**УНИВЕРЗИТЕТ „ГОЦЕ ДЕЛЧЕВ" - ШТИП**
**ФАКУЛТЕТ ЗА ПРИРОДНИ И ТЕХНИЧКИ НАУКИ**

**UNIVERSITY GOCE DELCEV - STIP**
**FACULTY OF NATURAL AND TECHNICAL SCIENCES**

UDC: 622:55:574:658

ISSN:1857-6966
DOI: 10.46763/NRT

# Природни ресурси и технологии
# Natural resources and technology

**Број 1**
**No 1**

**Година 15**
**Volume XV**

**Јуни 2021**
**June 2021**

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**DOI: https://www.doi.org/10.46763/NRT21151**

# ПРИРОДНИ РЕСУРСИ И ТЕХНОЛОГИИ
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**UDC: 553.63/.64:546.296.064(497.713)**
**DOI: https://www.doi.org/10.46763/NRT211510051j**

# RADON FOOTPRINT FROM THE PHOSPHOGYPSUM WASTE STACK NEAR ZGRPOLCI LOCALITY, VELES, REPUBLIC NORTH MACEDONIA

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**Abstract.** Five locations and five samples of materials from the phosphogypsum waste stack near Zgrpolci locality, in the vicinity of the city of Veles, were checked for their radon concentrations in air and phosphogypsum radon exhalation rate. The accumulation method using AlphaGUARD DF2000 device was used for specific exhalation rate determinations as well as for radon concentrations in air. The activity concentrations of $^{222}$Rn at 5 different sampling locations of the anthropogenically introduced phosphogypsym waste stack near the Zgrpolci locality ranged from 21.02 up to 142.20 Bq kg$^{-3}$. The $^{222}$Rn exhalation rates from these materials (from the same 5 locations) were in the range of 592.27-897.99 mBq m$^{-2}$ h$^{-1}$ .

**Key words:** radon, air, phosphogypsum waste.

# КАРАКТЕРИСТИКИ НА РАДОНОТ ОД ФОСОФИГИПСНИОТ ОТПАД ВО БЛИЗИНА НА ЛОКАЛИТЕТОТ ЗГРПОЛЦИ, ВЕЛЕС, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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**Апстракт.** Пет локации и пет примероци на материјали од јаловиштето со фосфогипсен отпад во близина на месноста Згрполци, во близина на градот Велес, беа проверени за нивната концентрација на радон во воздухот и стапката на есхалација на радон од фосфогипсот. Методот на акумулација со употреба на уредот AlphaGUARD DF2000 се користеше за специфични одредби на опсегот на есхалации на радон од форсфогипсот, како и за концентрациите на радон во воздухот. Концентрациите на активност на $^{222}$Rn на 5 различни места на опробување на примероци во антропогено создаденото јаловиште на фосфогипс во близина на месноста Згрполци се движеа од 21,02 до 142,20 Bq kg$^{-3}$. Стапките на есхалација на $^{222}$Rn од овие материјали (од истите 5 локации) беа во опсег од 592,27-897,99 mBq m$^{-2}$ h$^{-1}$.

**Клучни зборови:** радон, воздух, фосфогипсен отпад.

## 1. Introduction

Radioactive elements in nature are present in a wide range of concentrations in all rocks, soils and waters. The presence and distribution of radionuclides in the air is primarily a matter of local geology and chemical composition of rocks and water. Among the heavy radioactive elements, the most common are $^{238}$U and $^{232}$Th, which produce other radioactive isotopes, such as radium and radon. Radon ($^{222}$Rn) and thoron ($^{220}$Rn) are radioactive gases emanating from geological materials. Inhalation of these gases is closely related to an increase in the probability of lung cancer if the levels are high. Although in our environment people and institutions are still not sufficiently aware of the health problems that radon gas can cause, this does not reduce the need for its monitoring in water, air and soils. Radon has a half-life of 3.8 days, while thoron has a half-life of 55.6 seconds, which means that in this time period, on average, one half of the given amount of radon/thoron atoms will decompose. Nevertheless, despite thoron indoor concentration is generally lower than for the radon, the $^{212}$Pb thoron progeny (half-life of 10.6 h) can accumulate to significant levels in breathable air, aggravating its inhalation risk (World Health Organization, 2009). Some studies (Doi et al., 1994; Milić et al., 2010; De With and De Jong, 2011; Kudo et al., 2015) have demonstrated that thoron concentrations can be comparable to radon and its progeny in some areas of elevated radiological risk. Radon and thoron are significant contributors to the average dose from natural background sources of radiation. They represent approximately half of the estimated dose from exposure to all natural sources of ionizing radiation (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2008). Inhalation of these radioactive gases and their decay products can cause health risks, especially in poorly ventilated areas. Long-term exposure to high levels of radon/thoron in home and working area increases risk of developing lung cancer (World Health Organization, 1988; Brenner, 1994). Radon is the second leading cause of increase of the probability of lung cancer after tobacco smoke (World Health Organization, 2009).

Phosphogypsum, a waste by-product derived from the wet process production of phosphoric acid, represents a serious problem facing the worldwide phosphate industry. Phosphogypsum can be classified as a Naturally Occurring Radioactive Material (NORM) residue of the phosphate fertilizer industry. It may therefore contribute to the presence of radon in the environment away from the phosphogypsum landfill. There is no radon concentration factor around phosphogypsum deposits. Diffusion and convection (wind) usually remove any large accumulation / concentration of radon near phosphogypsum landfills (FDHBRC and EPCHCAMD, 2011).

In some previous work, were studied Zgrpolci phosphogypsum mean values of gross alpha and beta specific activities and their standard deviation values (950±104) Bq/kg and (1694±220) Bq/kg, respectively (Jancev et al., 2019; Jancev et al., 2020), as well as the mean values of the specific activities of $^{238}$U and $^{226}$Ra were (360±55) Bq/kg and (280±84) Bq/kg, respectively. Also, estimated annual outdoor effective dose, at 1m received by adults was calculated at 0.25 mSv/y, which is below a dose limit of 1 mSv/y for members of general public (Jancev et al., 2020). If we take into account the fact that radon is the second leading cause of lung cancer worldwide after active smoking, as well as a common cause of gastric cancer, which somehow imposed the need to record the current state of radon in the air in the area of the landfill for phosphogypes near Zgrpolci. Such a need is indicated by the fact that radon belongs to the group of inert gases, which means that it is very difficult to chemically communicate with other elements, and above all it is a radioactive gas, which makes it a factor that has a detrimental effect on public health. In the context of the above, the main objectives of these measurements are emphasized, which refer to the provision / analysis of radon concentrations in the ambient air of the phosphogypum landfill near Zgrpolci.

