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Measuring and modelling the radiological impact of a phosphogypsum deposition site on the surrounding environment

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Phosphogypsum (PG) is a waste product (residue) from the production of phosphoric acid characterized by technologically enhanced natural radioactivity. Croatia's largest PG deposition site is situated at the edge of Lonjsko Polje Nature Park, a sensitive ecosystem possibly endangered by PG particles. This field study investigates two aspects relevant for the general radiological impact of PG: risk assessment for the environment and risk assessment for occupationally exposed workers and local inhabitants. Activity concentrations of natural radionuclides (^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K) were measured in the PG (at the deposition site), soil, and grass samples (in the vicinity of the site). The ERICA Assessment Tool was used to estimate the radiological impact of PG particles on non-human biota of the Lonjsko Polje Nature Park. The average annual effective dose for occupationally exposed workers was 0.4 mSv which was within the worldwide range.

KEY WORDS: *dose assessment; ERICA Tool; occupational dosimetry; radioactivity*

Phosphogypsum (PG) is a Naturally Occurring Radioactive Material (NORM) generated as a waste product during the "wet process" of phosphoric acid production (1-3). PG radioactivity originates from the natural radioactivity of phosphate ore – a raw material used in the production. PG contains different quantities of natural radionuclides, mostly ^{226}Ra, which incorporate into it during phosphate ore processing (4). As a waste product, PG is usually deposited near factories; however, during the last decade, investigations have focused on its use in agriculture, as building material, and as backfill for road construction (2, 4, 5-9). The Republic of Croatia has only one PG deposition site, located at the edge of the Lonjsko Polje Nature Park. So far, ~4 million tonnes of PG have been deposited there (10). In 2009, the production of phosphoric acid ceased, barring any new PG deposition. However, the plundering of PG with machinery continues and this may lead to exposure for the workers.

Investigations on the spread of PG from this deposition site to the environment were performed recently (11). The results showed that PG particles spread across the surroundings of the deposition site. Therefore, higher activity concentrations of natural radionuclides were to be expected in the soil and biota sampled outside the very site..

The specific location of the deposition site required a close examination of the surrounding ecosystem. Natural radionuclides in PG may affect the complex ecosystem of the Lonjsko Polje Nature Park, which is home to different wild and domestic animals that graze in the vicinity of the site on a daily basis, as the site is not fenced. Also, doses originating from the natural radionuclides in PG may cause health problems for occupationally exposed workers as well as the local population since there is a village about 200 m from the site. Apart from radioactivity, chemical compounds, trace elements, as well as PG acidity are also reason for concern (3).

Due to the specific location of the site and the quantity of the PG, continuous and thorough investigations of the deposition site and its surroundings are vital. The general objective should be to preserve the stability of the specific ecosystem surrounding the site as well as protect the health of the workers. This study aims to contribute to this goal.

MATERIALS AND METHODS

Study design

The present study examined the activity concentrations of natural radionuclides (^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K) measured in 15 surface and 20 in-depth PG samples. In addition, soil and grass samples from various locations

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on the earth embankment dam surrounding the site were analyzed. The results were compared to measurements of radioactivity in soil samples from the Zagreb region (NW Croatia) (12, 13).

The nearby area of the PG deposition site is used by local inhabitants for pasture (cattle and sheep). The most important pathway of animal contamination by radionuclides is through the ingestion of contaminated soil and feed. Ingestion of feed gives the highest contribution to animal contamination since the availability of radionuclides from ingested soil is low (14). To evaluate the suitability of the studied area for pasture, an assessment of radionuclide transfer from grass to animal products (milk and meat) was done using concentration ratios provided by the International Atomic Energy Agency (IAEA) (15).

The radiological risk of PG on non-human biota in the vicinity of the deposition site was estimated by the ERICA (Environmental Risk from Ionizing Contaminants: Assessment and Management) Assessment Tool. This software enables the assessment of radiological risk from ionising radiation to wildlife by calculating dose rates received by different groups of animals and plants – so-called reference animals and plants. This includes a database of default radionuclides, distribution coefficients, concentration ratios, and dose conversion coefficients that enable dose rate calculations from input data. Also, the software is able to identify radionuclides that contribute to the dose rate the most as well as the most exposed organisms (16-19). It is important to note that, within the ERICA Tool, the list of reference organisms is formed by amalgamating terrestrial ecosystems into a single representative semi-natural ecosystem. ERICA uses default geometries of the corresponding reference organisms proposed by the ICRP (20). Hence, reference organisms do not directly represent specific animal or plant species in the ecosystem under consideration. In addition, the ERICA Tool includes a number of methods for addressing various types of uncertainties during ecological risk assessment (21). Different tiers can have different approaches to dealing with uncertainties. In Tier 2, (the screening tier) the uncertainties can be large, so quantitative uncertainty analysis is impossible, hence conservative estimates and assumptions result in a worst-case estimate of risk and ensure that exposure, even if uncertain, is overestimated (21).

The determined activity concentrations of soil and grass in the vicinity of the PG deposition site were used as input parameters for dose assessment to terrestrial animals and plants within the Tool. All of the reference animals and plants available within the software were selected for screening possible radiological risks to the terrestrial biota.

Since PG is widely used as an additive in building and construction industry, and the planning of remediation of the site is in progress, the radiological effects of PG were estimated by calculating the radium equivalent index (Ra_{eq}), activity concentration index (I), external absorbed dose rate ($\dot{D}$), and annual effective dose (E).

Sampling site

The studied deposition site (Figure 1) is located in the central part of Croatia, at the edge of the Lonjsko Polje Nature Park, some 4 km south from a fertilizer plant (45°26'38.67'' N and 16°44'40.76'' E).

The deposition site is not fenced and, although there is a surveillance on site, animals and humans can walk on the site and the earth embankment dam freely.

The waste pile has a surface area of 1.6 km² and an average depth of 4 m.

Workers use machinery to plunder the deposited PG on a daily basis.

