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Original Research

Radiological Assessment in the Premises of the Phosphate Fertilizer Plant of the Industrial Complex "Trepça"

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Abstract

Mining, through technological processes, creates large amounts of industrial residues that potentially contain high concentrations of radionuclides. The radiological impact on the health of employees on the premises of the phosphate fertilizer plant of the industrial complex "Trepça" - Mitrovica, is investigated by measuring gamma dose rates, total alpha/beta and gamma, and radionuclide concentrations in residues. The results show that the gamma radiation dose rates are comparable with background radiation, ranging from 70 to 285 nSv/h. Activity concentrations of gross alpha, gross beta, and gross gamma are found to vary between 380-610 Bq/kg, 354-570 Bq/kg, and 162-375 Bq/kg, respectively. The highest activity concentration is found in the phosphogypsum residue, which is further analyzed by means of gamma-ray spectrometry, with the concentration levels ranging from 6±1 Bq/kg (^{228}Th) to 350±30 Bq/kg (^{226}Ra).

Based on the results presented, we can conclude that the relevant radiological risk for workers at the location of the phosphate fertilizer plant of the industrial complex "Trepça" – Mitrovica, may result from phosphogypsum residue.

Keywords: NORM, radiological assessment, environmental radioactivity, radiation protection

Introduction

Mining, through technological processes, creates large amounts of residue. Through industrial processing, products and residues may contain higher levels of radionuclides. These minerals in their raw form contain uranium, which has an activity of about 15 Bq/kg. In fact, it is natural that the raw materials contain radionuclides due to the presence of ^{40}K, ^{238}U, and ^{232}Th in the earth. The average content of radioactivity at world levels in the earth's crust is 727±60 Bq/kg, 33±7 Bq/kg,, and 43±4 Bq/kg, respectively for ^{40}K, ^{238}U, and ^{232}Th [1]. Minerals during their processing lead to the concentration of radionuclides, which can cause an increase in human exposure and widespread environmental pollution.

Several types of industries have been identified that deal with materials that contain elevated levels

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of natural radionuclides. The most important component of the dose rate received by humans comes from ^{40}K, ^{232}Th, and ^{238}U as the progeny of the radioactive decay chain, accounting for a worldwide average of 58 nGy/h [2]. Human activity can increase the presence of radiation, to which not only the persons directly involved in these activities are exposed, but also the general population and the environment in general.

Exposures of workers during the handling of these materials can be of very high radiation levels. According to the EU Council Directive [3], residues from mineral processing are proposed in a priority list of industrial sectors that can lead to the concentration of Natural Radioactive Materials (NORM) in by-products and industrial residues. According to the EU Council Directive, the concentration values of solid materials for reuse, recycling, conventional disposal, or incineration are discussed in each case. The International Atomic Energy Agency (IAEA), based on the recommendations of the International Commission for Radiation Protection, has published Basic Safety Standards, whose recommendations have been approved by all European Union countries as Basic Safety Standards [4]. Based on these recommendations, some countries have introduced their own classification regulations, setting rules for those radionuclides that have been discharged into the environment or are planned to be discharged. The Republic of Kosovo still does not have any regulations dealing with this topic, but the Law on Radiation Protection and Nuclear Safety is in force [5]. In the absence of regulation, the Republic of Kosovo has taken as a basis the Basic Safety Standards, in which exposure limits and exemptions from various sources of radioactivity, including NORM, are recommended. The purpose of this work was to monitor environmental radioactivity and the radiological impact on the health of workers in the facility of the phosphate fertilizer factory of the Industrial Complex "Trepça" - Mitrovica (Fig. 1a).

These results will provide basic data for the creation of a national policy for the management of NORM in order to protect the health of employees in this production sector.