## 2. Materials and methods

The measurement of radon concentrations ($^{222}$Rn) in the air at the phosphogypsum landfill, Zgrpolci was performed at 5 locations that cover the total area (~ 28545 m2), and they are positioned in a so-called zigzag layout (Figure 1).

Fig. 1. Sampling locations of radon concentrations in the air and radon exhalation from the locality of phosphogypsum landfill, Zgrpolci

The analysis of radon concentrations in the air was performed at a height of 0.5 m from the ground (deposited material) using the AlphaGUARD DF2000 professional radon monitor for multi-parametric analysis with gas impermeable chamber for pulsating ionization (0, 6 l).

The radon measurement range was from min 2 to max 2 000 000 Bq / $m^3$ $^{222}$Rn. Radon sensitivity is: 1 cpm at 20 Bq / $m^3$ (0.5 pCi / l). Sensitivity for radon determination in relation to toron: radon minimum 1 cpm at 60 Bq / $m^3$ (1.6 pCi / l); thoron (1 l / min) minimum 1 cpm at 200 Bq / $m^3$ (5.5 pCi / l) and thoron (2 l / min) minimum 1 cpm at 140 Bq / $m^3$ (3.8 pCi / l).

Also, five samples from the phosphgypsum waste stack, have been collected for the necessities of exhalation measurements. These samples were collected from the exact points where the radon in the air concentration measurements took place. The mass of each sample labeled as samples 1, 2, 3 and 5 was 1 kg while the sample 4 had a mass of 2 kg. Figure 1 shows the spatial location of sampled materials. The aforementioned materials were classified as materials incorporating residues from industries processing naturally-occurring radioactive material (phosphogypsum) in accordance to directives by the European Parliament (2014). Sample preparation consisted of hand crushing and drying of sampled materials for 48 h at $105^{O}$C, prior to proceeding with their exhalation measurements. Among the methods to measure exhalation rate of radon and thoron isotopes in different materials such as passive methods, that use solid-state nuclear track detector and accumulation chamber methods and active methods with radon/thoron monitors, we used the later one. The method is schematized in Fig. 2.

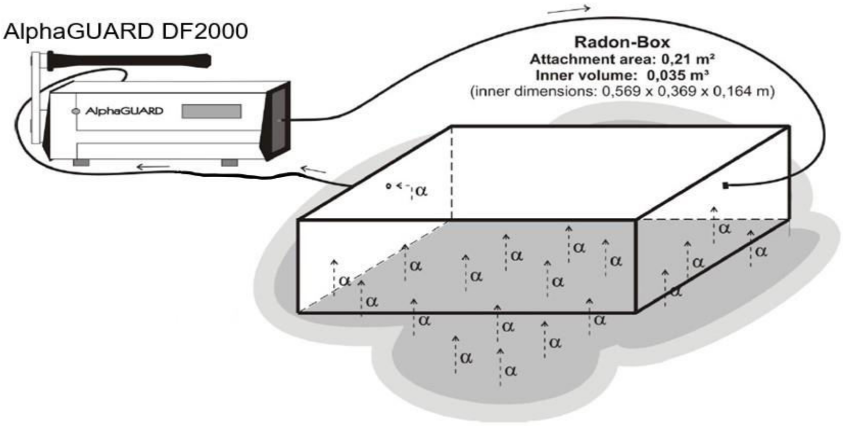


Fig. 2. *AlphaGUARD* operating outside the Radon-Box in flow-through mode

Accumulation method technique consisted of attaching the Radon Box to the phosphogypsum surface with its opening. The edges of the opening were sealed by duct tape to avoid exchange of the medium to be measured with the surrounding atmosphere. The AlphaGUARD monitor placed outside the Radon Box was connected in a closed loop with the container and its internal AlphaPUMP allows continuous measurement of the radon and thoron concentration within the box. Exhalation is the amount of radon/thoron as obtained from a given layer (geological material on the surface/surface exposure) mainly the outer thinner part of the crust and it is given in Bq $h^{-1}$, according to the Netherlands Standardization Institute (Netherlands Standardization Institute, 2001). Exhalation can be related to the mass of the samples (massic radon/thoron exhalation, and its value is expressed Bq $kg^{-1}$ $h^{-1}$) as well as to areal exhalation related to the area of exhalation expressed as Bq $m^{-2}$ $h^{-1}$ (Miro et al., 2014; Hassan et al., 2011; Frutos-Puerto et al., 2018).

### 3. Results of concentration measurements of radon in the air and radon/thoron exhalation measurements

Measurements of radon concentrations in ambient air in the area of interest, as already mentioned, were followed by detection of alpha particles in the ionization chamber during air flow /

circulation in the system. The results of the measurements of the radon concentration (in Bq · m$^{-3}$) in the air during the measurements are given in Table 1.

