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Original scientific paper

RADON AND RADIUM CONCENTRATION IN WATER FROM PUBLIC FOUNTAINS AT THE CENTRAL PARTS OF THE KRATOVO-ZLETOVO VOLCANIC AREA, REPUBLIC OF NORTH MACEDONIA

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A b s t r a c t: The paper presents information about our latest study of radon and radium in drinking water from the public water fountains situated in central parts of the Kratovo-Zletovo volcanic area. Results for the radon in water measurements were as follows: Fountain 1 to Fountain 4 samples, ranged from 6.63 up to 157.73 Bq l^{-1}. Obtained results for the radium in water, Fountain 1 to Fountain 4 samples, ranged from 0.20 up to 1.08 Bq l^{-1}. Both, radon and radium measurements, in water samples from certain fountains have shown significantly higher values than the strictest standards given by the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO). The committed effective doses for the population consuming the water directly from the fountains or as self-bottled waters from the Kratovo-Zletovo volcanic area were estimated using the concentration of ^{222}Rn and ^{226}Ra in water samples, ranged from 45.47 μSv y^{-1} to 709.36 μSv y^{-1}, which once again for some fountains were higher than the WHO recommended values of max. 100 μSv y^{-1}.

Key words: radon; radium; water; fountains; effective dose; Kratovo; Zletovo

INTRODUCTION

As already mentioned elsewhere radiation from a variety of sources (natural and anthropogenic) has always been a potential danger to humans (Ilani et al., 2006; Sannappa et al., 2006). The average world annual dose is about 2.4 μSv, so although it is inevitable, its control is necessary (UNSCEAR, 1993; WHO, 2011; WHO 2018)**.**

It is an inevitable fact that surface and underground waters contain radionuclides as natural components in various concentrations depending on their origin (Tasev et al., 2022). The radionuclides are part of the terrestrial composition where they could be found in different concentrations (Di Carlo et al., 2019). The radioactive series ^{238}U, ^{235}U, and ^{232}Th as well as their radionuclides are continuously present in the human body and contribute to internal radiation emitting alpha and beta particles. The major fraction of the internal dose received by humans from naturally occurring radionuclides can be easily attributed to radium (^{226}Ra) and its daughter products, especially radon (^{222}Rn). As a result of natural processes like decay and dissolution from the surrounding geological environment (rocks, soils) of its parent nuclide radium (^{226}Ra) and consecutively radon (^{222}Rn) are released into waters (Moreno et al., 2014; Fonollosa et al., 2016). Radon in water may originate from dissolution of airborne radon into water and other higher radon bearing water in-flows in the catchment area, too. It has long been known that many mineral springs contain significant concentrations of naturally occurring radionuclides (mostly radium and radon) in higher concentration (in the range of 200–300 Bq·l^{-1}; Najeeb et al., 2014) than the usual drinking water (Moldovan et al., 2009). During the last decades, radon and radium concentration in ground water and its variability with time and space have been studied more intensively (Alshamsi et al., 2013; Eröss et al., 2015). Radium is known as more chemically active and it can easily be absorbed from the soil by plants and transported to the food chain to humans when it may affect the tissues (bone marrow that produces red blood cells) and can cause bone cancer, also. The radioactive gas radon, as a decay product of ^{226}Ra, is very important from the point of view of health risk. ^{222}Rn is an inert gas whose concentrations in ground water are reportedly related to a number of factors including its emission from surrounding rocks, temperature, pressure, rainfall and earthquake activities (Ilani et al., 2006; Sannappa et al., 2006). The alpha radiation emitted by radon and its progeny polonium is considered a significant health hazard by the United State Environmental Protection Agency because at elevated levels it causes lungs cancer (Lubin et al., 1995; UNSCEAR, 2006).