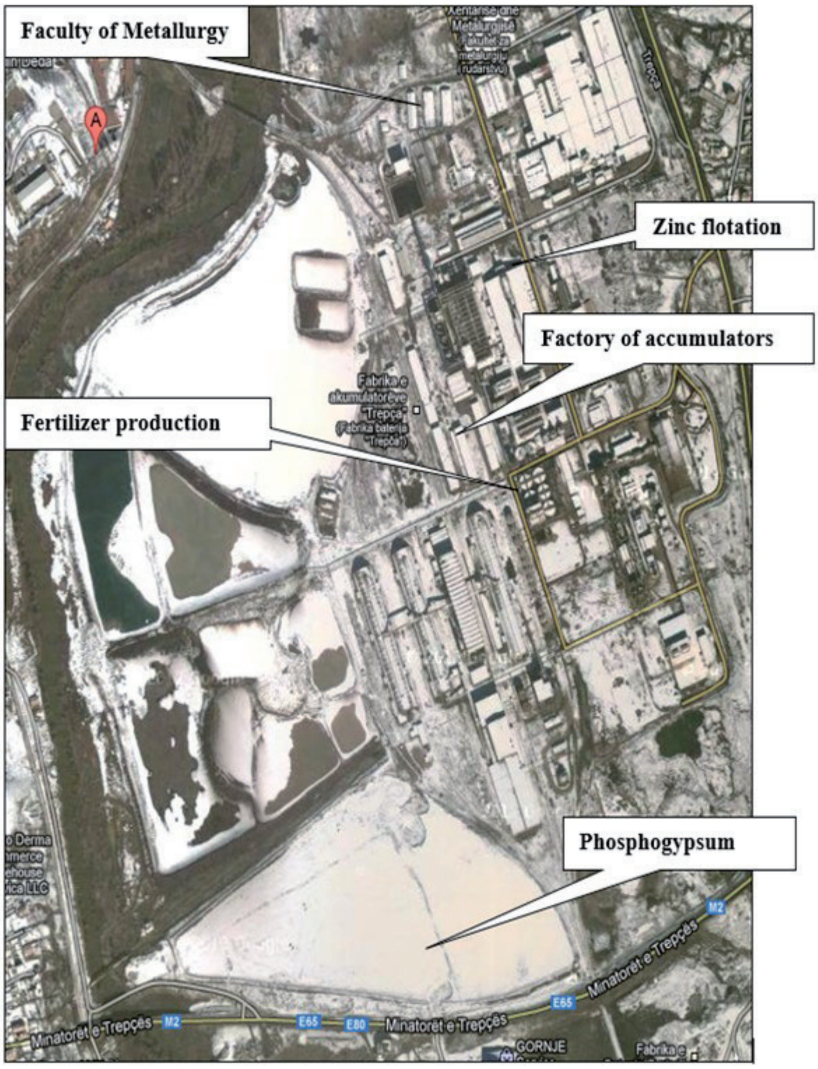


Fig. 1. a) Industrial complex "Trepça" – Mitrovica.

Material and Methods

Description of the Industrial Process

The industrial complex "Trepça" is located in the city of Mitrovica, in the north of Kosovo. Some of the industrial departments that have been in operation in the past were the lead smelter, the production of chemical fertilizer, the "Trepça" battery factory, the electrolysis of zinc, and the factory for the production of sulfuric acid. Most of the sectors are currently not in operation due to severe damage that occurred during the 1999 war. In the absence of maintenance, most of the sectors are in a bad state, and they are "contributing" to the pollution of groundwater and land due to the large area with phosphogypsum residues. This area has an area of over 12 hectares and over 280,000 tons of industrial residues [6]. This area, because of the phosphogypsum landfill, has the potential for the release of radon gases, and this part should be considered a problem for the future that needs to be solved [7]. For this reason, the former production of chemical fertilizers and the processing of other minerals have been identified as relevant NORM processes [8]. The industrial process begins (Fig. 1b) with the grinding (crushing) of phosphate rock in a grinding mill, as such material is introduced into a mixer where certain additives are added, such as phosphoric acid, sulfuric acid, ammonia, zinc sulfate, sulfate ammonia, ammonium phosphate, magnesium salts and potassium salts, boron, dolomite, and calcium.

Phosphate rock (or phosphorite) is the raw material used in the production of chemical fertilizers