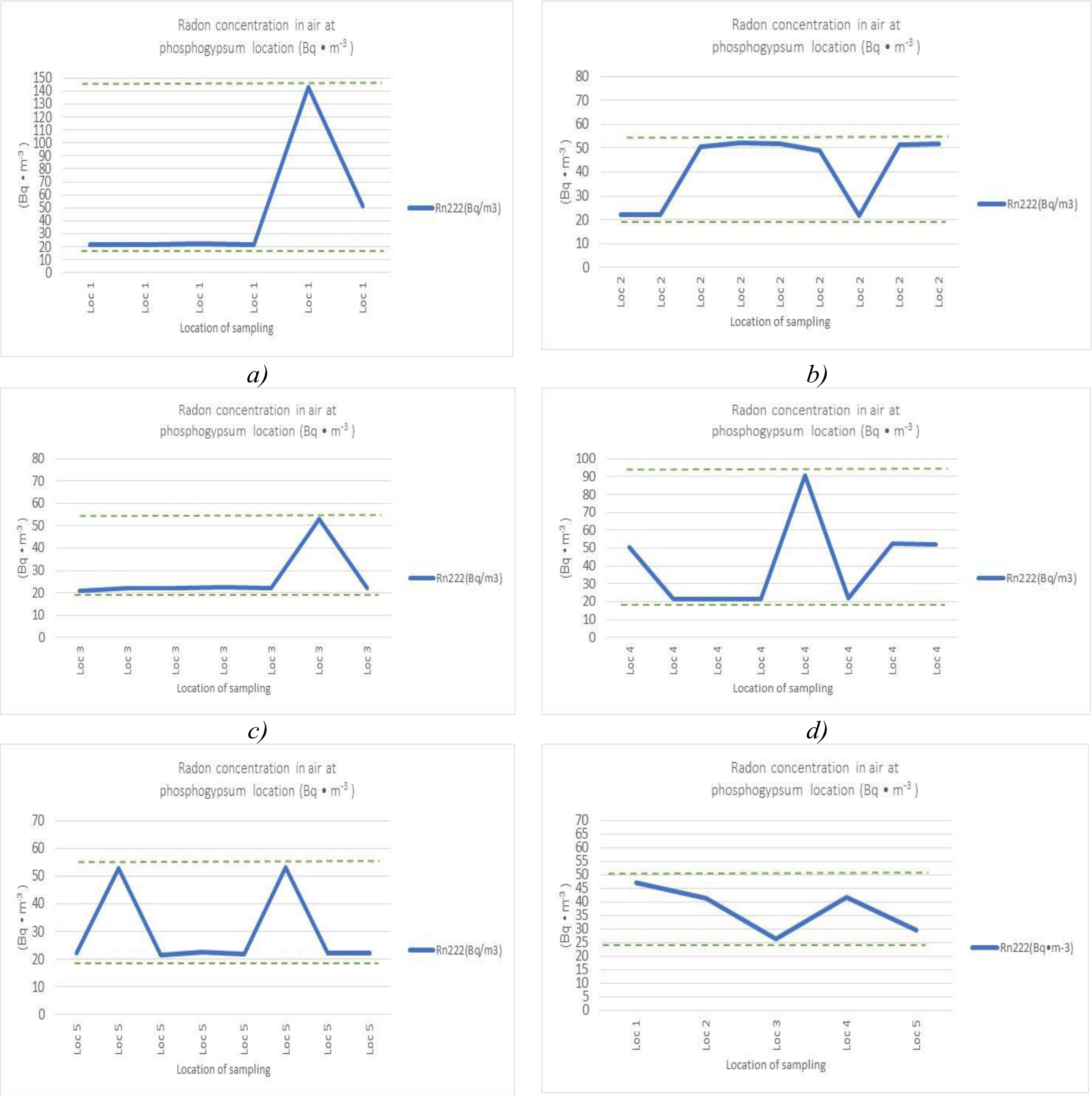
Table 1. Measurements of the concentration of radon in the ambient air in the space of the phosphogypsum landfill in the locality Zgrpolci (Bq • m$^{-3}$)

| | Measurement time | Rn$^{222}$ (Bq•m$^{-3}$) | Air pressure Mbar (mbar) | Temperature (°C) |
|---|---|---|---|---|
| Loc 1 | 18.6.2020 07:52 | 21,77 | 985,37 | 25,76 |
| Loc 1 | 18.6.2020 07:53 | 21,92 | 985,35 | 25,82 |
| Loc 1 | 18.6.2020 07:58 | 22,36 | 985,26 | 26,10 |
| Loc 1 | 18.6.2020 07:59 | 21,51 | 985,25 | 26,19 |
| Loc 1 | 18.6.2020 08:00 | 143,20 | 985,22 | 26,27 |
| Loc 1 | 18.6.2020 08:02 | 51,50 | 985,23 | 26,41 |
| Loc 2 | 18.6.2020 08:08 | 21,94 | 985,56 | 27,09 |
| Loc 2 | 18.6.2020 08:09 | 21,94 | 985,56 | 27,27 |
| Loc 2 | 18.6.2020 08:10 | 50,78 | 985,52 | 27,46 |
| Loc 2 | 18.6.2020 08:13 | 52,35 | 985,54 | 27,91 |
| Loc 2 | 18.6.2020 08:14 | 51,69 | 985,58 | 28,05 |
| Loc 2 | 18.6.2020 08:15 | 49,11 | 985,55 | 28,19 |
| Loc 2 | 18.6.2020 08:16 | 21,55 | 985,58 | 28,31 |
| Loc 2 | 18.6.2020 08:18 | 51,56 | 985,63 | 28,59 |
| Loc 2 | 18.6.2020 08:20 | 51,65 | 985,68 | 28,93 |
| Loc 3 | 18.6.2020 08:25 | 21,02 | 986,54 | 29,60 |
| Loc 3 | 18.6.2020 08:27 | 21,97 | 986,62 | 29,85 |
| Loc 3 | 18.6.2020 08:28 | 21,95 | 986,63 | 30,02 |
| Loc 3 | 18.6.2020 08:32 | 22,35 | 986,69 | 30,50 |
| Loc 3 | 18.6.2020 08:33 | 22,26 | 986,68 | 30,66 |
| Loc 3 | 18.6.2020 08:35 | 52,93 | 986,72 | 30,88 |
| Loc 3 | 18.6.2020 08:36 | 22,05 | 986,73 | 30,97 |
| Loc 4 | 18.6.2020 08:40 | 50,54 | 987,03 | 31,23 |

| | | | | |
|---|---|---|---|---|
| Loc 4 | 18.6.2020 08:42 | 21,64 | 987,03 | 31,37 |
| Loc 4 | 18.6.2020 08:43 | 21,67 | 987,01 | 31,49 |
| Loc 4 | 18.6.2020 08:44 | 21,70 | 987,01 | 31,59 |
| Loc 4 | 18.6.2020 08:45 | 90,71 | 986,98 | 31,68 |
| Loc 4 | 18.6.2020 08:48 | 21,85 | 987,00 | 32,00 |
| Loc 4 | 18.6.2020 08:51 | 52,51 | 986,95 | 32,30 |
| Loc 4 | 18.6.2020 08:52 | 51,80 | 986,93 | 32,41 |
| Loc 5 | 18.6.2020 08:57 | 22,34 | 987,71 | 32,53 |
| Loc 5 | 18.6.2020 08:58 | 52,74 | 987,68 | 32,54 |
| Loc 5 | 18.6.2020 09:00 | 21,40 | 987,67 | 32,63 |
| Loc 5 | 18.6.2020 09:03 | 22,37 | 987,67 | 32,90 |
| Loc 5 | 18.6.2020 09:06 | 21,73 | 987,64 | 33,21 |
| Loc 5 | 18.6.2020 09:07 | 53,19 | 987,67 | 33,29 |
| Loc 5 | 18.6.2020 09:08 | 22,14 | 987,62 | 33,41 |
| Loc 5 | 18.6.2020 09:09 | 22,10 | 987,63 | 33,52 |
| **Loc 1-5 stat** | **Min** | 21,02 | 985,22 | 25,76 |
| **Loc 1-5 stat** | **Max** | 143,20 | 987,71 | 33,52 |
| **Loc 1-5 stat** | **Average** | 37,10 | 986,47 | 29,97 |
| **Loc 1-5 stat** | **Median** | 22,30 | 986,68 | 30,58 |