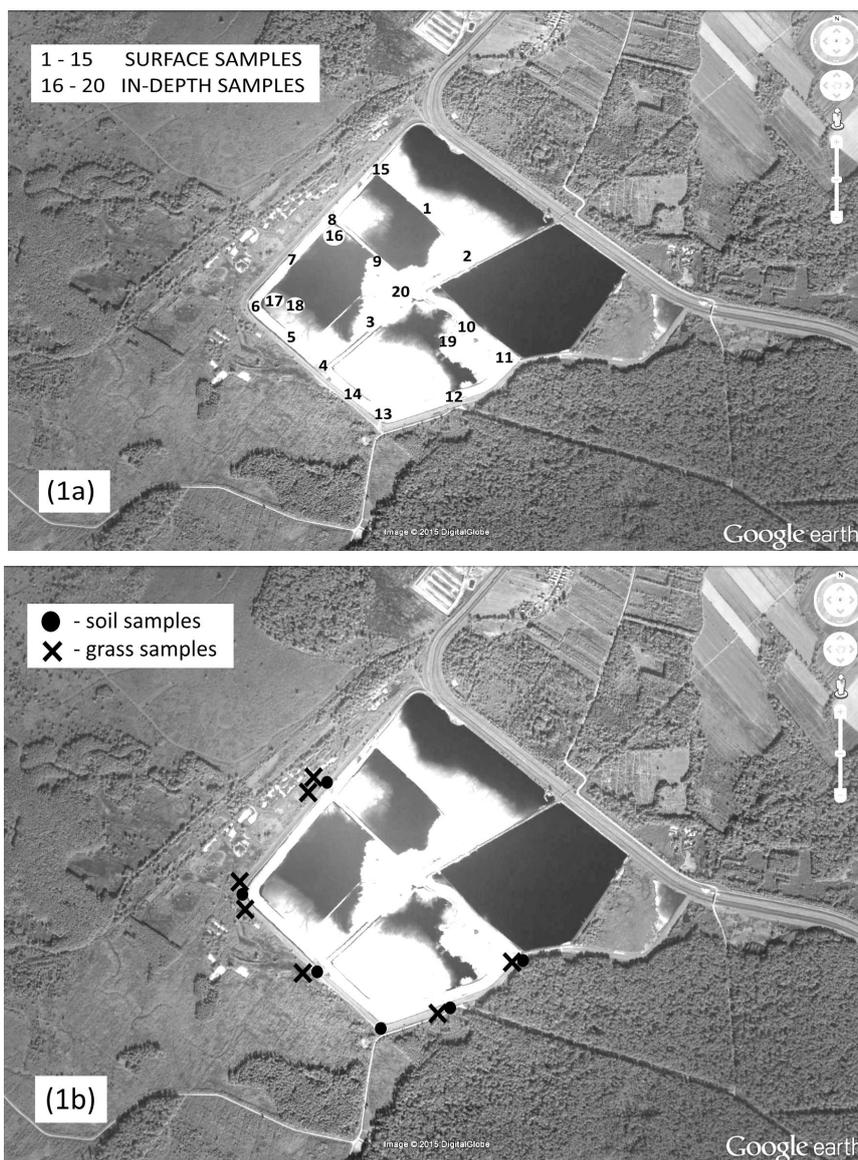## Sample collection, preparation, and measurements

PG samples were collected at the deposition site according to Figure 1a. The measurement grid was set to cover most of the surface of the deposition site. Since PG is constantly plundered and moved from one side of the pile to another, it was important to measure the radioactivity of both surface and in-depth samples to get better overall status of the activity concentrations thorough the pile.

Surface samples (0-20 cm) were collected at 15 locations, while in-depth samples were collected at 50, 100, 150, and 200 cm at 5 locations.

The samples were dried at 105 °C for 24-72 h and packed in Marinelli beakers of 1 L. Soil and grass samples were collected across the earth embankment dam according to Figure 1b. Soil samples were collected from an uncultivated surface using a corer tool (Ø=10 cm; 10 cores; depth 20 cm) from a surface area of 1 m², sieved (2 mm), dried at 105 °C for 3 days and ashed at 450 °C. Soil samples were packed in Marinelli beakers of 1 L. Grass samples were cut 5 cm above the ground, dried at 105 °C for 24 hours and ashed at 450 °C. The samples were packed in sealed plastic cylindrical containers of 100 or 200 mL.

All of the samples were stored for at least 30 days to allow the re-establishment of secular equilibrium conditions between ²²⁶Ra and its short-lived decay products. All sampling and sample preparation were performed according to the standardized procedures of the IAEA (22). The measurement time was set to at least 24 h.

The samples were gamma-spectrometrically analysed in the laboratory using an HPGe detector (ORTEC, USA) (FWHM 2.24 keV at 1.33 MeV ⁶⁰Co and relative efficiency of 74.2 % at 1.33 MeV ⁶⁰Co). The detector was calibrated using sources supplied by the Czech Metrological Institute covering an energy range between 40 and 2000 keV (23). ²²⁶Ra was determined using the photopeak of its daughter nuclide ²¹⁴Bi at 609.32, 1120.28, and 1764.51 keV. ²³⁸U was determined from ²³⁴Th at 63.29, 92.38, and 92.80 keV. ²³⁵U was calculated from ²³⁸U and directly at 185.72 keV. ²³²Th was determined using 209.40, 338.40, 911.07, 964.60, 968.90, and 1587.90 keV emissions from ²²⁸Ac. ²¹⁰Pb and ⁴⁰K were calculated directly from 46.52 keV and 1460.75 keV, respectively.

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Figure 1 *Phosphogypsum sampling locations at the deposition site (1a); soil and grass sampling locations surrounding the phosphogypsum deposition site (1b) (Google Earth, 2014)*

Quality assurance was implemented through international inter-calibration programmes organized by the IAEA, World Health Organization (WHO), and Joint Research Centre (JRC). The applied method has been officially accredited according to the ISO/IEC 17025 Standard.

