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RADIOACTIVITY IN SAMPLES OF IMPORTED MINERAL FERTILIZER ANALYZED IN THE PERIOD 2020–2022

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Abstract

In the period 2020–2022 the Institute for the Application of Nuclear Energy – INEP received 677 samples of mineral fertilizer for gamma spectroscopic investigation of various compositions. In all investigated samples different activity levels of natural (^{40}K, ^{232}Th, ^{226}Ra, ^{238}U) and artificially produced (^{137}Cs) radionuclides were determined. The activity levels of ^{137}Cs in all samples were very low. Depending on the type and composition of the fertilizer, different levels of natural radionuclides were registered. All analized samples were in accordance with activity levels prescribed by the Regulations and were imported into Serbia.

Keywords: mineral fertilizer, radionuclides, gamma-spectrometry.

INTRODUCTION

In the XXI century the human population faces the issue of hunger and lack of food. In 1840 Justus von Liebig presented the results of his research on the significance of nutrients for plant growth in the British Royal Society and set the basis of modern agriculture and production of mineral fertilizers. In the last 100 years the use of mineral fertilizers is constantly increasing [1].

According to their origin, fertilizers can be organic and inorganic (mineral). Inorganic are composed of artificially obtained materials and minerals. They can be solid, water-soluble and with controlled release of chemical elements; simple (nitrogen, phosphorus and potassium, less often calcium) and complex (produced by mixing simple ones) that can be mixed and complex [2]. Inorganic fertilizers contain macro and micronutrients. Nitrogen, phosphorous and potassium are primary macronutrients, consumed in large quantities and are present in plant tissue. Calcium, sulfur and magnesium are secondary macronutrients, while boron, chlorine, manganese, iron, zinc, copper, molybdenum and selenium are micronutrients (trace elements) [3]. Excessive or too little amount of fertilizer can be harmful. Excessive amounts of fertilizer can lead to the burning of plant crops (drying of the roots, damage or even the death of the plant).

Phosphorus fertilizers are the most interesting for our research and they are used in plant production in different quantities depending on the supply of phosphorus to the soil and the needs of plant species. Phosphorus fertilizers are produced from phosphorus ores: apatite and phosphorite [4]. Depending on the geographical origin of the ores from which they are produced and the chemical composition of fertilizers in them, the level of activity of natural radionuclides varies [5,6]. When producing phosphorus mineral products from phosphorus ores, over 90% of uranium remains in the final products. In countries producing phosphoric acid, the problem of extracting uranium from it is being worked on, either for economic and technical or environmental reasons. Three extraction procedures for uranium extraction are known in the World. The procedure known as DENTRA-TORO has been applied in Serbia in the semi-industrial installation located close to the IHP Prahovo factory. The efficiency of uranium extraction from phosphorous acid was 90 to 95% [7].

Radioactive substances from mineral fertilizers that are deposited on the soil can be adopted by grown plants, both the above-ground parts of the plant and the root system. The adoption of natural radionuclides from phosphorus fertilizers by plants depends on many factors [8]. The use of phosphorus mineral fertilizers in agriculture constitutes the largest anthropogenic source of ^{226}Ra, ^{232}Th and ^{238}U in soil [9]. Studies have shown that radionuclides that are introduced into the soil through mineral fertilizers that contain phosphorous can lead to an increase in basic radiation levels in certain regions and can represent significant local risks of exposing the population to ionizing radiation [10–12].

