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RADIONUCLIDES CONTENT IN SELECTED MINERAL FERTILIZERS AVAILABLE IN POLAND*

ZAWARTOŚĆ RADIONUKLIDÓW W WYBRANYCH NAWOZACH MINERALNYCH DOSTĘPNYCH NA POLSKIM RYNKU

Abstract: Mineral fertilizers, commonly used in agriculture, contain natural radionuclides. Fertilizers are responsible both for external and internal exposure to human beings. They supply the soil and are consumed by plants, therefore, they pose one of the main source of radionuclides in the human diet. Moreover, due to the storage of large amount of fertilizers in warehouses they can be responsible for the external exposure. The gamma spectrometric measurements of radioactive isotopes content (potassium ^{40}K, uranium ^{238}U, thorium ^{232}Th) and the measurements of gamma dose rate for over a dozen types of mineral fertilizers available in Poland, were performed. The measurements were conducted in fertilizer warehouses by means of portable gamma spectrometers with BGO detectors. The results were registered as potassium content K [%], equivalent uranium content eU [ppm], equivalent thorium content eTh [ppm] and absorbed dose rate $D_{K, U, Th}$ [nGy h^{-1}] generated by radionuclides of uranium and thorium decay series as well as potassium ^{40}K. Radium ^{226}Ra, thorium ^{232}Th and potassium ^{40}K activities range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively.

Keywords: radionuclides, mineral fertilizers, gamma spectrometry

Mineral fertilizers are commonly used in agriculture. They enrich the soil mainly in nitrogen N, phosphorus P and potassium K. Various types of fertilizers with various concentrations of these chemical compounds are available [1].

Fertilizers contain also naturally occurring radionuclides, such as radioisotopes of uranium ^{238}U and thorium ^{232}Th decay series as well as the isotope of potassium ^{40}K. The concentration of these radionuclides in fertilizers is related to the raw material used for manufacturing the fertilizer. In the case of phosphate fertilizers an important raw material is phosphate rock. It can be enriched with naturally occurring radionuclides coming from uranium ^{238}U and thorium ^{232}Th decay series as well as from potassium ^{40}K. Thorium ^{232}Th and potassium ^{40}K concentrations in phosphate rocks are similar to those observed naturally in soil. But uranium ^{238}U concentration is connected with the origin of the rock and can be enhanced in phosphate deposits of sedimentary origin [2]. A typical concentration of uranium ^{238}U in sedimentary phosphate rocks is 1500 Bq kg^{-1} [3]. A direct correlation between P_2O_5 concentration and uranium concentration in various mineral fertilizers has been noticed [2, 4].

The knowledge of uranium, thorium and potassium concentrations in fertilizers is relevant due to the fact that these radionuclides can reach human beings via various pathways and affect them. Fertilizers are responsible both for external and internal exposure to human beings. Radionuclides contained in fertilizers are consumed by plants and subsequently by man. They can also get into the water and finally cause the internal radiation exposure of the people [4]. Both, the internal (related to radon activity

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concentration in the air) and the external exposure, can occur in warehouses where large amount of fertilizers are stored [5].

To reflect an external exposure rate and to evaluate a radiation risk, an activity concentration index (*I*) is commonly used [1, 4, 7, 8]. It includes combined activities of natural radioisotopes and is defined by the following formula:

$$I = A_1 C_{Ra} + A_2 C_{Th} + A_3 C_K \tag{1}$$

where: A_1, A_2, A_3 are coefficients representing different impact factors and C_{Ra}, C_{Th}, C_K are activities of uranium ^{238}U, thorium ^{232}Th decay series and potassium ^{40}K, respectively.

Various values of A_1, A_2, A_3 coefficients are acceptable in different countries. In Poland they are equal to 1/300, 1/200 and 1/3000, respectively. An activity concentration index (*I*) should not exceed the value equal to 1 which was established on the basis of the assumption that the gamma dose rate should not exceed the value equal to 1 mSv a^{-1} over the natural background radiation dose [6].

To assess a radiation risk, also the total gamma dose rate [mSv a^{-1}] is used. According to European Commission [6] the excess of 0.3-1 mSv a^{-1} of gamma dose rate over the natural background radiation dose is acceptable.

The main aim of the survey was to evaluate the radionuclides content in selected mineral fertilizers available and used in Poland and to estimate their radiological impact on human beings.