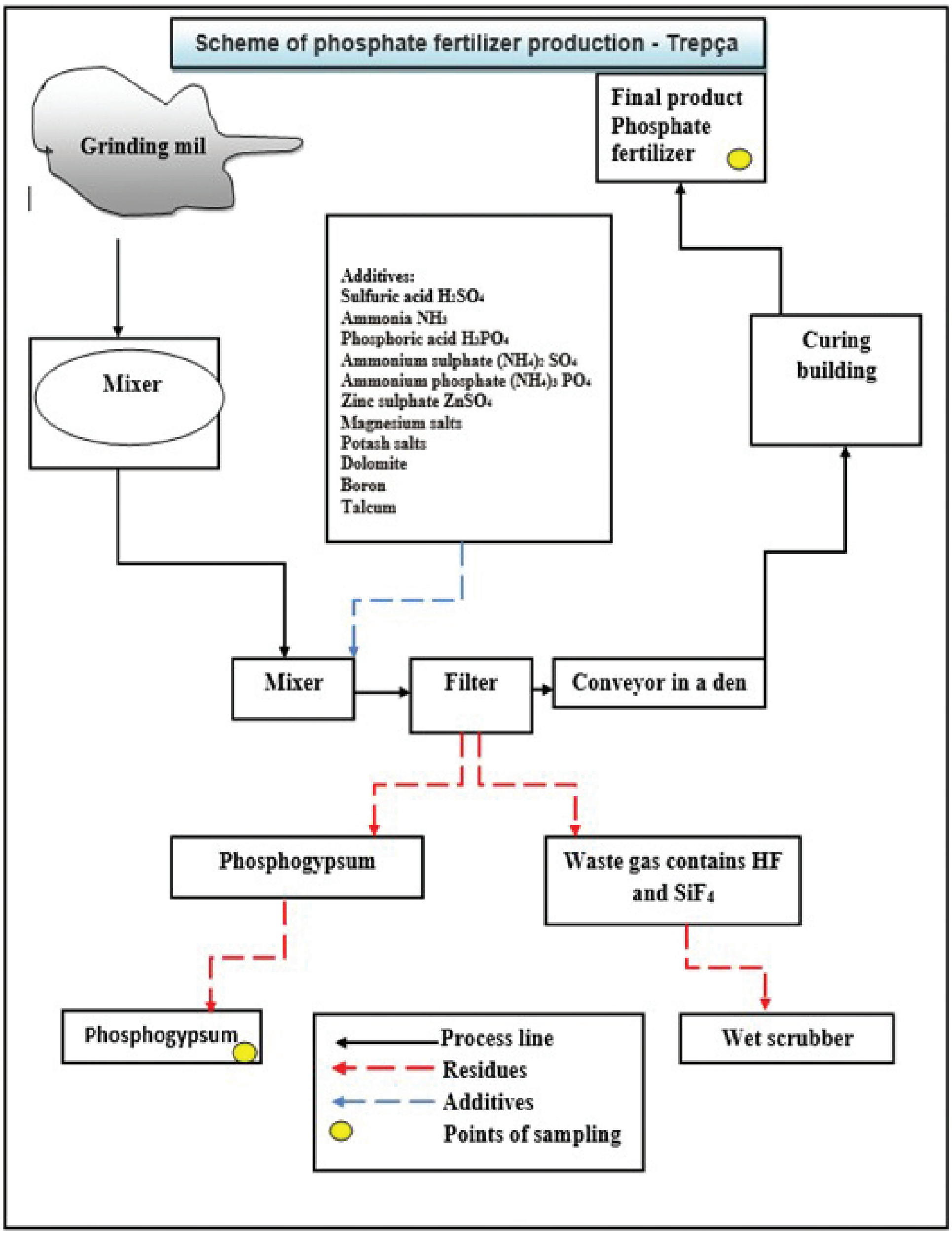


Fig. 1. b) Simplified scheme of the technological process,

(phosphates). Phosphate rock contains varying amounts of naturally occurring radioactive elements. The by-product of phosphogypsum, in addition to trace metals and fluorides, also contains radionuclides (especially radon gas). Practically all radioisotopes, which are included in phosphogypsum, and in particular ^{226}Ra, become the main source of radioactivity [9]. Phosphate minerals are processed through technological processes such as acid leaching for the production of phosphoric acid and thermal processes for the production of elemental phosphorus. The first method is more common for the production of phosphogypsum ($CaSO_4 \times H_2O$). In the process of thermal processing of the mineral, calcium silicate ($CaSiO_3$) is formed in the product residue, which contains uranium and radium. During the production process of phosphoric acid, the main by-product produced is phosphogypsum.

About 80% of ^{226}Ra is found in phosphogypsum, while about 86% of uranium and 70% of thorium are found in phosphoric acid [10]. During the technological process, natural radionuclides may result in their enrichment; therefore, these radionuclides should be investigated to identify possible processes that may lead to the radiological exposure of workers [11].