The mineral fertilizer factories in each country are one of the pillars of the overall economy and part of the national strategy of each country, as this production is in the function of food the Chemical Products Industry in Prahovo (IHP-Prahovo) was founded by the Bor Mining and Smelting Basin on September 19, 1960. In 2008, the factory was privatized by the Greek company Neochimiki-Athens, but in 2011 IHP Prahovo was introduced into bankruptcy. The Elixir Group Šabac, created from the family company Narcis Popovići (1998), on 02.08.2012 purchased the bankrupted factory and on 01.02.2013 became its formal owner. In 2011 the Elixir Group bought Zorka Šabac. With the purchase of two chemical companies, the Elixir Group has become a major producer of chemical components based on phosphorus, primarily phosphoric acid, complex mineral fertilizers and feed additives. Investment in capacities for the production of mineral fertilizers, as a development potential of this branch of the chemical industry, already in 2015 made the Elixir Group the undisputed leader in the region. By purchasing two large chemical companies the Elixir Group took over a great responsibility of protecting the environment [13]. The Elixir group in 2023 was the only producer of artificial NPK fertilizer. Serbia has moved from being a serious producer of fertilizers to a serious importer, as many factories producing mineral fertilizers have stopped working.

NP and NPK fertilizers with different formulations are most often imported into Serbia. When importing into the Republic of Serbia, gamma spectrometric analysis of mineral and organic fertilizers that have the macronutrient element phosphorus in their composition is mandatory. Fertilizers that are produced in our country are not subject to mandatory control before [14]. According to the Regulations on the limits of the content of natural radionuclides in mineral phosphate fertilizers containing the macronutrient element phosphorus, placed on the market, the permitted level of activity for ^{238}U is 1600 Bq kg^{-1} for mineral fertilizers and 3200 Bq/kg for raw materials for the production of mineral fertilizers, and for ^{226}Ra 1000 Bq kg^{-1}. The permitted activity level for ^{40}K is 27000 Bq kg^{-1} for mineral fertilizers containing the macronutrient elements K and/or P, placed on the market and applied as raw materials for their production. According to the Regulations fertilizer samples in which the measured levels of natural radionuclides are higher than these stated values cannot be imported into country [14]. The purpose of this work is to show the activity levels of natural (^{40}K, ^{232}Th, ^{226}Ra, ^{238}U) and artificially created (^{137}Cs) radionuclides in imported mineral fertilizers.

MATERIALS AND METHODS

In the period 2020–2022 the Institute for the Application of Nuclear Energy – INEP followed activity levels of the artificial (^{137}Cs) and natural (^{40}K, ^{232}Th, ^{226}Ra, ^{238}U) radionuclides in fertilizer samples containing the phosphorous macronutrient element and imported from; Russian Federation, Spain, Greece, France, Italy and other countries.

Fertilizer samples (677) were taken by the phytosanitary inspection and sent to be analyzed in INEP, where they were homogenized, puted in 1 L Marinelli containers and measured. Gamma spectrometric measurements of fertilizer samples were performed according to the standard method of the International Agency for Atomic Energy [15]. The semiconducting high purity germanium detector of the n-type, produced by ORTEC-AMETEK, USA was used. The 8192 channel detector has a resolution of 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co. The samples were measured for 60000 seconds and spectral analysis was performed using the Gamma Vision 32 software. The activity level of ^{238}U on the lines: ^{234}Th (63 and 93 keV) and ^{234}Pa (1000 keV), ^{226}Ra on the lines: ^{214}Bi (609, 1120 and 1764 keV) and ^{214}Pb (295 and 352 keV), while ^{232}Th on the lines ^{228}Ac (338, 911 and 969 keV). The activity level of ^{40}K was determined based on the gamma line at 1460.8 keV, while for ^{137}Cs it was at 661.6 keV [16]. Detector calibration was performed using two different radioactive reference materials in Marinelli geometry. The total measurement uncertainty that includes many elements was lower than 20%. Quality control of gamma spectrometric measurements used for the analysis was performed using a calibration standard and reference materials and also by yearly participation in comparisons organized by the International Atomic Radiation Agency.