Method

The measurements were conducted by means of portable gamma spectrometers RS230 with BGO detectors and automatic gain stabilization based on thallium ^{208}Tl emission at 2615 keV. The results were registered as potassium content K [%], equivalent uranium content eU [ppm], equivalent thorium content eTh [ppm] and absorbed dose rate $D_{K,\,U,\,Th}$ [nGy h^{-1}] generated by radionuclides of uranium and thorium decay series and potassium ^{40}K [9]. Because of the fact that uranium ^{238}U is not a gamma emitter, its content is estimated on the basis of gamma photons emitted by bismuth ^{214}Bi which is a product of uranium ^{238}U decay. This procedure is based on the assumption of the equilibrium within uranium ^{238}U decay series and uranium ^{238}U content obtained in this way is denoted as equivalent uranium eU. Similarly thorium ^{232}Th content is estimated on the basis of gamma photons emitted by thallium ^{208}Tl and thorium ^{232}Th content is denoted as equivalent thorium eTh.

87 measurements on 14 various types of fertilizers were performed in fertilizer warehouses. The devices were located at the top of piles of fertilizers placed loose directly on the floor of warehouses or packed into the bags.

Results

The average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (in [Bq kg^{-1}]) and average dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) with the respective standard deviations have been calculated for particular investigated types of mineral fertilizers. Summary of the results is presented in the Table 1.

Table 1

Mean activity concentration [Bq kg^{-1}] of Ra-226, Th-232 and K-40 and dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) for various types of mineral fertilizers

Ferti-lizer	No of measure-ments	N	P	K	Activity concentration [Bq kg^{-1}]			Dose rate	
		composition [%]			Ra-226	Th-232	K-40	[nGy h^{-1}]	[mSv a^{-1}]
F 1	3	27.5	0	0	17.4±1.2	9.2 ± 2.1	141.6 ± 35.0	19.8 ± 14.4	0.2 ± 0.1
F 2	10	0	40	0	827.0±90.1	38.9 ± 5.0	922.3 ± 148.8	426.6 ± 12.9	3.7 ± 0.1
F 3	5	3	22	0	416.7±30.5	14.3 ± 2.5	267.0 ± 25.4	202.5 ± 48.9	1.8 ± 0.4
F 4	12	4	12	12	347.9±61.3	32.4 ± 9.3	3494.1 ± 265.1	323.7 ± 31.0	2.8 ± 0.3
F 5	5	3.5	8	15	31.1±4.2	29.7 ± 5.1	4089.8 ± 362.4	209.6 ± 40.4	1.8 ± 0.4
F 6	3	16	16	16	37.3±8.6	35.0 ± 3.8	3610.4 ± 189.5	193.3 ± 56.9	1.7 ± 0.5
F 7	5	4	10	17.5	151.9±6.2	29.0 ± 2.3	4702.7 ± 333.7	288.2 ± 26.0	2.5 ± 0.2
F 8	3	0	12	20	328.6±27.7	27.8 ± 2.5	7028.7 ± 464.4	464.9 ± 45.4	4.1 ± 0.4
F 9	5	5	16	24	71.6±9.7	34.4 ± 2.0	7142.0 ± 995.6	361.3 ± 2.4	3.2 ± 0.02
F 10	5	5	10	25	144.5±15.8	31.0 ± 1.8	8422.3 ± 631.9	446.5 ± 35.2	3.9 ± 0.3
F 11	5	9.5	25	25	32.3±5.2	44.9 ± 3.7	7057.0 ± 1220.5	347.6 ± 82.7	3.0 ± 0.7
F 12	3	5	15	30	61.7±2.6	16.6 ± 3.7	6209.5 ± 569.5	305.6 ± 37.1	2.7 ± 0.3
F 13	10	0	0	40	65.2±77.1	19.1 ± 5.8	10743.0 ± 1678.7	504.3 ± 16.0	4.4 ± 0.1
F 14	13	0	0	60	62.0±9.0	24.2 ± 4.3	12068.2 ± 1898.3	564.1 ± 10.8	4.9 ± 0.1

Also minimum, maximum and average radionuclides concentrations and dose rate for all of the fertilizers have been estimated (Table 2). Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in investigated mineral fertilizers range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively with the average of 22.1 ± 257.2, 28.2 ± 10.1 and 6081.6 ± 4176.9 Bq kg^{-1}, respectively. The dose rate range between 0.2-6.7 mSv a^{-1} with the average of 3.3 ± 0.4 mSv a^{-1}.