Estimation of radiological risk on non-human biota

Tier 2 from the ERICA Assessment Tool was used. Key differences in the tiered approach (there are 3 tiers in the ERICA Tool) are flexibility in calculations, data requirements, and the provision of concomitant contextual information (16). The purpose of Tier 2 is to identify and screen out situations with low probability of significant radiological impact on non-human biota (16, 24). It was therefore used for the calculation of the radiation exposure dose rate for terrestrial organisms due to radionuclide

content of the soil and grass in the vicinity of the PG deposition site. As input data, average soil and grass activity concentrations for specific radionuclides were used, since field data did not show high diversity in activity concentrations between sampling points. Inputs of the best estimated activity concentrations for media and organisms are also recommended by the software guidance document for Tier 2 (25). In the software database, there is no data for ^{40}K; therefore it was excluded from the calculation. All of the terrestrial reference organisms were included in the assessment. A dose rate of 10 μGy h^{-1} was used as the screening confidence level below which radiological risks are negligible (26). This value is lower than the value proposed by the IAEA (27) and UNSCEAR (28) for terrestrial animals (40 μGy h^{-1}). The ratio between the estimated total dose rate for reference organisms, tand the selected screening dose rate produces a risk quotient (*RQ*)

for each organism included in the assessment (16). Other parameters were left at their default values: concentration ratios for reference organisms (other than grass and herbs), occupancy factors, radiation weighting factors, and uncertainty factor.

Estimation of radiological effect on workers and the general population

The radiological effect of phosphogypsum and soil on occupationally exposed workers and the local population was calculated through the radium equivalent index, activity concentration index, external absorbed dose rate, and annual effective dose.

The radium equivalent index (Ra_{eq}) is used to define a uniform value in respect to radiation exposure. It is used to present the radioactive hazard of building materials and is calculated using the following formula (29, 30):

$$Ra_{eq} = A_{Ra} + 1.43 A_{Th} + 0.077 A_K \qquad (1)$$

where A_{Ra}, A_{Th} and A_K (in Bq kg^{-1}) are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K, respectively. The weights are based on the estimation that 370 Bq kg^{-1} of ^{226}Ra, 259 Bq kg^{-1} of ^{232}Th, and 4810 Bq kg^{-1} of ^{40}K produce the same gamma ray dosage (30, 31).

The activity concentration index (I) for the gamma radiation emitted by building materials must be less than unity in order to keep the radiation hazard insignificant, i.e. the annual radiation exposure due to the radioactivity from building materials is limited to 1 mSv. European Council Directive 2013/59/EURATOM (32) defines I as follows:

$$I = \frac{A_{Ra}}{300 Bq/kg} + \frac{A_{Th}}{200 Bq/kg} + \frac{A_K}{3000 Bq/kg} \leq 1 \quad (2)$$

The guidelines provided by UNSCEAR (33) provide the absorbed dose rates ($\dot{D}$) in nGy h^{-1} due to gamma radiation in air at 1 m above the ground for uniform distribution of naturally occurring radionuclides (^{226}Ra, ^{232}Th, and ^{40}K). The absorbed dose rates are calculated as follows:

$$\dot{D} = 0.462 A_{Ra} + 0.621 A_{Th} + 0.0417 A_K \qquad (3)$$

The annual effective dose (E) in mSv was calculated according to UNSCEAR (33):

$$E = \dot{D}(nGy h^{-1}) \times 8760 (h yr^{-1}) \times 0.2 \times 0.7 (Sv Gy^{-1}) \quad (4)$$

where 0.7 Sv Gy^{-1} is the conversion coefficient from the absorbed dose in air to the effective dose received by adults, while 0.2 is the outdoor occupancy factor.

Additionally, the transfer of radionuclides from grass grown in the studied area to animal products, meat and milk, was assessed by concentration ratios (CR). The CR is the ratio of the radionuclide activity in a food product (Bq kg^{-1}

f.w.) divided by the radionuclide concentration in feed (Bq kg^{-1} dry matter). It is useful in field studies because the dietary intake does not need to be calculated (15). Therefore, our assumption was that animals were fed solely by the grass grown at the investigated location. The average activity concentrations of radionuclides in grass were used. Since the IAEA (15) does not include data on CR for ^{226}Ra in cow's milk, the transfer coefficients (F_m) and daily dry matter intake values were applied, according to the IAEA (14). The transfer of ^{232}Th from grass to milk was not assessed due to a lack of available data, as was also the case with the transfer of ^{226}Ra to sheep milk.

RESULTS AND DISCUSSION

The impact of the phosphate industry on the natural environment is the focus of investigations worldwide. The specific location of the studied deposition site also calls for a close examination of the surrounding ecosystem.

The data presented here might be of relevance for the scientific community dealing with radioecological assessments. By using the ERICA Tool, the radiological risk to biota could be assessed regardless of obtained knowledge on the activity concentrations of radionuclides in the analysed samples. A similar approach was also used in previous studies (19, 34).

One of the main reasons for adopting such a study approach was the fact that some of the plans regarding the future management of this deposition site include its possible remediation; through the use of PG as a building material in road construction and in gypsum board production. Therefore, we used a conservative approach of calculating the risks for local inhabitants, workers, animals, and biota.

Activity concentrations

To extend the investigations covered by our previous publication (11) which reports the extent of the PG spread, the present study focused only on the natural radionuclides ^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K, which we found important for the assessments.

The activity concentrations of ^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K measured in PG, soil, and grass samples are shown in Table 1. Activity concentrations of ^{226}Ra in PG varied from 507±12 Bq kg^{-1} to 1054±22 Bq kg^{-1} in surface samples and 473±9 Bq kg^{-1} to 1626±29 Bq kg^{-1} in the in-depth samples. Usually, the activity concentrations of ^{226}Ra vary depending on the origin of the phosphate rock used in the process. The results obtained in this study are in accordance with the investigations of PG radioactivity in samples from phosphate industries in other countries that use phosphate rock of sedimentary origin (1, 3, 4, 35).