Due to fact that they have always been regarded as a voluptuary good, bottled mineral waters intended for human consumption until recently were excluded from national and international regulations. But being aware that in the recent years consumption of bottled mineral waters, without any doubts, has become very popular and even a significant segment of the population (due to a higher standard of living) drinks exclusively only mineral water as drinking water, approximately 1 $l \cdot d^{-1}$ (Statista, 2016) arise an idea of their monitoring in regards to radon and radium. This is very similar to the average individual consumption of bottled mineral water is 0.36 $l \cdot d^{-1}$ in Europe (Di Carlo et al, 2019). Population exposure to radon concentration in such waters is usually low because its half-life (3.8 days), which is much shorter than the typical time needed by bottled waters to reach consumers' houses. As a consequence, radon concentration measured in mineral bottled waters is usually lower or much lower than its above-mentioned parametric value (Kralik et al., 2003). Opposite to that scenario, in non-industrially bottled mineral waters, radon exposure can be not negligible when consumers fill bottles and containers directly from public fountains thus reducing significantly the time elapsing between mineral water bottling and subsequent consumption. As we all already know, water for human consumption should be free from chemical, microbiological, and radiological contamination (UNSCEAR, 2000). It is a decades long tradition that inhabitants in rural settlements in the Republic of North Macedonia are self-bottling water for individual use from the public fountains. Those waters are believed to have positive effects to human's health due to an idea that they are located in industrially non-polluted areas and should be free any substances harmful to humans health. However, scientific approach and analyses of such waters are quite scarce.

STUDY AREA

Public fountain waters radon and radium activity concentration measurements were carried out on 4 samples from the Kratovo-Zletovo volcanic area, Republic of North Macedonia. Water that was sampled is regularly used for direct human consumption. As it is already known elevated radon concentrations are often encountered in water coming from wells drilled in bedrocks, containing medium to high uranium content. Radon in drinking water supplies derived from drilled wells is entirely dependent on the geochemistry of the bedrock or sands and gravels into which the well is drilled and the recharge rate of the bedrock fractures or the sand and gravel aquifer. In that regard, here we are giving brief preview of the local geology.

Geological characteristics of the Kratovo-Zletovo area.

The Kratovo-Zletovo volcanic area, situated in the eastern part of the country, is the largest magmatic area in the Republic of North Macedonia, which occupies a surface of about 1200 km^2 (Serafimovski, 1993). Opposing opinions for its regional geotectonic position are published. Some of them locate the area in the Serbo-Macedonian massif (Ivanov, 1966), while others say that it is situated in the Vardar zone (Arsovski and Petkovski, 1975; Dimitrijević, 1974). The Kratovo-Zletovo volcanic area includes the ore region of the same name, which is of great interest from magmatic and metallogenic point of view. According to (Arsovski, 1997; Serafimovski, 1993) and other researchers the volcanic activity in the Kratovo-Zletovo area started at the end of the Eocene or in the Early Oligocene, and with some pauses lasted up to the Early Pliocene. During its active period, volcanic activity successively shifted from north-east to south-west direction (Boev and Yanev, 2001). The Kratovo-Zletovo region volcanism was generally controlled by deep sub-meridional dislocations, activated by Paleogene east-west extension. Until the end of the Miocene, the volcanic activity was reestablished along longitudinal neotectonic dislocations, starting with younger north-south extension. Geomorphologically, in Kratovo-Zletovo area there are about 20 volcanic centres and calderas, highly eroded by post-volcanic denudation processes. The volcanic rocks in the Kratovo-Zletovo area belong to a large Eocene-Oligocene magmatic belt which can be traced from Serbia to the west and to Bulgaria and Turkey to the east (Harkovska et al., 1989). The explosive magmatism generated abundant volcanic rocks (lavas and pyroclastic materials) and subvolcanic bodies of predominantly andesite, trachy-andesite, dacite, and rhyolite composition (Figure 1).