Environmental Radiological Assessment

Dose Rate Measurements

The equipment used to measure ambient gamma dose rates includes an energy-sensitive radiation detector and amplifier connected to data readout equipment. Sodium iodide (NaI-1.4’ x 2’ / 35 x 51 mm) scintillation counters are the most common devices, which are activated by thallium (Tl), with gamma energy range: 20 keV to 3 MeV and dose range: 0.01 µSv to 1 Sv. These devices use crystals that emit light when gamma photons interact with atoms in the crystals. The light produced in the crystal has an intensity proportional to the energy deposited in the crystal by gamma photons. During the measurement procedures, we performed 15-20 measurements within a short time, at one point of a material, and calculated the average radiation dose level of that material. The dose rate measurements were made at a distance of 20 m. The dotted lines in Fig. 2 show the path of dose rate gamma radiation measurement. All data is in nSv/h. The red dotted line shows the running direction (trajectories). The doses of radiation levels were measured at a height of 0.05 m - 1 m from the ground surface.

Gross Alpha, Beta, and Gamma Measurements

The main purpose of measuring gross alpha, beta, and gamma is to provide sufficient information about the activity of the sample and thus determine if more detailed analysis is necessary. Proportional and scintillation detectors are mainly used to measure sources with general (gross) activity. This counting technique is based on the ability of proportional counters to differentiate between the appearance of ionization due to alpha and beta particles, which depend on the voltage applied to the counter.

There are a variety of counters available that provide measurements for alpha and beta particles [12]. Total alpha/beta measurement techniques are applicable to alpha emitters having energy above 3 MeV and beta emitters having energy above 0.1 MeV. The density of the sample should not exceed 10 mg cm^{-2} for total alpha and 20 mg cm^{-2} for total beta. Moisture must be removed from the dried sample because this interferes with the results.

For total alpha/beta measurements, the detector must be calibrated in advance in order to obtain the counting efficiency, namely the ratio of the counting rate to the decay rate. Alpha-emitting radionuclides such as ^{240}Am, ^{230Th}, or ^{238}Pu and beta-emitting radionuclides such as $^{90}Sr/^{90}Y$. These radionuclides are presented as reference standards, which are prepared in geometrically identical samples, and their weights will be used for efficient calibration.

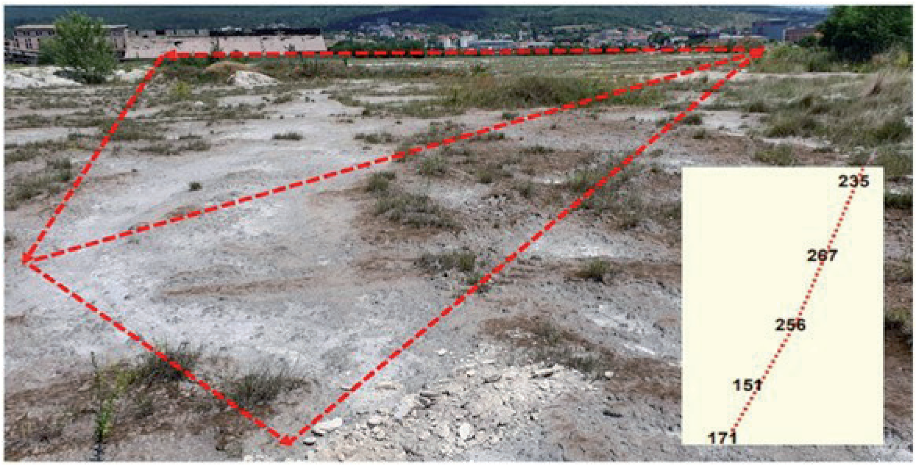
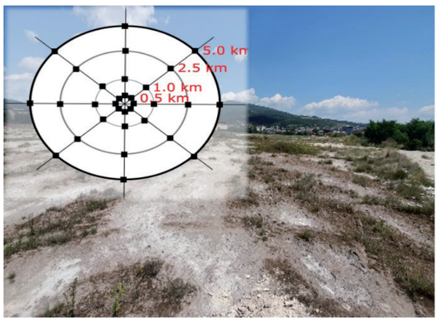
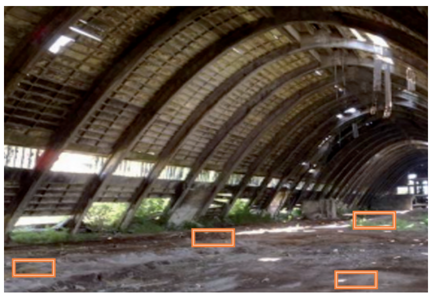


Fig. 2. Measurement of ambient gamma dose rate.