Table 2

Minimum, maximum and average activity concentrations [Bq kg^{-1}] of Ra-226, Th-232 and K-40 and minimum, maximum and average dose rate (in [nGy h^{-1}] and [mSv a^{-1}]) for investigated mineral fertilizers

	Activity concentration [Bq kg^{-1}]			Dose rate	
	Ra-226	Th-232	K-40	[nGy h^{-1}]	[mSv a^{-1}]
Min	16.2	7.0	121.4	18.0	0.2
Max	973.4	50.9	16777.9	762.9	6.7
Average	22.1 ± 257.2	28.2 ± 10.1	6081.6 ± 4176.9	377.4 ± 142.3	3.3 ± 0.4

The frequency distributions (Fig. 1a-c) prepared for ^{226}Ra, ^{232}Th and ^{40}K activities showed that the majority of the results are placed between the ranges 0-100, 20-40 and 0-4000 Bq kg^{-1}, respectively.

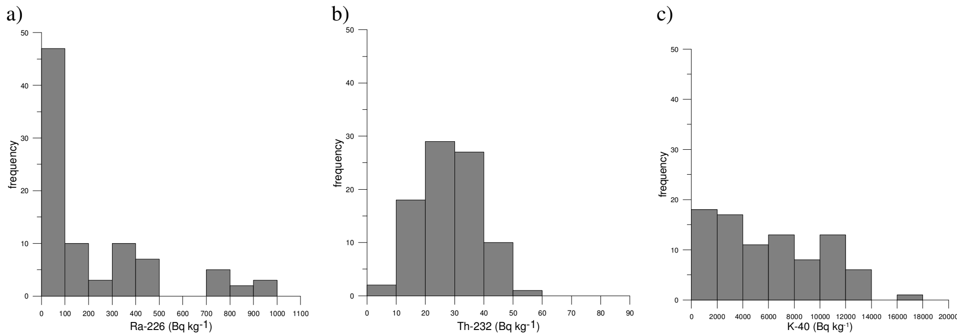


Fig. 1. Frequency distribution of radium ^{226}Ra (a), thorium ^{232}Th (b) and potassium ^{40}K (c) activities for all the investigated mineral fertilizers

Assessment of radiation hazard

To assess a radiological impact on human beings, the activity concentration index (*I*) was calculated for all types of investigated fertilizers (Table 3).

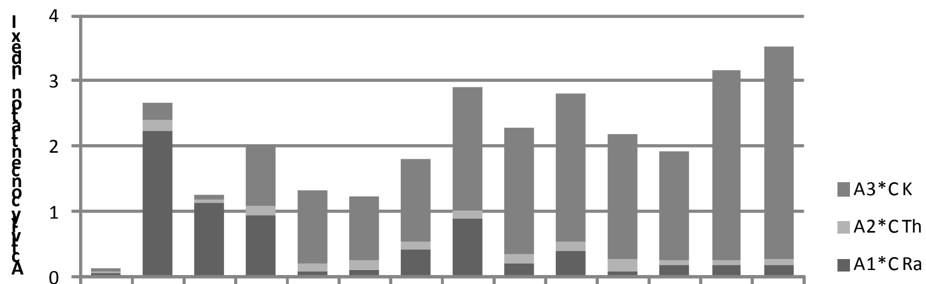
Table 3

The activity concentration index (*I*) for various types of mineral fertilizers

Fertilizer	**N**	**P**	**K**	**Activity concentration index (*I*)**
	composition [%]			
F 1	27.5	0	0	0.1
F 2	0	40	0	2.7
F 3	3	22	0	1.3
F 4	4	12	12	2.0
F 5	3.5	8	15	1.3
F 6	16	16	16	1.2
F 7	4	10	17.5	1.8
F 8	0	12	20	2.9
F 9	5	16	24	2.3
F 10	5	10	25	2.8
F 11	9.5	25	25	2.2
F 12	5	15	30	1.9
F 13	0	0	40	3.2
F 14	0	0	60	3.5

The activity concentration index ranges between 0.1-3.5 (Table 3). In 13 of 14 surveyed fertilizers the activity concentration index (*I*) exceeds the value equal to 1. The most significant values of these two indices are observed in the case of typically potassium fertilizers (F 13 and F 14) and they can pose a radiation hazard if they are stored in large amount.