Numerous studies showed the calc-alkaline to shoshonitic character of the magmatism, and only few of them refer it to the tholeiitic series [Serafimovski, 1993]

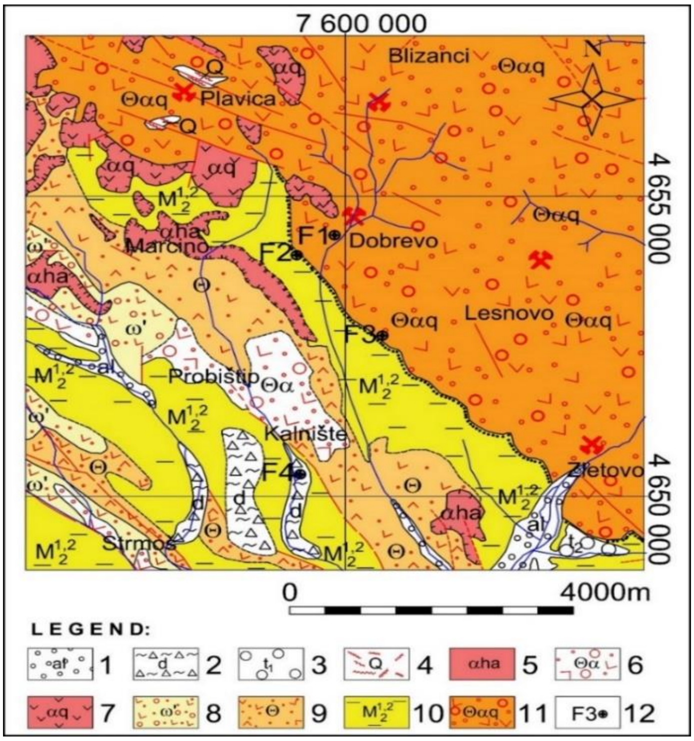


Fig. 1. Sketch of the Kratovo-Zletovo area geological map (excerpt from the Basic Geological Map of the Republic of North Macedonia; modified 2023)

Legend: ***Holocene:*** 1 – Alluvium, 2 – Deluvium, 3 – Lower river terrace; ***Pleistocene:*** 4 – Hydrothermal quartzites – silex, 5 – Horblenda – augite andesites, 6 – Ignimbrites of andesitic composition; ***Pliocene:*** 7 – Dacytoids, 8 – Andesitic breccias, 9 – Tuffs; ***Miocene:*** 10 – Marlstones, tuffaceous sandstones and claystones, 11 – Plated grey-green ignimbrites of dacite composition. 12 – *F1-F4* fountain water sampling points

METHODOLOGY

Here we explain the water fountain sampling, measurement system and the process of radon and radium analysis.

Water sampling procedure. The radon concentration is evaluated at the point where the drinking water is put into bottles for two main reasons:

i. The radon concentration in samples collected directly at the public water fountains is higher than in any other scenario interesting the same source (Figure 2). Indeed, referring to bottled water, the radon concentration in water stored in containers for transport and subsequent consumption (after a certain period of time) decreases due to the natural radioactive decay of Rn and the leakage through the sealing of the bottles. Also, radon concentration in water is significantly reduced during the processes of bottling and packing in plant operations.

ii. Sampling the water directly consumed, in a matter of an hours elapsing between the collection and the first opening of the bottle and water consumption.

For our research water was collected in polyethylene terephthalate (PET) bottles due to fact that such a material has lower radon loss during storage (Leaney et al., 2006; Lucchetti et al., 2016) than some other usually practiced types of polyethylene (Jobbágy et al., 2017), which also are compliant with ISO 13164–1:2013 (ISO, 2013a) and ISO 13164–3:2013 (ISO, 2013b) principles to be practiced in water sampling and its storage, and transport (Figure 2).

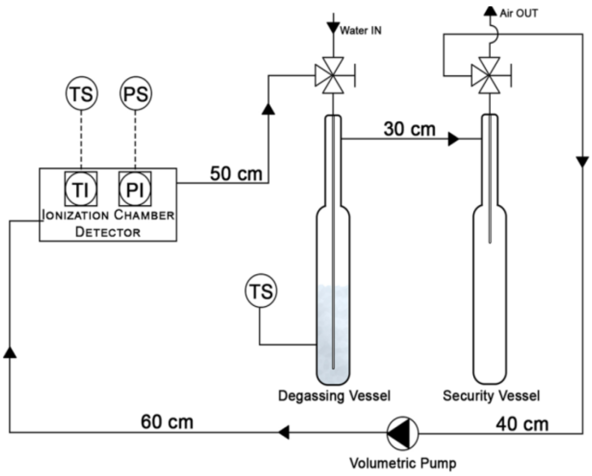
For the drinking water public fountains of interest, four samplings were carried out in the so-called *typical way* (Di Carlo et al., 2019), with a medium water flux and by simply placing the bottle in vertical position during filling operation, as a common user would have done (Figures 2b, 2c, 2d and 2e). The sealed samples were then transported to the University "Goce Delčev", Faculty of Natural and Technical Sciences in Štip, where the radon concentration measurements were performed. An effective time delay between the sample collection and measurements was kept below 6 h in order to increase measurements precision and to reduce radon loss due to diffusion through PET.