The values of activity concentrations of natural radionuclides in soil samples for all of the analysed natural radionuclides except for ^{226}Ra were similar or higher than

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Table 1 *Activity concentrations (Bq kg⁻¹) of natural radionuclides in phosphogypsum (PG), soil, and grass samples*

	Activity concentrations (Bq kg⁻¹)			
	PG samples		soil samples	grass samples
Radionuclide	Surface samples (n=15)	in-depth samples (n=20)		
^{238}U	104±7 (46-172)	125±10 (70-207)	62.6±0.6 (52-76)	0.93±0.04 (0.2-1.9)
^{235}U	7.9±0.4 (3-21)	10.5±0.5 (5-16)	3.23±0.05 (3-4)	0.46±0.02 (0.2-0.8)
^{232}Th	7.5±0.3 (4-14)	8.4±0.3 (3-15)	54.2±0.1 (44-68)	0.94±0.03 (0.3-1.5)
^{226}Ra	757±4 (507-1054)	962±4 (473-1626)	57.1±0.8 (44-69)	1.80±0.02 (0.9-4.4)
^{210}Pb	746±7 (532-1281)	865±18 (401-1089)	57±1 (40-80)	21.6±0.4 (15-29)
^{40}K	12.7±0.6 (7-23)	12.5±0.5 (10-17)	663±1 (601-774)	491±1 (157-779)

ᵃthe range is given in parentheses and the errors of the range are of the order up to 15 %

those in soil samples from the Zagreb region (12, 13). If we compare the results with investigations from other countries (2, 4, 36, 37), most of the values from this study were within the range of those obtained in other countries (10-99 Bq kg⁻¹; 16-44 Bq kg⁻¹; 12-54 Bq kg⁻¹; 9-99 Bq kg⁻¹, and 54-627 Bq kg⁻¹ for ^{238}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K, respectively).

The activity concentrations of natural radionuclides in grass samples collected at the earth embankment dam showed that the average values were comparable with grass samples for the Zagreb region for all natural radionuclides (12). Also, the values are comparable with investigations conducted in other countries (2, 36).

Radiological effects on non-human biota

The results of the radiological risk assessment performed with the ERICA Tool are shown in Table 2 and Figures 2a and 2b. The total dose rates (internal and external) for all of the radionuclides measured in soil and grass (^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, and ^{210}Pb, except for ^{40}K) are presented in Table 2. Dose rates for all of the reference organisms were lower than the selected screening dose rate limit of 10 μGy h⁻¹. The maximum dose rates were estimated for lichen and bryophytes (1.97 μGy h⁻¹), and minimum for trees (0.03 μGy h⁻¹). Total dose rates for specific radionuclides and reference organisms are shown in Figure 2a. It is evident that the most important contributor to the total dose rate was ^{226}Ra (91 %). ^{226}Ra is a radionuclide with higher dose conversion coefficients, especially for internal alpha radiation.

All of the studied radionuclides showed maximum dose rates for lichen and bryophytes, which confirms their unique role as bioindicators of radioactive contamination (38).

The expected risk quotient (*RQ*) values are shown in Figure 2b. The expected *RQ* for reference terrestrial organisms in the area of investigation was low (the highest *RQ*<0.2). Together with the uncertainty factor, it indicates

that there was a less than 5 % probability that the absorbed dose rate to any organism will exceed the screening dose rate.

Based on these results, it could be concluded that the spread of PG particles from the investigated PG deposition site into the environment did not affect the terrestrial environment in such a way that would raise concerns from the radioecological point of view (the highest calculated value was five times lower than the set screening dose rate limit).

Radiological effect on workers and general population

Using values obtained from measurements of activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K, the radium equivalent

Table 2 *Total dose rates (μGy h⁻¹) to reference terrestrial organisms estimated using ERICA Tool*

Organism	Total dose rate per organism (μGy h⁻¹)
Amphibian	0.30
Bird	0.32
Bird egg	0.30
Detritivorous invertebrate	0.79
Flying insects	0.75
Gastropod	0.42
Grasses & Herbs	0.09
Lichen & bryophytes	1.97
Mammal (Deer)	0.22
Mammal (Rat)	0.25
Reptile	0.30
Shrub	0.24
Soil Invertebrate (worm)	0.78
Tree	0.03
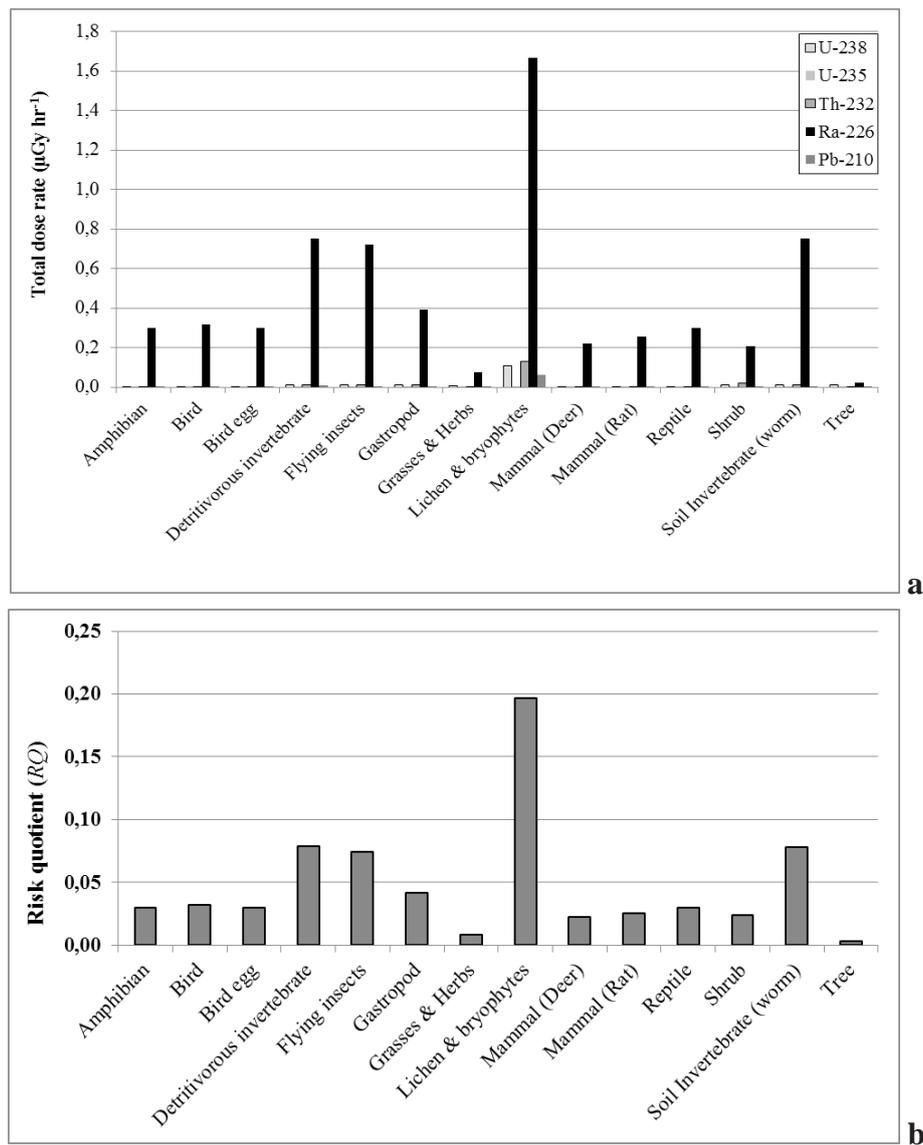
Figure 2 *Total dose rates for specific radionuclides and reference animals and plants (a) and expected risk quotient (RQ) for reference terrestrial organisms (b) calculated with the ERICA Tool*