RESULTS AND DISCUSSION

This work presents the activity levels of radionuclides in imported fertilizer samples (677). All samples contained natural radionuclides (^{40}K, ^{232}Th, ^{226}Ra, ^{238}U) and the artificial radionuclide (^{137}Cs). During 2020–2022 INEP received 384 samples of NPK fertilizer (75 formulations 15-15-15, 171 formulations 16-16-16, 30 formulations 20-20-20, 41 formulation 16-16-8, 67 different formulations). Low levels of activity of ^{226}Ra and ^{238}U were measured in 104 samples of NPK fertilizer and 36 NPK fertilizer samples had a low ^{40}K content. Imports also included 69 samples of NP fertilizer and 84 samples of MAP.

Table 1 shows the type of investigated fertilizer, import year, average radionuclide activity levels (Bq kg^{-1}), minimal and maximal values for fertilizers imported between 2020 and 2022. The activity levels of ^{137}Cs in all samples were low and can be ignored (<4.0 Bq kg^{-1}). The activity levels of ^{232}Th in fertilizers were up to 43.0 Bq kg^{-1}, and the average activity levels are higher than the values shown in previous research [17].

Table 1 *Fertilizer type, investigation year, average radionuclide activity levels (Bq kg^{-1}), minimal and maximal values of radionuclide activity levels (Bq kg^{-1})*

Fertilizer type	**Year**	**^{137}Cs**	**^{40}K**	**^{226}Ra**	**^{232}Th**	**^{238}U**
				Bq kg^{-1}		
15-15-15 (75)	2020 (12)	1.3	3683	20.5	9.1	39.9
	2021 (21)	0.8	3685	32.9	7.6	93.0
	2022 (42)	0.7	2812	70.0	8.0	125
	Min-max	0.3–2.3	1256–4147	7.0–409	4.0–29.0	10.0–510
16-16-16 (171)	2020 (83)	1.2	4096	23.1	20.8	49.4
	2021 (65)	0.9	3800	66.6	23.0	107
	2022 (23)	0.7	2951	19.9	20.7	33.2
	Min-max	0.4–1.8	1390–4622	10.0–674	2.0–41.0	4.0–826
20-20-20 (30)	2020 (6)	1.3	4292	17.3	6.3	25.7
	2021 (9)	1.0	4823	16.8	9.1	32.1
	2022 (15)	0.9	3833	17.9	6.5	29.9
	Min-max	0.3–2.5	587–6248	6.0–40.0	4.0–13.0	2.0–66.0
16-16-8 (41)	2020 (0)	---	---	---	---	---
	2021 (26)	0.6	1625	15.7	23.5	33.0
	2022 (15)	0.6	1944	19.6	24.9	39.9
	Min-max	0.3–1.1	848–2571	5.0–29.0	11.0–36.0	8.0–76.0
MAP (84)	2020 (32)	0.5	44.3	43.7	4.2	125
	2021 (21)	0.4	33.6	14.5	5.7	79.2
	2022 (31)	0.3	39.6	64.5	4.2	143
	Min-max	0.1–0.8	6.0–143	5.0–300	1.0–22.0	1.0–685
NP (69)	2020 (5)	0.5	17.4	25.0	4.2	31.6
	2021 (10)	0.4	59.1	113	7.4	305
	2022 (56)	0.4	142	157	7.0	303
	Min-max	0.1–0.9	13.0–763	7.0–542	1.6–27.0	5.0–991
NPK (67)	2020 (8)	1.3	5217	128	19.3	209
	2021 (19)	0.9	4356	106	11.5	231
	2022 (40)	0.7	3420	170	14.0	341
	Min-max	0.3–1.6	23.0–10927	8.0–578	2.0–33.0	20.0–944
NPK small participation of ^{226}Ra and ^{238}U (104)	2020 (31)	1.3	5680	15.5	8.3	35.8
	2021 (52)	0.9	4798	16.6	7.3	31.0
	2022 (21)	0.8	4064	17.8	8.7	30.5
	Min-max	0.2–3.1	1038–11175	3.0–57.0	1.0–25.0	4.0–82.0
NPK small participation of ^{40}K (36)	2020 (0)	---	---	---	---	---
	2021 (15)	0.9	420	11.5	3.3	21.9
	2022 (21)	0.6	423	124	12.9	164
	Min-max	0.2–1.6	5.0–954	1.0–637	1.0–43.0	3.0–930