Gamma-Ray Spectrometry Measurements

Gamma-ray measurement techniques are the mainstay for estimating the concentration of radionuclides in environmental samples because most radionuclides emit gamma rays. The most important detectors for detecting and measuring gamma rays are inorganic scintillator detectors, such as NaI(Tl). The measurement was performed with a gamma spectrometer with a NaI(Tl) scintillation detector and with an energy resolution of 7.3% for 661.6 keV (^{137}Cs) and 5.2% for 1172 keV and 1332 keV (^{60}Co) [13, 14]. The activity concentrations of ^{226}Ra were determined by averaging the measured concentrations of ^{214}Pb (295 and 351 keV gamma-ray energies). The activity concentrations of ^{232}Th were determined by averaging the measured concentrations for ^{212}Pb (238 keV gamma-ray energy) [15-17]. In this study, we investigated the premises of the industrial complex "Trepça" - Mitrovica. The radiological impact on the environment and human health of the materials before and after the technological process is assessed. In particular, the samples taken in this study are presented in Table 1. The samples for the phosphogypsum residue (T-2) and from the depot (warehouse) for final phosphate fertilizer products (T-3) were taken in several places, at a depth of up to 0.25 m.

Table 1. Solid samples from the industrial complex "Trepça" - Mitrovica

Research material	Sample ID	Sample foto
Map of Kosovo	Mitrovica	
Sample from the ore	T-1	
Sample from the Phosphogypsum residue	T-2	
Sample from the depot for final phosphate fertilizer products	T-3	

Results and Discussion

Gamma Dose Rate Measurement

The natural background dose rate in the area of the site is 70-80 nSv/h. The results of radiation dose rate measurements for NORM are in the range of 113-285 nSv/h (see Table 2). These results show that the phosphogypsum residue deposition area is characterized by higher radioactivity than the natural background.

We have made 45 measurements: 7 measurements in ore sites, 11 measurements in warehouses for final phosphate fertilizer products, and 27 measurements in the location with phosphogypsum residues (see Table 3). Within a short time, at one point of a material, and calculated the average radiation dose level of that material.

The radiological risk was assessed by determining the annual effective dose, which is calculated by taking a factor of 0.7 Sv/Gy, which calculates the biological effect of the dose to cause damage to human tissues and an outdoor residence time of 20%.

$$E = H T * t * 0.2 * 0.7 \quad (1)$$

E - annual effective dose (Sv)
HT - dose rate level (Gy h-1)
t - time (1 year, or 8,760 hours)
0.2 - the external factor of residence
0.7 - the conversion coefficient (Sv Gy-1)

The experiment site is located in a region with a low natural background. The usual natural background radiation can be estimated to be about 70-80 nSv/h. The resulting dose values ranged from

Table 2. Data of ambient gamma dose rate measurement of natural background, raw material, and residues.

Location: Industrial complex “Trepça” Mitrovica	Sample ID	Distance [m]	Gamma dose rate [nSv/h]	Calculated annual effective dose levels [mSv/year]
Natural background dose rate		1	70-80	
Ore	T-1	0.05	113	0.14
Phosphogypsum residue	T-2	0.05	285	0.35
The depot for final phosphate fertilizer products	T-3	1	150	0.18

Table 3. Measurements and the average value of measurements of the Gamma dose rate [nSv/h]

	Sample ID	Ore	Phosphogypsum residues	The depot for final phosphate fertilizer products	The average value of measurements of the Gamma dose rate [nSv/h]
1	T-1	115			
2	T-1	116			
3	T-1	111			
4	T-1	114			
5	T-1	114			
6	T-1	112			
7	**T-1**	**109**			**113**
8	T-2		189		
9	T-2		171		
10	T-2		151		
11	T-2		256		
12	T-2		267		
13	T-2		235		
14	T-2		268		
15	T-2		310		
16	T-2		323		
17	T-2		292		

Table 3. Continued.