index, activity concentration index, absorbed dose rates, and annual effective doses from PG were calculated and summarized in Table 3.

The radium equivalent index for PG samples was calculated using equation (1). Both minimal (146 Bq kg^{-1}) and maximal (1649 Bq kg^{-1}) Ra_{eq} values were calculated from in-depth samples (2 m depth). The wide range of Ra_{eq} values could have resulted from the deposited PG, which originates from phosphate ores of different radioactivity; therefore, the diversity in the distribution of the Ra_{eq} values was expected. Except for one location (146 Bq kg^{-1}), all of the Ra_{eq} values exceeded the threshold value of 370 Bq kg^{-1}.

As seen from Table 3, the average value for the activity concentration index (2.53 and 2.73 for surface and in-depth samples, respectively) exceeded unity. We have concluded that PG by itself must not be used as a material for building. However, if PG was to be mixed with other materials (not

NORM) and the resulting composite achieved $I<1$, it could be used as such.

The calculated absorbed dose rates were high. The average value for surface samples was 350 nGy h^{-1} and for in-depth samples 380 nGy h^{-1} with a range of up to 761 nGy h^{-1}. These results are in accordance with earlier direct dose rate measurements conducted on the same deposition site using electronic dosimeters (11). However, all of the calculated annual effective dose values were lower than reported in UNSCEAR (33). Figures 3a and 3b show the annual effective doses for surface and in-depth samples, respectively. The values ranged from 0.08 to 0.93 mSv. The worldwide average annual effective dose is 0.43 mSv, with the results for individual countries being within the range of 0.3-0.6 mSv (33). As seen in Figure 3a, almost all of the surface samples were within the range of 0.3-0.6 mSv (dotted lines), while some annual effective doses calculated for in-depth samples (Figure 3b) slightly exceeded the

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Table 3 *Phosphogypsum (PG) and soil samples (SS) – average values for radium equivalent index (Ra$_{eq}$), activity concentration index (I), absorbed dose rate ($\dot{D}$), and annual effective dose (E)*

		Ra$_{eq}$(Bq kg^{-1})[a]	*I*[a]	$\dot{D}$ (nGy h^{-1})[a]	*E* (mSv y^{-1})[a]
PG	surface samples (n=15)	758 (512-1068)	2.53 (1.71-3.56)	350 (237-493)	0.43 (0.29-0.60)
	in-depth samples (n=20)	822 (146-1649)	2.73 (0.49-5.50)	380 (67-761)	0.47 (0.08-0.93)
SS	earth embankment dam (n=6)			90 (78-109)	0.11 (0.1-0.13)