Analyzing the contribution of the radioisotopes in forming the activity concentration index (*I*) it has been noticed that radionuclides of uranium decay series play the most significant role in the case of typical phosphate fertilizers (Fig. 2, fertilizer F 2) and NP fertilizers (Fig. 2, fertilizer F 3). In the case of NPK fertilizers (Fig. 2, fertilizers F 4-F 12, without F 8), PK fertilizers (Fig. 2, fertilizer F 8) and typical potassium fertilizers (Fig. 2, fertilizers F 13 and F 14), naturally occurring ^{40}K has the main participation in forming the activity concentration index (*I*). Radioisotopes of thorium decay series has a minor contribution to the radioactivity of mineral fertilizers (Fig. 2).



	F 1	F 2	F 3	F 4	F 5	F 6	F 7	F 8	F 9	F 10	F 11	F 12	F 13	F 14
A3*C K	0,04	0,25	0,07	0,94	1,11	0,98	1,27	1,90	1,93	2,28	1,91	1,68	2,90	3,26
A2*C Th	0,04	0,17	0,06	0,14	0,13	0,15	0,12	0,12	0,15	0,13	0,19	0,07	0,08	0,10
A1*C Ra	0,05	2,24	1,13	0,94	0,08	0,10	0,41	0,89	0,19	0,39	0,09	0,17	0,18	0,17

Fertilizers

Fig. 2. The contribution of radioisotopes in forming the activity concentration index (*I*) for particular types of mineral fertilizers

In some cases of investigated fertilizers (Table 1) also the annual gamma dose rate generated by radionuclides present in fertilizers exceeds the limit value 1 mSv over the natural background radiation dose (2.4 mSv a^{-1}).

Conclusions

1. Activity concentrations of Ra-226, Th-232 and K-40 in mineral fertilizers available in Poland range between 16.2-973.4, 7.0-50.9 and 121.4-16777.9 Bq kg^{-1}, respectively with the average of 22.1 ± 257.2, 28.2 ± 10.1 and 6081.6 ± 4176.9 Bq kg^{-1}, respectively.
2. The annual dose rate range between 0.2-6.7 mSv with the average of 3.3 ± 0.4 mSv.
3. Calculated activity concentration index for investigated mineral fertilizers range between 0.1-3.5.
4. Some types of fertilizers stored in a large amount can pose a radiological hazard for human beings.

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ZAWARTOŚĆ RADIONUKLIDÓW W WYBRANYCH NAWOZACH MINERALNYCH DOSTĘPNYCH NA POLSKIM RYNKU

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Abstrakt: Nawozy mineralne, powszechnie stosowane w rolnictwie, zawierają naturalne pierwiastki promieniotwórcze. Środki te stanowią zarówno zewnętrzne, jak i wewnętrzne źródło napromieniowania człowieka. Nawozy zasilają glebę i pobierane są przez rośliny, przez co stanowią jedno z głównych źródeł radionuklidów w ludzkiej diecie. Natomiast na skutek składowania dużych ilości nawozów w magazynach może dojść do narażenia na promieniowanie zewnętrzne. Przeprowadzono gamma spektrometryczne pomiary zawartości izotopów promieniotwórczych (potasu ^{40}K, uranu ^{238}U i toru ^{232}Th) oraz pomiar mocy dawki promieniowania dla kilkunastu nawozów mineralnych dostępnych na polskim rynku. Pomiary wykonano w magazynach nawozów mineralnych za pomocą przenośnych gamma spektrometrów z detektorami BGO. Wyniki badań były rejestrowane jako zawartość potasu K [%], równoważne zawartości uranu eU [ppm] i toru eTh [ppm] oraz moc dawki pochłoniętej $D_{K,\ U,\ Th}$ [nGy h^{-1}] generowanej przez radionuklidy szeregów uranu i toru oraz potas ^{40}K. Zawartość radu ^{226}Ra, toru ^{232}Th i potasu ^{40}K w nawozach wahała się w granicach odpowiednio 16.2-973.4, 7.0-50.9 i 121.4-16777.9 Bq $\cdot$ kg^{-1}.

Słowa kluczowe: radionuklidy, nawozy mineralne, gamma spektrometria