As can be seen from Table 1 above, the range of radon concentrations ranged from 21.51 to 143.20 Bq • m$^{-3}$ (mean 47.04 Bq • m$^{-3}$) at location 1, from 21.55 to 52.35 Bq • m$^{-3}$ ( mean value 41.40 Bq • m$^{-3}$) at location 2, from 21.02 to 52.93 Bq • m$^{-3}$ (mean value 26.36 Bq • m$^{-3}$) at location 3, from 21.64 to 90.71 Bq • m$^{-3}$ (mean value 41.55 Bq • m$^{-3}$) at location 4, as well as from 21.40 to 53.19 Bq • m$^{-3}$ (mean 29.75 Bq • m$^{-3}$) at location 5. As can be seen from the measured values, the range of measured radon concentrations , except for two "hurricane values", moved within narrow limits with mutual differences of about 30 Bq • m$^{-3}$. This statement becomes even more pronounced if we take into account the sum values for all 5 locations, where the mean value of 37.10 Bq • m$^{-3}$ and the median of 22.30 Bq • m$^{-3}$ point out to the relatively narrow range of measured radon concentrations (Table 1).

For greater illustrativeness of the measurements performed in the diagram given in Figure 3, the radon concentrations in the ambient air during the measurements are graphically shown, both at each location separately (Figure 3a-3d), and collectively for all locations with their mean values ( Figure 3f).



*a)* *b)*

*c)* *d)*

*e)* *f)*

Fig. 3. Diagrams for the course of the measurements of the radon concentrations in the ambient air in the phosphogyps landfill at the locality Zgrpolci (Bq • m-3)
a) Location 1; b) Location 2; c) Location 3; d) Location 4; e) Location 5; f) Average presentation of the values from the measurements of radon concentrations in all 5 locations; dashed lines in green give the range of measured radon concentrations (upper and lower limit)

Based on the measurements and calculations (Table 1 and Figure 3), we can conclude that radon concentrations in the measured samples undoubtedly indicate the uniformity of the deposited phosphogypsum masses, the existence of similar conditions in the measurements, such as air pressure, ambient humidity. air, temperature (Table 1), but also uniformity of moisture of the material phosphogypsum, compaction of the material, grain size, porosity, diffusion characteristics and similar parameters that have a great influence on the concentrations of radon in the space of interest. This influence is primarily manifested in the possibility of radon spreading through the material before it can leave it, and its velocity of discharge from the material is related to its diffusion characteristics. When equilibrium is not reached in the diffusion process, because if the radon needs too much time to reach the surface (half-life 3.8 days), it will decompose before it can reach the air. All of the above slightly affects the rate of diffusion through the material, and thus the rate of radon emission. The displayed radon concentrations in the air above the phosphogypsum deposit near Zgrpolci are at least two magnitudes higher than the usual average of 10 Bq • m$^{-3}$, determined as the annual average for open radon concentrations (UNSCEAR, 1993), but certainly higher that radon concentrations (average 12 Bq • m$^{-3}$) in the air around Belgrade, R. Serbia (Kolarž et al., 2020), the People's Republic of China (average ~ 13-14 Bq • m$^{-3}$; Wu et al., 2016) and others.

Also, going one step further, based on the average, measured radon values, we calculated the exposure to radon inhalation, ie, the annual effective doses of ionizing radiation exposure that would be received (from radon) by individuals annually ( Table 2), as outdoor stay and indoor stay. The annual effective dose due to radon exposure (inhalation), $E_{Rn}$, is:

a) in open space

$$E_{Rn}(mSv/y) = 6{,}7 * 10^{-6} * C_{Rn}\ (Bq * m^{-3}) * 2000(\frac{h}{y})$$

b) indoors (in closed space)

$$E_{Rn}(mSv/y) = 6{,}7 * 10^{-6} * C_{Rn}\ (Bq * m^{-3}) * 7000(\frac{h}{y})$$

where: $E_{Rn}(mSv \cdot y^{-1})$ – is an effective dose for radon exposure (inhalation) on an annual basis

$C_{Rn}(Bq * m^{-3})$ - is the measured concentration of radon in the subject area 6.7 * 10$^{-6}$ mSv at Bq h m$^{-3}$ dose coefficient

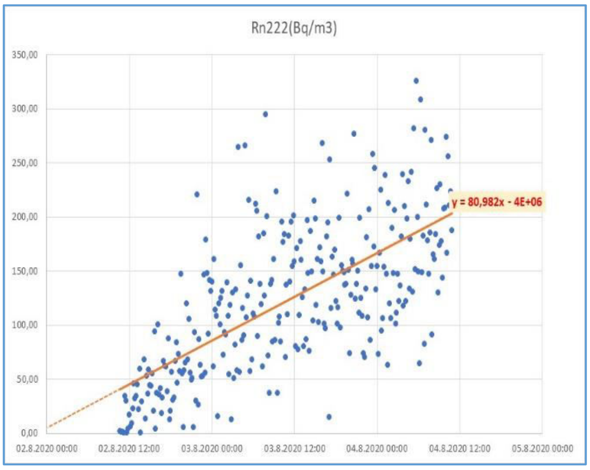
Table 2. Calculated values for the exposure during the inhalation of radon from the ambient air at the phosphogyps landfill at the locality Zgrpolci

| Sampling location | Location 1 | Location 2 | Location 3 | Location 4 | Location 5 |
|---|---|---|---|---|---|
| Number of measurements | 6 | 9 | 7 | 8 | 8 |
| $^{222}$Rn (Bq m$^{-3}$) | 47,04 | 41,4 | 26,36 | 41,55 | 29,75 |
| Annual effective dose for inhalation of $^{222}$Rn (mSv y$^{-1}$) indoors | 1,19 | 1,04 | 0,66 | 1,05 | 0,75 |
| Annual effective dose for inhalation of $^{222}$Rn (mSv y$^{-1}$) outdoors | 0,45 | 0,39 | 0,25 | 0,39 | 0,28 |
| Total (Σ) effective dose outdoors+indoors (mSv y$^{-1}$) | 1,63 | 1,44 | 0,91 | 1,44 | 1,03 |