[a]*The range is given in parentheses*
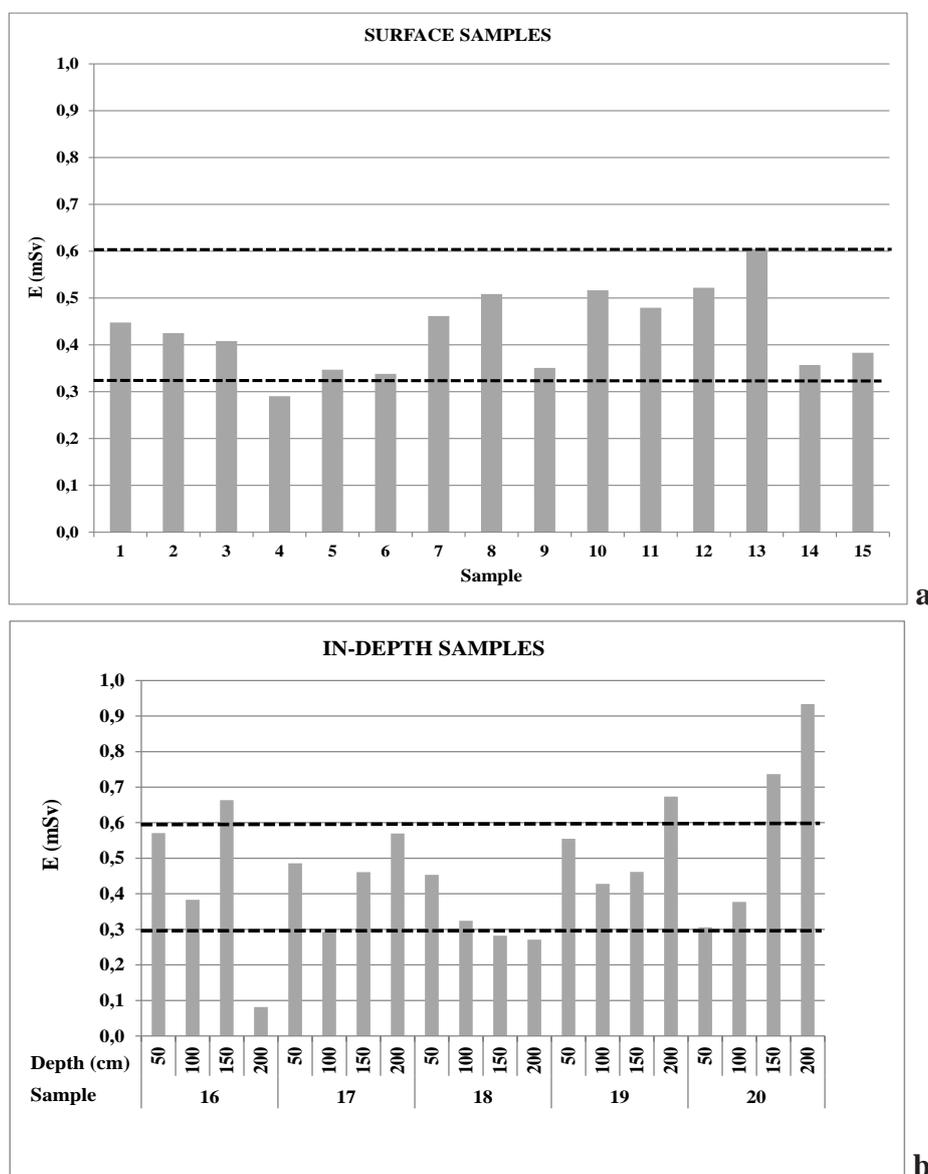
Figure 3 *Annual effective doses (E, mSv) of phosphogypsum surface samples (a) and of phosphogypsum in-depth samples (b). The dotted lines represent the worldwide range*

Table 4 *Calculated activity concentrations of different radionuclides in meat and milk of animals that graze in the vicinity of the phosphogypsum deposition site*

Radionuclide	Meat (Bq kg^{-1} f.w.)		Milk (Bq L^{-1})	
	Cattle	Sheep	Cattle	Sheep
^{238}U	0.3	0.3	0.005	0.005
^{235}U	0.2	0.2	0.002	0.002
^{232}Th	0.006	0.006	n.d.[a]	n.d.[a]
^{226}Ra	0.3	0.3	0.01	0.01
^{210}Pb	1.7	0.3	0.05	0.6

[a]*n.d.-there are no data on transfer from animal feed to milk for ^{232}Th*

worldwide averages. The risk for occupationally exposed workers could be significant; however, since plundering PG with machinery is not performed on an hourly basis, the workers are not exposed constantly.

The radiological effects were also calculated for soil samples collected from the earth embankment dam surrounding the PG deposition site (Table 3). The results showed lower values for Ra_{eq} and I (<1 in all samples).

Dose rates and annual effective doses were lower compared to world averages. There is no radiation hazard for occupationally exposed workers. Compared to the soil samples from the Zagreb region (0.07 mSv), the calculated doses were slightly higher, which could be explained by the spread of PG particles across the earth embankment dam (11).

This study did not calculate the inhalation dose for occupational workers, because according to the ICRP (39) such a calculation is generally recommended for particles 1 and 5 μm in diameter. Considering that the average PG particle size was ~40 μm, they were likely withheld in the upper part of the respiratory tract.

The results of radionuclide transfer from grass to animal products are shown in Table 4. Maximum activity concentrations in meat were calculated for ^{210}Pb in cattle meat (1.7 Bq kg^{-1} f.w.), and minimum for ^{232}Th (0.006 Bq kg^{-1} f.w.). Values for ^{238}U, ^{235}U, and ^{226}Ra were similar in both cattle and sheep meat. For milk, the maximum activity concentration was calculated for ^{210}Pb in sheep milk (0.6 Bq L^{-1}), and minimum for ^{235}U (0.002 Bq L^{-1}) in cattle and sheep milk.

Due to the lack of data on natural radionuclides in local meat and milk, we compared our results data from other sources and established that they are reasonably similar (40-42). Also, they are below the internationally maximum permitted levels of radioactive contamination in foodstuffs and below or similar to the proposed safe values of radionuclides in food and feed (43). It can therefore be concluded that the area surrounding the PG deposition site is suitable for agricultural use, e.g. for pasture.

CONCLUSIONS

The allocation of a deposition site near an ecologically sensitive environment is not specific to Croatia. PG is commonly deposited worldwide in rivers, sea water, lakes, near forests, etc. (1, 2, 4, 44).

This study covered measurements of activity concentrations for natural radionuclides (^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{40}K) in soil, PG, and grass samples. Results showed that activity concentrations in PG vary with the origin of the phosphate rock used in production, which is in accordance with investigations performed in other countries. The PG deposited at the studied location cannot be used as a building material by itself. However, if it is mixed with other materials and the resulting composite has I<1, it could. The average annual effective dose for occupationally exposed workers (with regard to the time spent on the site) was 0.4 mSv, which is within the worldwide range. Some annual effective doses calculated for in-depth samples exceeded worldwide averages due to differences in activity concentrations of the deposited PG.

It must be noted, however, that due to uncertainties arising from estimations and assumptions our conclusions are conservative estimates and can only serve for screening purposes.