18	T-2		327		
19	T-2		312		
20	T-2		303		
21	T-2		298		
22	T-2		315		
23	T-2		293		
24	T-2		329		
25	T-2		342		
26	T-2		339		
27	T-2		275		
28	T-2		278		
29	T-2		259		
30	T-2		285		
31	T-2		296		
32	T-2		313		
33	T-2		346		
34	**T-2**		**325**		**285**
35	T-3			195	
36	T-3			185	
37	T-3			183	
38	T-3			165	
39	T-3			169	
40	T-3			155	
41	T-3			148	
42	T-3			139	
43	T-3			130	
44	T-3			125	
45	**T-3**			**145**	**158**

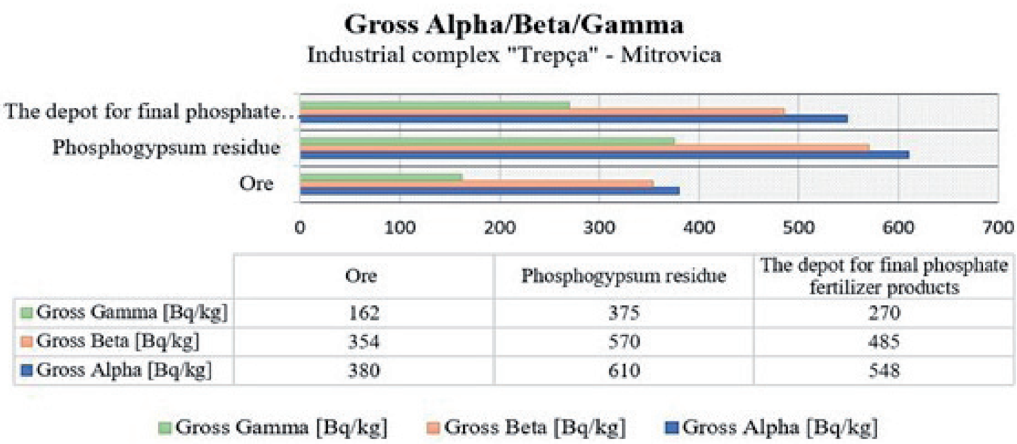


Fig. 3. Presentation of concentration levels of Gross Alpha, Beta, and Gamma.

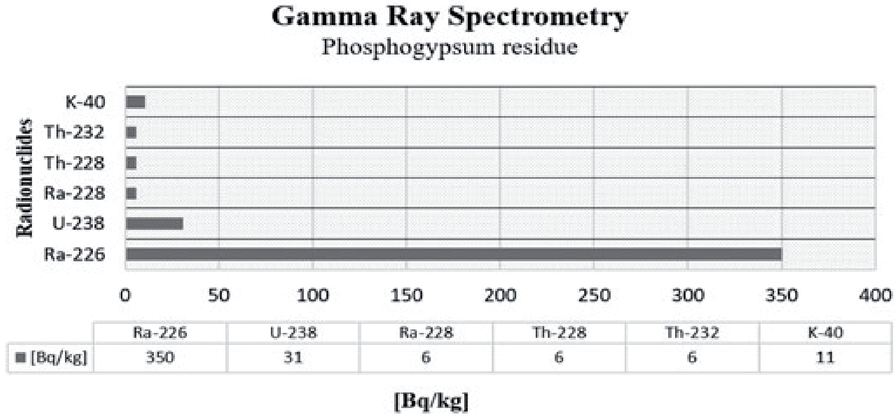


Fig. 4. Activity concentration of radionuclides from phosphogypsum residue [Bq/kg].

Table 4. Presentation of concentration levels of Gross Alpha/Beta and Gamma.

Location: Industrial complex “Trepça” Mitrovica	Sample ID	Gross Alpha [Bq/kg]	Gross Beta [Bq/kg]	Gross Gamma [Bq/kg]
Ore	T-1	380	354	162
Phosphogypsum residue	T-2	610	570	375
The depot for final phosphate fertilizer products	T-3	548	485	270

0.14 mSv-0.35 mSv/year, which is higher than the worldwide average annual effective dose rate of 0.07 mSv/year, but within the global range, which for terrestrial radiation is 0.50 mSv. At the same time, the annual average effective dose worldwide is 2.4 mSv, respectively: Radon-1.20 mSv, internal-0.30 mSv, terrestrial-0.50 mSv, and cosmic-0.40 mSv. The results show that the highest annual doses result from phosphogypsum residues (0.35 mSv/year).