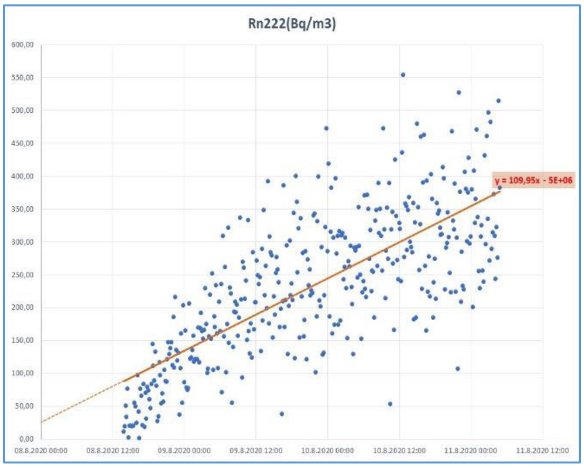
The effective doses ($E_{Rn}$) indoors ranged from 0.66 mSv·y$^{-1}$ to 1.19 mSv · y$^{-1}$ (mean 0.94 mSv · y$^{-1}$), while the calculations of values for eventual outdoor stay were in the range of 0.25 mSv · y$^{-1}$ to 0.45 mSv · y$^{-1}$ (mean 0.35 mSv · y$^{-1}$). The cumulative, ie, the sum absolute absolute values of the cumulative effective doses ($E_{Rn}$), ranged from 0.91 mSv · y$^{-1}$ to 1.63 mSv · y$^{-1}$ (mean 1.29 mSv · y$^{-1}$) . The analysis of these effective doses certainly showed that the mean value for indoor spaces very close to the maximum recommended for individual doses in the general population (1 mSv · y$^{-1}$), the mean value for outdoor stay is below the maximum recommended doses, while the combined doses outside / indoor space annually exceed that value in the whole range of trials (location 1- location5). Doses from other sources of radiation sources such as $^{40}$K, $^{232}$Th and $^{238}$U at the same site (in the amount of 0.24537 mSv· y$^{-1}$; Jancev et al., 2020) should certainly be taken into account here.

However, here we want to emphasize that the estimated mean annual effective dose should not be taken too seriously, as the mean values are widely used. For example, according to UNSCEAR estimates (2000), as many as 65% of people are exposed to doses of 1 to 3 mSv, while 25% of people are exposed to doses below 1 mSv and only 10% of them are exposed to doses above 3 mSv, which would classify our site of interest in the most numerous group of people with exposure to doses from 1 to 3 mSv.

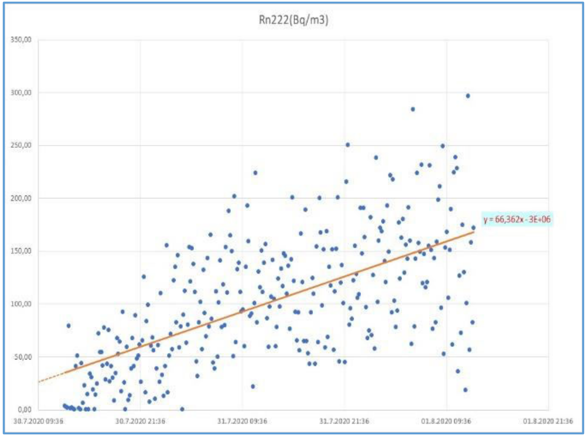
As we already mentioned above, the $^{222}$Rn and $^{220}$Rn exhalation rates from Zgrpolci phosphogypsum materials (from the same 5 locations) were measured, also (Figure 4).



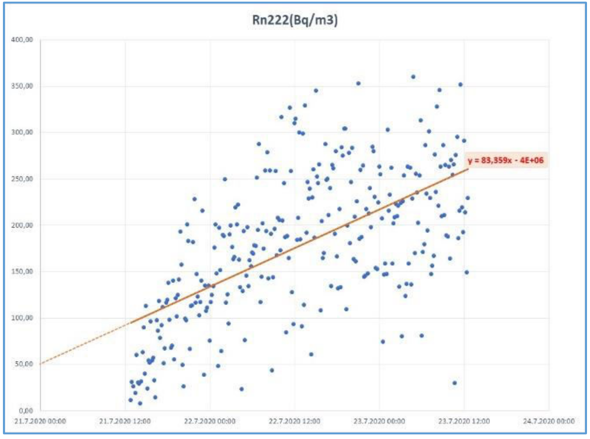
Sample 1



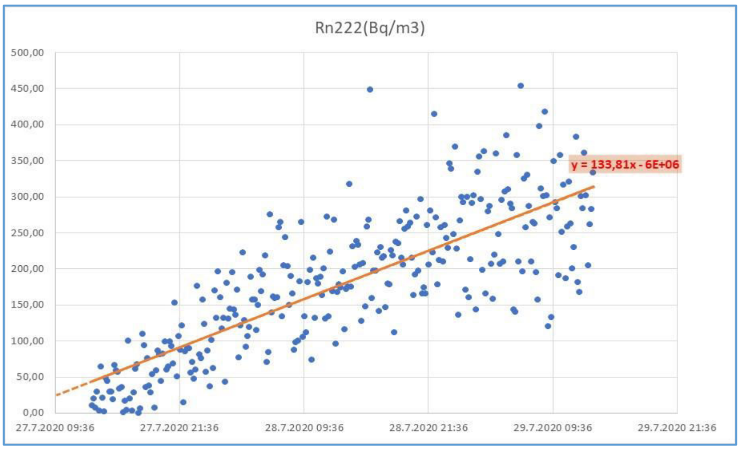
Sample 2



Sample 3



Sample 4



Sample 5

Fig. 4. Exhalation measurements of radon and thoron from Zgrpolci phosphogypsum

### 4. Radon Exhalation Calculation

Conventionally, $^{222}$Rn exhalation rate, $E_{222}$, [Bq $h^{-1}$] is calculated according to the following equation, which is equation 1 solved with respect to E (Tuccimei et al., 2009):

$$E_{Rn222} = \frac{(C - C_o e^{-\lambda_{222} t})}{1 - e^{-\lambda_{222} t}} \cdot \lambda_{222} \cdot V$$

where C is the equilibrium concentration [Bq $m^{-3}$],
$C_0$ is the initial radon concentration [Bq $m^{-3}$],
$\lambda_{222}$ is $^{222}$Rn decay constant [$h^{-1}$],
V is the free total volume of the analytical system [$m^3$] and
t is time [h].