REFERENCES

1. Abril JM, Garcia-Tenorio R, Manjon G. Extensive radioactive characterization of a phosphogypsum stack in SW Spain: ^{226}Ra, ^{238}U, ^{210}Po concentrations and ^{222}Rn exhalation rate. J Hazard Mater 2009;164:790-7. doi: 10.1016/j.jhazmat.2008.08.078

Bituh T, et al. Measuring and modelling the radiological impact of a phosphogypsum deposition site on the surrounding environment
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2. Al Attar L, Al-Oudat M, Kanakri S, Budeir Y, Khalily H. Radiological impact of phosphogypsum. J Eviron Manage 2011;92:2151-8. doi: 10.1016/j.jenvman.2011.03.041

3. Rutherford PM, Dudas MJ, Samek RA. Environmental impact of phosphogypsum. Sci Total Environ 1994;149:1-38. doi: 10.1016/0048-9697(94)90002-7

4. Papastefanou C, Stoulos S, Ioannidou A, Manolopoulou M. The application of phosphogypsum in agriculture ant the radiological impact. J Environ Radioact 2006;89:188-98. doi: 10.1016/j.jenvrad.2006.05.005

5. Degirmenci N, Okucu A, Turabi A. Application of phosphogypsum in soil stabilization. Build Environ 2007;42:3393-8. doi: 10.1016/j.buildenv.2006.08.010

6. Fuding M, Jiaojiao H, Zude L. Research on activity characteristics on composite cementitious materials based on phosphogypsum. Procedia Engin 2012;43:9-15. doi: 10.1016/j.proeng.2012.08.003

7. Kuryatnyk T, Angulsky da Luz C, Ambroise J, Pera J. Valorization of phosphogypsum as hydraulic binder. J Hazard Mater 2008;160:681-7. doi: 10.1016/j.jhazmat.2008.03.014

8. Reijnders L. Cleaner phosphogypsum, coal combustion ashes and waste incineration ashes for application in building materials: A review. Build Environ 2007;42:1036-42. doi: 10.1016/j.buildenv.2005.09.016

9. Zhou J, Gao H, Shu Z, Wang Y, Yan C. Utilization of waste phosphogypsum to prepare non-fired bricks by novel Hydration-Recrystallization process. Constr Build Mater 2012;34:114-9. doi: 10.1016/j.conbuildmat.2012.02.045

10. Bituh T, Marović G, Franić Z, Senčar J, Bronzović M. Radioactive contamination in Croatia by phosphate fertilizer production. J Hazard Mater 2009;162:1199-203. doi: 10.1016/j.jhazmat.2008.06.005

11. Bituh T, Vučić Z, Marović G, Prlić I. A new approach to determine the phosphogypsum spread from the deposition site into the environment. J Hazard Mater 2013;261:584-92. doi: 10.1016/j.jhazmat.2013.08.012

12. Marović G. Praćenje stanja radioaktivnosti životne sredine u Republici Hrvatskoj, Izvještaj za 2011. godinu. [Results of environmental radioactivity monitoring in the Republic of Croatia. Annual Report 2011, in Croatian]. Zagreb: Institute for Medical Research and Occupational Health; 2012.

13. Šoštarić M, Petrinec B, Babić D. ^{137}Cs u tlu i oborini Zagrebačke regije [^{137}Cs in soil and fallout of the Zagreb region, in Croatian]. In: Knežević Ž, Majer M, Krajcar Bronić I, editors. Proceedings of the Ninth Symposium of the Croatian Radiation Protection Association; 10-14 Apr 2013; Krk, Croatia. Zagreb: HDZZ-CRPA; 2013. p. 395-400.

14. International Atomic Energy Agency (IAEA). Quantification of Radionuclide Transfer in Terrestrial and Freshwater Environments for Radiological Assessments. TECDOC Series No 1616. Vienna: IAEA; 2009.

15. International Atomic Energy Agency (IAEA). Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments. Technical Report Series 472. Vienna: IAEA; 2010.

16. Brown JE, Alfonso B, Avila R, Beresford NA, Copplestone D, Prohl G, Ulanovsky A. The ERICA Tool. J Environ Radioact 2008;99:1371-83. doi: 10/1016/j.jenvrad.2008.01.008

17. Mrdakovic Popic J, Salbu B, Skipperud L. Ecological transfer of radionuclides and metals to free-living earthworm species in natural habitats rich in NORM. Sci Total Environ 2012;414:167-76. doi: 10.1016/j.scitotenv.2011.10.064

18. Oughton DH, Stromman G, Salbu B. Ecological risk assessment of Central Asian mining sites: application of the ERICA assessment tool. J Environ Radioact 2013;123:90-8. doi: 10.1016/j.jenvrad.2012.11.010

19. Petrinec B, Štrok M, Franić Z, Smodiš B, Pavičić-Hamer D. Radionuclides in the Adriatic sea and related dose-rate assessment for marine biota. Radiat Prot Dosim 2013;154:320-30. doi: 10.1093/rpd/ncs234

20. International Commission on on Radiological Protection (ICRP). Environmental Protection: the Concept and Use of Reference Animals and Plants. 2008 ICRP Publication 108. Ann ICRP 2008;38(4-6).

21. Oughton DH, Aguero A, Avila R, Brown JE, Copplestone D, Gilek M. Addresing uncertainties in the ERICA integrated approach. J Environ Radioact 2008;99:1384-92. doi: 10.1016/j.jenvirad.2008.03.005

22. International Atomic Energy Agency (IAEA). Measurement of Radionuclides in Food and the Environment. Technical Report Series No 295. Vienna: IAEA; 1989.

23. Petrinec B, Franić Z, Bituh T, Babić D. Quality assurance in gamma-ray spectrometry of seabed sediments. Arh Hig Rada Toksikol 2011;62:17-23. doi:10.2478/10004-1254-62-2011-2078

24. Wood MD, Marshall WA, Beresford NA, Jones SR, Howard BJ, Copplestone D, Leah RT. Application of the ERICA Integrated Approach to the Drigg coastal sand dunes. J Environ Radioact 2008;99:1484-95. doi:10.1016/j.jenvrad.2008.03.008

25. Beresford N, Brown J, Copplestone D, Garnier-Laplace J, Howard BJ, Larsson C-M, Oughton D, Pröhl G, Zinger I. D-ERICA: An INTEGRATED APPROACH to the assessment and management of environmental risks from ionising radiation. 2007 [displayed 20 February 2015]. Available at https://wiki.ceh.ac.uk/download/attachments/115017395/D-Erica.pdf

26. Anderson P, Garnier-Laplace J, Beresford NA, Copplestone D, Howard BJ, Howe P, Oughton D, Whitehouse P. Protection of the environment from ionizing radiation in a regulatory context (protection): proposed numerical benchmark values. J Environ Radioact 2009;100:1100-8. doi: 10.1016/j.jenvrad.2009.05.010

27. International Atomic Energy Agency (IAEA). Effects of Ionizing Radiation on Plants and Animals at Levels Implied by Current Radiation Protection Standards. Technical Report Series No. 332. Vienna: IAEA; 1992.

28. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Sources and Effects of Ionizing Radiation. Report to the general assembly with scientific annex A/AC.82/R.54. New York: United Nations; 1996.

29. Hirchi H, Baccouche S, Belgaied JE. Evaluation of radiological impacts of tenorm in the Tunisian petroleum industry. J Environ Radioact 2013;115:107-13. doi: 10.1016/j.jenvrad.2012.07.012

30. Szabo Zs, Volgyesi P, Nagy HE, Szabo Cs, Kis Z, Csorba O. Radioactivity of natural and artificial building materials – a comparative study. J Environ Radioact 2013;118:64-74. doi: 10.1016/j.jenvrad.2012.11.008

31. Farai IP, Ademola JA. Radium equivalent activity concentrations in concrete building blocks in eight cities in

40

Bituh T, et al. Measuring and modelling the radiological impact of a phosphogypsum deposition site on the surrounding environment
Arh Hig Rada Toksikol 2015;66:31-40

Southwestern Nigeria. J Environ Radioact 2005;79:119-25. doi:10.1016/j.jenvrad.2004.05.016

32. European Council (EC). Directive 2013/59/EURATOM: Basic safety standards for protection against the dangers arising from exposure to ionizing radiation. European Union, Bruxelles, 2014 [displayed 20 February 2015]. Available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2014:013:FULL:EN:PDF

33. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Exposures from natural radiation sources. Vol. 1. Annex B. New York: United Nations; 2000.

34. Vandenhove H, Vives I Batlle J, Sweeck L. Potential radiological impact of the phosphate industry on wildlife. J Environ Radioactiv 2015;141;14

35. Azouazi M, Ouahidi Y, Fakhi S, Andres Y, Abbe JCh, Benmansour M. Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. J Environ Radioact 2001;54:231-42. doi: 10.1016/S0265-931X(00)00153-3

36. Khater AEM, Higgy RH, Pimpl M. Radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits. Egypt. J Environ Radioact 2001;55:255-67. doi: 10.1016/S0265-931X(00)00193-4

37. Mas JL, San Miguel EG, Bolivar JP, Vaca F, Perez-Moreno JP. An assay on the effect of preliminary restoration tasks applied to a large TENORM wastes disposal in the South-west of Spain. Sci Total Environ 2006;364:55-66. doi: 10.1016/j.scitotenv.2005.11.006

38. Marović G, Franić Z, Senčar J, Bituh T, Vugrinec O. Mosses and some mushroom species as bioindicators of radiocaesium contamination and risk assessment. Coll Antropol 2008;32(Suppl 2):109-14. PMID: 19138015

39. International Commission on on Radiological Protection (ICRP). Compendium of Dose Coefficients based on ICRP Publication 60. 2012 ICRP Publication 119. Ann. ICRP 2012;41(Suppl.).

40. Santos AJG, Silva PSC, Mazzilli BP, Favaro DIT. Radiological characterization of disposed phosphogypsum in Brazil: Evaluation of the occupational exposure and environmental impact. Radiat Prot Dosim 2006;121:179-85. doi: 10.1093/rpd/ncl011

41. Akher P, Rahman K, Orfi SD, Ahmad N. Radiological impact of dietary intakes of naturally occurring radionuclides on Pakistani adults. Food Chem Toxicol 2007;45:272-7. doi: 10.1016/j.fct.2006.08.006

42. Meli MA, Cantaluppi C, Desideri D, Benedetti C, Feduzi L, Ceccotto F, Fasson A. Radioactivity measurements and dosimetric evaluation in meat of wild and bred animals in central Italy. Food Control 2013;30:272-9. doi: 10.1016/j.foodcont.2012.07.038

43. Varga B. Regulations for radioisotope content in food- and feedstuffs. Food Chem Toxicol 2008;46:3448-57. doi: 10.1016/j.fct.2008.08.019

44. Santos EE, Lauria DC, Amaral ECS, Rochedo ER. Daily ingestion of ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Pb in vegetables by inhabitants of Rio de Janeiro City. J Environ Radioact 2002;62:75-86. doi: 10.1016/S0265-93X(01)00152-7

Mjerenje i modeliranje radiološkog utjecaja odlagališta fosfogipsa na okoliš

Fosfogips je nusproizvod koji nastaje tijekom proizvodnje fosforne kiseline, a karakteriziran je tehnološki povišenom prirodnom radioaktivnošću. Odlagalište fosfogipsa u Hrvatskoj nalazi se na rubu Parka prirode Lonjsko polje, osjetljivom ekosustavu potencijalno ugroženom od čestica fosfogipsa. Istraživanje opisano u ovom radu sagledava dva aspekta značajna za radiološki utjecaj fosfogipsa: procjenu rizika za okoliš te procjenu rizika za profesionalno izložene radnike i lokalno stanovništvo. Koncentracije aktivnosti prirodnih radionuklida (^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, ^{210}Pb i ^{40}K) izmjerene su u uzorcima fosfogipsa uzetima s odlagališta te u uzorcima tla i trave uzetima u blizini odlagališta. Za modeliranje utjecaja fosfogipsa na okoliš (biotu) korišten je program *ERICA Assessment Tool*. Prosječna godišnja efektivna doza za profesionalno izložene radnike iznosila je 0,4 mSv, što je na razini svjetskog prosjeka.

KLJUČNE RIJEČI: *dozimetrija profesionalno izloženih radnika; ERICA; procjena doze; radioaktivnost*