Gross Alpha, Beta, and Gamma Measurements

Samples are analyzed to determine levels of radioactivity, which includes measurements of total alpha, total beta, and total gamma activity. If the screening gives relatively high values, then qualitative and quantitative radiometric analysis of a sample is done. From Table 4, the results show that in the industrial complex “Trepça” - Mitrovica the values of gross alpha range from 380-610 Bq/kg. The lowest values are found in raw materials, while the highest values are found in residues. The highest values are found in the phosphogypsum residue (610 Bq/kg). The total gross beta concentration ranges from 354 Bq/kg-570 Bq/kg, where again the highest values are found in the residues, especially in the residues of phosphogypsum. Finally, the total gross gamma concentration is found to vary from 162 Bq/kg to 375 Bq/kg (Fig. 3).

From these results, it can be seen that in all cases, we have higher levels of technological residues compared to unprocessed material (ore). This justifies the purpose of the objective that, after the technological processes, the enrichment of radioactive materials is possible.

Gamma-Ray Spectrometry Measurements

Taking into account that the measurement values of gamma dose rate, gross alpha, gross beta, and gross gamma for samples were higher in sample residues from the phosphogypsum, we analyzed that sample by means of gamma-spectrometry for these radionuclides: ^{226}Ra, ^{238}U, ^{228}Ra, ^{228}Th, ^{232}Th, and ^{40}K. The results are presented in Fig. 4 and Table 5, with uncertainties corresponding to the 2σ statistical uncertainties.

Based on the results obtained, we see that the concentration levels range from $6^{\pm}1$ Bq/kg (^{228}Th) to 350+30 Bq/kg (^{226}Ra). Therefore, higher levels of ^{226}Ra are found in these phosphogypsum residues, and

Table 5. Concentration of radionuclides from phosphogypsum residue [Bq/kg].

Phosphogypsum residues	Phosphate fertilizer plant of the industrial complex “Trepça” - Mitrovica
Radionuclide	[Bq/kg]
Ra-226	350 ± 30
U-238	31 ± 6
Ra-228	6 ± 1
Th-228	6 ± 1
Th-232	6 ± 1
K-40	11 ± 3

we consider that this radionuclide is responsible for increasing the level of radiation dose in the natural background in their locations [18].

Conclusions

The results of the measurements show that:

The industrial complex "Trepça" - Mitrovica is located in a region with a low natural background. The dose rate in the area of the site is 70-80 nSv/h.

Unprocessed minerals are characterized by relatively low natural radioactivity concentrations. The residues of phosphogypsum deposited in a location near the former processing facilities show an increased gamma dose up to 285 nSv/h.

Relatively higher concentrations of total activities (gross alpha/beta and gamma) are found in technological residues such as phosphogypsum residues (610 Bq/kg, gross alpha).

The activity concentrations of ^{226}Ra, ^{238}U, ^{228}Ra, ^{228}Th, ^{232}Th, and ^{40}K in the sample from the phosphogypsum residue are higher than 200 Bq/kg; ^{226}Ra has activity of 350±30 Bq/kg.

In Table 5, the concentration of radionuclides from phosphogypsum residues in Bq/kg is represented. The results of the gamma-spectrometric analysis show that the radionuclides of the ^{232}Th series are in decay equilibrium. Therefore, ^{232}Th can be estimated as the average of ^{228}Ra and ^{228}Th.

Processing results in phosphogypsum as residue, which contains ^{226}Ra, or fertilizer as a product containing concentrations of uranium ^{238}U up to values of 31 + 6 Bq/kg.

Phosphogypsum residue contains radionuclides, especially radon gas. Practically all ^{226}Ra is incorporated into phosphogypsum and becomes the main source of radioactivity.

Based on the results presented, we can conclude that the relevant radiological risk for workers at the location of the phosphate fertilizer plant of the industrial complex "Trepça" – Mitrovica, may result from phosphogypsum residues. It is also possible to contaminate underground water with radionuclides because, as is known, radium (Ra) is very soluble in water [19].

The results obtained from the research reflect the situation of a recent period of time, and any changes in raw materials or changes in technological processes can significantly change the activities of the materials and therefore should be investigated.

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Conflict of Interest

The authors declare no conflict of interest.

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