**Thoron** ($^{220}$Rn) exhalation rate, $E_{220}$ [Bq $h^{-1}$], was calculated according to the following equation (Tuccimei et al., 2009):

$$E_{Rn220} = (\lambda_{220} \cdot V_o) \frac{(C_m)}{e^{-\lambda_{220}\left(\frac{V_1}{Q}\right)}}$$

where $\lambda_{220}$ is $^{220}$Rn decay constant ($h^{-1}$),
$V_0$ is the volume of the accumulation chamber ($m^3$),
$C_m$ is the measured $^{220}$Rn concentration [Bq $m^{-3}$],
$V_1$ is the volume between the outflow of the accumulation chamber and the inflow of the radon monitor, and
Q is the flow rate in the system.

The second term of the equation corrects for the decay of $^{220}$Rn during the transport in the closed system, because thoron half-life (55.61 s) is comparable with time required to complete a whole loop, causing the underestimation of thoron activity concentration.

Table 3. Measurements of the radon and thoron accumulation concentration (Bq • m$^{-3}$), exhalation from the phosphogypsum landfill in the locality Zgrpolci (mBq • kg$^{-1}$ h$^{-1}$) and annual effective dose (mSv y$^{-1}$)

| Sample | | No.of meas. | C (Bq m$^{-3}$) range | Mean | SD | t (h) | m (kg) | $E_{Rn222/Rn220}$ (mBq kg$^{-1}$h$^{-1}$) | Annual effective dose (mSv y$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $^{222}$Rn | 288 | 0.14-325.37 | 90.331 | 69.847 | 48 | 1 | 281.539 | 2.34 |
| | $^{220}$Rn | 288 | 0.60-398.18 | 59.935 | 77.753 | 48 | 1 | 13040.3 | 3.18 |
| 2 | $^{222}$Rn | 378 | 1.34-553.82 | 192.093 | 112.489 | 63 | 1 | 381.948 | 3.99 |
| | $^{220}$Rn | 378 | 0.26-721.92 | 83.708 | 108.512 | 63 | 1 | 18032.2 | 5.77 |
| 3 | $^{222}$Rn | 288 | 0.13-296.86 | 69.849 | 61.259 | 48 | 1 | 255.746 | 2.14 |
| | $^{220}$Rn | 288 | 1.27-410.48 | 57.805 | 76.034 | 48 | 1 | 13421.76 | 3.27 |
| 4 | $^{222}$Rn | 288 | 7.90-360.14 | 153.477 | 78.816 | 48 | 2 | 153.153 | 2.59 |
| | $^{220}$Rn | 288 | 0.89-452.61 | 79.676 | 102.681 | 48 | 2 | 7408.02 | 3.61 |
| 5 | $^{222}$Rn | 288 | 0.14-453.67 | 135.565 | 97.977 | 48 | 1 | 387.760 | 3.27 |
| | $^{220}$Rn | 288 | 1.59-623.11 | 80.732 | 95.554 | 48 | 1 | 20385.35 | 4.97 |

**Note:** Volume of the RadonBox (exhalation box) 0.035 m$^3$, area of exhalation within the box 0.21 m$^2$.

Exhalation measurements of radon from the phosphogypsum samples showed range of values going from 153.153 up to 387.78 mBq • kg$^{-1}$ h$^{-1}$ and averaging 292.029 mBq • kg$^{-1}$ h$^{-1}$, from more than of 1530 cumulative measurements. Comparison with literature data showed that measurements of radon exhalations from phosphogypsum at the tailing (waste stack) near Zrgopolci showed that the values were several times higher than in some common building materials (Frutos-Puerto et al., 2020). On average, the measured values for phosphogypsum exhalation were 22 times higher than those of concrete, 12 times higher than those of cement, 10 times higher than those of marble, 10 times higher than those of marble, 16 times higher than those of shale, 3 times higher those of granite and even 193 times higher than those of gypsum. We obtained very similar findings when comparing the results for the exhalation of radon from phosphogypsum from the tailings near Zgrpolci compared to some building materials originating in Italy (tuff, pyroclastic flow, lapilli and cement; Tuccimei et al., 2009), where our measured values were higher in the range of 3 to 18 times. Without going any further into separate comparisons we would like to emphasize that the values of radon exhalation rates reported in Table 3 correspond well with the values reported by other authors (Rawat et al., 1991; Porstendörfer, 1994; Stoulos et al., 2003; Righi and Bruzzi, 2006; Perna et al., 2018). Also, we would like that radon exhalations from sampled phosphogypsum waste stack at Zrgopolci were approximately two times higher then respective ones in coals and related fly ashes from some part around the World (Singh et al., 2016)

In regards to exhalation measurements of thoron from the phosphogypsum samples we are emphasizing that they showed range of values going from 7408.1 up to 20385.4 mBq • kg$^{-1}$ h$^{-1}$ and averaging 14457.5 mBq • kg$^{-1}$ h$^{-1}$, from more than of 1530 cumulative measurements, also. Comparison with literature data showed that measurements of thoron exhalations from phosphogypsum at the tailing (waste stack) near Zrgopolci, opposite to radon one, were not that uniform. Namely, for some materials such as concrete, cement, marble, ceramic and gypsum (Frutos-Puerto et al., 2020), our phosphogypsum thoron exhalation average values were several times higher (2.2; 4.1; 3.9; 6.3 and 5.1 respectively). For some other building materials such are granite measured values for phosphogypsum exhalation were 2 times lower, 5 times lower than those of wood and approximately 0.5 times lower than those of slate. Comparison with some Italian produced building materials (Tuccimei et al., 2009) showed that thoron exhalation for Zrgopolci phosphogypsum were from 2 to 7 times lower magnitudes. These findings are similar to the ranges of results given in works of other authors (Ujić et al., 2010; Jónás et al., 2016). Contrary to the results for the exhalation of radon, the exhalation of the toron from the coals and ashes (Singh et al., 2016) was 3-12 magnitudes higher than the exhalations of the toron from the phosphogypsum in waste stack of Zgrpolci.