The NPK fertilizers with the formulation: 15-15-15, 16-16-16, 20-20-20 and 16-16-8, are the most significant for this research, as they are used the most for fertilizing soil. The average activity level of ^{40}K in these fertilizers was in the range 1625–4823 Bq kg^{-1}. The maximal level of activity of ^{40}K (6248 Bq kg^{-1}) was determined in a fertilizer with a 20-20-20 formulation imported in 2021. This value is still much lower than the maximal allowed value determined by the Regulations [14]. Maximal activity levels of ^{226}Ra and ^{238}U were measured in a fertilizer with a formulation 16-16-16 imported in 2021 (674, and 826 Bq kg^{-1}, respectively). In our research from 2014 the maximal activity level of ^{226}Ra was measured in a NPK fertilizer sample 15-15-15 (775 Bq kg^{-1}) [18]. Table 1 also gives the activity levels of radionuclides in NPK fertilizers (67 samples) with different formulations. The maximal activity level of ^{40}K in fertilizers was 11175 Bq kg^{-1}. In our research from 2014 the maximal activity level of ^{40}K was 12965 Bq kg^{-1} [18]. The maximal activity levels of ^{226}Ra and ^{238}U were 578 and 944 Bq kg^{-1}, respectively. The Table 1 also shows activity levels of radionuclides in NPK fertilizers with a small participation of ^{226}Ra and ^{238}U, and also a small participation of ^{40}K (140 samples in total 140). Maximal activity levels of ^{226}Ra, ^{238}U and ^{40}K in fertilizers with a small participation of potassium was 637, 930 and 954 Bq kg^{-1}, respectively. It can be concluded that the activity levels of ^{226}Ra and ^{238}U in this type of fertilizer are high. Activity levels of radionuclides in mono-ammonium phosphate were also monitored (MAP) and NP fertilizers. The maximal activity levels of ^{226}Ra and ^{238}U in MAP were 300 Bq kg^{-1} and 685 Bq kg^{-1}, respectively and this is lower than in our previous research (745 and 1450 Bq kg^{-1}). A high average activity level of ^{238}U was measured in MAP samples in 2001 (1348 Bq kg^{-1}) [17]. The maximal activity levels of ^{226}Ra and ^{238}U in NP fertilizers were 542 and 991 Bq kg^{-1}, respectively. These results are higher than previous results obtained for the same fertilizer type (450 and 750 Bq kg^{-1}) [18]. The average activity level of ^{238}U in MAP is significantly lower in this work than in previous research [18].

CONCLUSION

The following radionuclides: ^{40}K, ^{232}Th, ^{226}Ra, ^{238}U and ^{137}Cs were determined in all measured fertilizer samples (677) sent to INEP for gamma spectrometric analysis by the phyto-sanitary inspection. The activity level of ^{137}Cs in all measured fertilizer samples was negligible. The maximum activity level of ^{40}K was measured in NPK fertilizer with a small proportion of ^{226}Ra and ^{238}U (11175 Bq kg^{-1}). The maximum activity level of ^{226}Ra was measured in a sample of fertilizer with the formulation 16-16-16 (674 Bq kg^{-1}), and ^{238}U in a sample of NP fertilizer (991 Bq kg^{-1}). All fertilizer samples had activity levels that are allowed by the Regulations and allowed to be imported into our country. In order to observe the cumulative effect due to the increasing content of uranium arable land due to fertilization and the possibility of establishing a food chain, constant but systematic measurements of the radioactivity of mineral fertilizers are necessary. These measurements should allow a long-term forecast of the content of uranium in the soil, due to the constant and necessary application of fertilizers.

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