average dose of 0.87 mSv y^{-1} [9], which is comparable to results in this research.

The estimated values of radon mass exhalation rates (E_M) range from 1.48 ± 0.19 mBq kg^{-1} h^{-1} (sample No. 29 from Russia) to 233 ± 18 mBq kg^{-1} h^{-1} (sample No. 11 from Austria). The average value of radon mass exhalation rates (E_M) for all 36 analyzed fertilizer samples is 44 ± 9 mBq kg^{-1} h^{-1} (mean value ± standard deviation). The estimated values of radon mass exhalation rates (E_M) are comparable to the values given for fertilizers in Saudi Arabia, where the measured values ranged from (22.65–179.79) mBq kg^{-1} h^{-1} for 12 analyzed fertilizer samples [34]. While the obtained values of radon mass exhalation rates are lower than the values obtained for fertilizers used in Nigeria (12 analyzed samples) [35] and Egypt (5 analyzed samples) [5], where the obtained values are in the range (130–420) mBq kg^{-1} h^{-1} and (792–9333) mBq kg^{-1} h^{-1}, respectively.

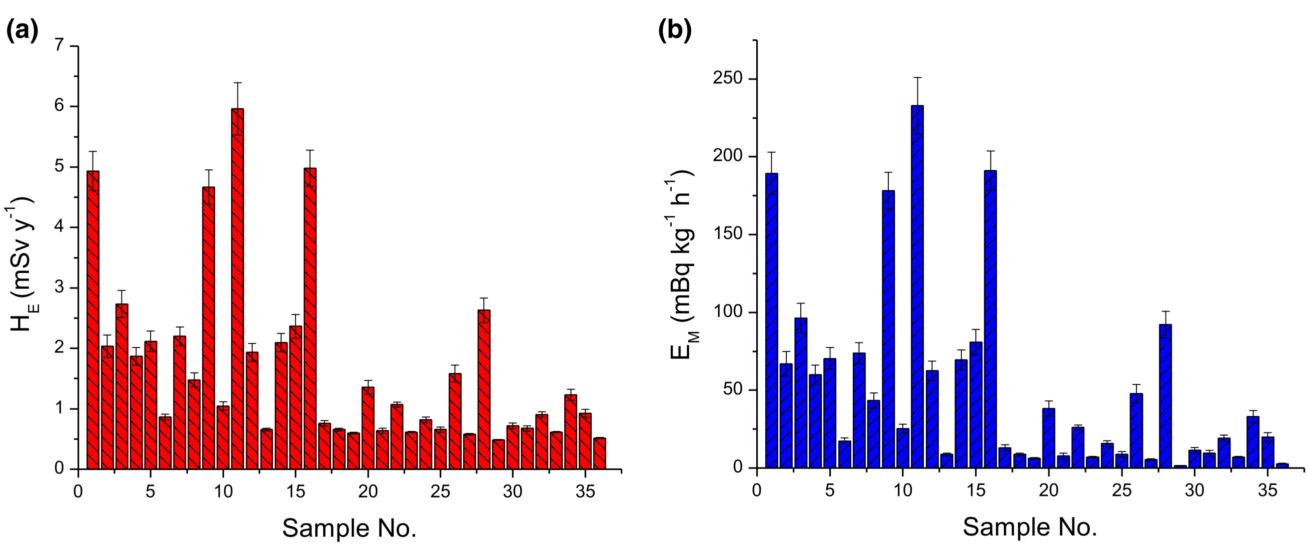

Fig. 5 The value of effective alpha dose equivalents (H_E) **(a)** and radon mass exhalation rates (E_M) **(b)** for fertilizers was obtained

Conclusion

This research presents the results of gamma spectrometric measurements for 36 samples of chemical fertilizers used in Serbia. Based on the measured values of ^{226}Ra, ^{232}Th, and ^{40}K, an assessment of the risk of radiation when working with these materials was made in terms of exposure to gamma radiation and radon.

Based on the measured values, it can be concluded that the activity concentration of ^{40}K is higher than that of fertilizer samples from other countries and that it contributes to the predominantly to exposure to gamma radiation. Annual effective doses do not exceed the permitted limit of 1 mSv per year, for all samples, but are still not negligibly small. The obtained ELCRs values are above the average values and indicate the existence of the risk of cancer as a stochastic effect during the life. The estimated values of alpha dose equivalents and radon mass exhalation rates for the analyzed fertilizer samples are comparable to the values from other research. Based on the assessments, it is assumed that the workers' exposure to radon is less than 100 Bq m^{-3}, which meets all the recommendations of the European Commission.

By implementing standard protective measures such as wearing protective gloves and masks, as well as maintaining personal hygiene, workers can significantly reduce the estimated risk to an acceptable level. This reduces the risk of inhalation and ingestion of dust in the air in production facilities. From this, it can be concluded that with the observance of protective measures and the regular wearing of adequate protective equipment, there is no particular danger for the exposure of workers in the fertilizer industry.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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