This radon concentration model can then be used to determinate the annual effective doses of $^{222}$Rn by the method recommended by the United Nations Scientific Committee on the Effects of Atomic Radiation (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2016):

$$D_{Rn222} = C_{Rn222} \cdot F_e \cdot T_a \cdot CF_{Rn222} \qquad (1)$$

where $D_{Rn222}$ is the annual effective dose of $^{222}$Rn (Sv y$^{-1}$);
$C_{Rn222}$ is the activity concentration for $^{222}$Rn (Bq m$^{-3}$);
$CF_{Rn222}$ is the dose conversion factor for $^{222}$Rn progeny (Sv per Bq h m$^{-3}$);
$F_e$ is the equilibrium factor for $^{222}$Rn and its progeny; and
$T_a$ is the annual work time.

The standard parameters were estimated using the RP 122 publication of EC 2002 (European Commission, 2002). The values of $CF_{Rn222}$ were assumed to be $9 \times 10^{-9}$ Sv per Bq h m$^{-3}$ and the $T_a$, 7 000 h y$^{-1}$. The value of $F_e$ was assumed to be 0.4 as reported in (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2008).

Similarly, for 220Rn:

$$D_{Rn220} = C_{Rn220} \cdot F_e \cdot T_a \cdot CF_{Rn220} \qquad (2)$$

where $D_{Rn220}$ is the annual effective dose of $^{220}$Rn (Sv y$^{-1}$);
$C_{Rn220}$ is the activity concentration for $^{220}$Rn (Bq m$^{-3}$);
$CF_{Rn220}$ is the dose conversion factor for $^{220}$Rn progeny (Sv per Bq h m$^{-3}$);
$F_e$ is the equilibrium factor for $^{220}$Rn and its progeny; and
$T_a$ is the annual work time.

The standard parameters were given as $CF_{Rn220}$ dose conversion factor for 220Rn progeny (40 × 10−9 Sv per Bq h m−3) and Ta as the annual work time, 2 000 h y$^{-1}$ (European Commission, 2002). $F_e$ is the equilibrium factor for $^{220}$Rn and its progeny, 0.1 (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 2008). Calculated annual effective dose, in aforementioned manner, for $^{222}$Rn ranged from 2.14 to 3.99 mSv y$^{-1}$, while for the $^{220}$Rn values ranged from 3.18 to 5.77 mSv y$^{-1}$, and all of them were of several magnited higher than allowed one of 1 mSv y$^{-1}$.

## 5. Conclusion

More than 40 measurements of radon in air concentration of the phosphogypsum waste stack near Zgrpolci showed range of 21.01 to 143.20 Bq • m$^{-3}$ , at all 5 locations respectively. The displayed radon concentrations in the air above the phosphogypsum deposit near Zgrpolci are at least two magnitudes higher than the usual average of 10 Bq • m$^{-3}$, determined as the annual average for open radon concentrations. Calculated annual effective doses for inhalation of $^{222}$Rn (mSv y$^{-1}$) outdoors were 0.45; 0.39; 0.25; 0.39 and 0.28, respectively for each sampling location and none of them were above the suggested values of 1 mSv • y$^{-1}$. Exhalation measurements of radon from the phosphogypsum samples showed range of values going from 153.153 up to 387.78 mBq • kg$^{-1}$ h$^{-1}$ , which values were several times higher than those of concrete, cement, marble, shale, granite and gypsum. Exhalation measurements of thoron from the phosphogypsum samples ranged from 7408.1 up to 20385.4 mBq • kg$^{-1}$ h$^{-1}$, which were several times higher than some materials such as concrete, cement, marble, ceramic and gypsum (2.2; 4.1; 3.9; 6.3 and 5.1 respectively).

## References

FDHBRC and EPCHCAMD, 2011. Ambient Air Radon Monitoring Report on Mosaic Riverview Phospogypsum Stack. Florida Department of Health Bureau of Radiation Control and Environmental Protection Commission of Hillsborough County Air Management Division, 16 p.

UNSCEAR, 1993. Sources and effects of ionizing radiation united nations. *Report to the General Assembly, with Scientific Annexes*. New York, (United Nations Scientific Committee on the Effects of Atomic Radiation).

UNSCEAR, 2000. SOURCES AND EFFECTS OF IONIZING RADIATION United Nations Scientific Committee on the Effects of Atomic Radiation, Report to the General Assembly, with Scientific Annexes VOLUME I: SOURCES, 654 p.

Kolarž, P., Stojanovska, Z., Ćurguz, Z., Žunić, S. Z., 2020. Diurnal and spatial variations of radon concentration and its influence on ionization of air Contemporary Materials, XI–1 , pp. 14-19.

Wu, Q., Pan, Z., Liu, S. and Wang. C., 2016. Outdoor radon concentration in China. NUKLEONIKA Vol 61, No. 3, pp. 373-378, doi: 10.1515/nuka-2016-0062

Brenner, D.J., 1994. Protection against radon-222 at home and at work (ICRP publication no 65). International Journal of Radiation Biology 66(4):314 DOI 10.1080/09553009414551371.

De With, G. and De Jong, P., 2011. CFD modelling of thoron and thoron progeny in the indoor environment. Radiation Protection Dosimetry 145(2–3):138–144 DOI 10.1093/rpd/ncr056.

Doi, M., Fujimoto, K., Kobayashi, S. and Yonehara, H., 1994. Spatial distribution of thoron and radon concentrations in the indoor air of a traditional Japanese wooden house. Health Physics 66(1):43–49 DOI 10.1097/00004032-199401000-00006.

European Parliament. 2014. Council Directive 2013/59/Euratom of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom. Official Journal of the European Union 57:1–73 DOI 10.3000/19770677.L_2013.124.eng.

Frutos-Puerto, S., Pinilla-Gil, E., Andrade, E., Reis, M., Madruga, M.J. and Miró Rodríguez, C., 2018. Radon and thoron exhalation rate, emanation factor and radioactivity risks of building materials of the Iberian Peninsula. PeerJ 8:e10331, pp. 1-18 (DOI 10.7717/peerj.10331)

Frutos-Puerto S, Pinilla-Gil E, Andrade E, Reis M, Madruga MJ, Miró Rodríguez C. 2020. Radon and thoronexhalation rate, emanation factor and radioactivity risks of building materials of the Iberian Peninsula.PeerJ 8:e10331DOI 10.7717/peerj.10331

Hassan NM, Hosoda M, Iwaoka K, Sorimachi A, Janik M, Kranrod C, Sahoo SK, Ishikawa T, Yonehara H, Fukushi M, Tokonami S. 2011. Simultaneous measurment of radon and thoron released from building materials used in Japan. Progress in Nuclear Sciencie and Technology 1(0):404–407 DOI 10.15669/pnst.1.404

Jónás, J., Sas, Z., Vaupotic, J., Kocsis, E., Somlai, J. and Kovács, T., 2016. Thoron emanation and exhalation of Slovenian soils determined by a PIC detector-equipped radon monitor. Nukleonika 61(3):379–384 DOI 10.1515/nuka-2016-0063.

Kudo, H., Tokonami, S., Omori, Y., Ishikawa, T., Iwaoka, K., Sahoo, S.K., Akata, N., Hosoda, M., Wanabongse, P., Pornnumpa, C., Sun, Q., Li, X. and Akiba, S., 2015. Comparative dosimetry for radon and thoron in high background radiation areas in China. Radiation Protection Dosimetry 167(1–3):155–159 DOI 10.1093/rpd/ncv235.

Milić, G., Jakupi, B., Tokonami, S., Trajković, R., Ishikawa, T., Čeliković, I., Ujić, P., Čuknić, O., Yarmoshenko, I., Kosanović, K., Adrović, F., Sahoo, S.K., Veselinović, N. and Žunić, Z.S., 2010. The concentrations and exposure doses of radon and thoron in residences of the rural areas of Kosovo and Metohija. Radiation Measurements 45(1):118–121 DOI 10.1016/j.radmeas.2009.10.052.

Miro C, Andrade E, Reis M, Madruga MJ. 2014. Development of a couple of methods for measuring radon exhalation from building materials commonly used in the Iberian Peninsula. Radiation Protection Dosimetry 160(1–3):177–180 DOI 10.1093/rpd/ncu063.

Netherlands Standardization Institute. 2001. Dutch standard: radioactivity measurement. Determination method of the rate of the radon exhalation of dense building materials. NEN

5699:2001. Available at https://infostore.saiglobal.com/en-us/Standards/NEN-5699-2001-785554_SAIG_NEN_NEN_1888053/

Tuccimei, P., Castelluccio, M., Soligo, M. and Moroni, M., 2009. Radon exhalation rates of building materials: experimental, analytical protocol and classification criteria. In: Building Materials (Editor: Donald N. Cornejo and Jason L. Haro,), 2009 Nova Science Publishers, Inc., Chapter 7, pp. 1-15.

Ujić, P., Čeliković, I., Kandić, A., Vukanac, I., Durašević, M., Dragosavac, D. and Žunić, Z.S., 2010. Internal exposure from building materials exhaling 222Rn and 220Rn as compared to external exposure due to their natural radioactivity content. Applied Radiation and Isotopes 68(1):201–206 DOI 10.1016/j.apradiso.2009.10.003.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). 2008. Sources, effects and risks of ionizing radiation, report to the General Assembly. New York. (https://www.unscear.org/unscear/en/publications/2008_1.html).

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). 2016. Sources, effects and risks of ionizing radiation, report to the General Assembly. New York. (https://www.unscear.org/unscear/en/publications/2016.html).

World Health Organization. 1988. IARC monographs on the evaluation of the carcinogenic risks to humans. (https://publications.iarc.fr/61).

World Health Organization. 2009. Indoor radon a public health perspective. Geneva: WHO Press.

Perna, A.F.N., Paschuk, S.A., Corrêa, J.N., Narloch, D.C., Barreto, R.C., Del Claro, F. and Denyak, V., 2018. Exhalation rate of radon-222 from concrete and cement mortar. Nukleonika 63(3):65–72 DOI 10.2478/nuka-2018-0008.

Porstendörfer, J., 1994. Properties and behaviour of radon and thoron and their decay products in the air. Journal of Aerosol Science 25(2):219–263 DOI 10.1016/0021-8502(94)90077-9.

Rawat, A., Jojo, P.J., Khan, A.J., Tyagi, R.K. and Prasad, R.., 1991. Radon exhalation rate in building materials. International Journal of Radiation Applications and Instrumentation. Part 19:391–394 DOI 10.1016/1359-0189(91)90223-5.

Righi, S. and Bruzzi, L., 2006. Natural radioactivity and radon exhalation in building materials used in Italian dwellings. Journal of Environmental Radioactivity 88(2):158–170 DOI 10.1016/j.jenvrad.2006.01.009.

Singh, L.M., Kumar, M., Sahoo, B. K., Sapra, B.K. and Kumar, R., 2016. Study of radon, thoron exhalation and natural radioactivity in coal and flyash samples of Kota superthermal power plant, Rajasthan, India. Radiation Protection Dosimetry (2016), pp. 1–4.

Stoulos S., Manolopoulou, M. and Papastefanou, C., 2003. Assessment of natural radiation exposure and radon exhalation from building materials in Greece. Journal of Environmental Radioactivity 69(3):225–240 DOI 10.1016/S0265-931X(03)00081-X.

Jancev, M., Boev, I., Stojanovska, Z. and Boev, B., (2019) *Characterization of phosphogypsum from dumps of Veles phosphate fertilizer factory (North Macedonia) and environmental implications.* Geologica Macedonica, 33 (2). pp. 111-124. ISSN 0352-1206

Jancev, M., Boev, I., Stojanovska, Z., Boev, B., (2020) *Evaluation of radioactivity in the phosphogypsum stockpile of "HIV" Veles, the Republic of North Macedonia.* Contemporary Materials, 1 (XI). pp. 27-32. ISSN 19868669