Fig. 2. a) Star denotes position of the sampling areas – the public water fountains in the Kratovo-Zletovo volcanic area (southeastern flank); b) Sampling the public fountain near the Dobrevo Pb-Zn mine; c) Sampling the public fountain near the Dobrevo village; d) Sampling the public fountain near the Dreveno village; e) Sampling the public fountain near the Kalnište village

Measurement system and procedure

Water quality parameters measurements such are pH, electrical conductivity and total dissolved solids (TDS) were performed using a glass electrode. The instrument used was the HANNA LF120 by HANNA Pvt. Ltd with an accuracy of 0.1 pH units and relative accuracy of 1% for the other two parameters.

Radiometric measurements were carried out by AlphaGUARD DF2000 (Bertin Instruments®) in order to measure radon/radium concentrations, and AquaKIT (Bertin Instruments®) accessory for samples degassing (Figures 3a, 3b). According to Jobbágy et al. (2017), the emanometry techniques relying on ionization chamber are characterized by a low detection limit (0.3 Bq l^{-1}) and a typical uncertainty (coverage factor $k = 1$) ranging between 5% and 12%.



a)

b)

Fig. 3. a) Scheme and b) illustration of radon in water concentration experimental setup. The diagram shows the position where temperature and pressure are monitored. Attention should be paid to tubes length and internal diameter when computing the inner volume of the whole apparatus (Saphymo GmbH, 2017)

The measuring set-up (Figure 3), consists of: (*i*) a degassing vessel, a custom gas washing vessel of DURAN® that hosts the degassing process; (*ii*) a security vessel, a DURAN® container to collect all the water drops in the gas flow; (*iii*) an active coal filter, used to reduce the radon content in the measurement set-up before injecting the sample; (*iv*) an Alpha Pump (Bertin Instrumens®); (*v*) six connecting tubes, Tygon® connections of different length and with an interior diameter of 4 mm (5/32″).

It is important to declare that:

• the lower nozzle of the degassing vessel is connected to the lower nozzle of the security vessel;

• the upper nozzle of security vessel is connected to the volumetric pump inlet;

• the volumetric pump outlet is connected to the inlet of ionization chamber;

• the ionization chamber outlet is connected with the upper nozzle of the degassing vessel such to close the circuit.

When all previous requirements are satisfied, the pressure head by the volumetric pump over comes the hydraulic head of the circuit preventing the water from flowing backward the ionizing chamber of the continuous radon monitor.

The radon concentration in water results from the following equation:

$$C_{\text{water}} = \frac{C_{\text{Air}} \cdot \left[\frac{V_{\text{system}} - V_{\text{sample}}}{V_{\text{sample}}} + k\right] - C_o \cdot \left[\frac{V_{\text{system}} - V_{\text{sample}}}{V_{\text{sample}}}\right]}{1000}$$

where:

• C_{water} is the radon concentration in the water sample [Bq l^{-1}];

• C_{air} is the radon concentration [Bq m^{-3}] of the air flowing in the measuring system during the degassing process of water samples. The radon concentration is monitored by the detector, whose functioning mode is set to 1 min FLOW, for 20 minutes. The air flow rate is set to 0.5 l min^{-1}.

• C_0 is the radon concentration [Bq m^{-3}] of the air contained in the measuring system before the injection of the sample inside the degassing vessel. The radon concentration is monitored by the detector, whose functioning mode is set to 1 min FLOW, for 10 minutes. The air flow rate is set to 0.5 l min^{-1}.

• V_{system} is the total volume [ml] of the complete measuring system, 1150 ml ± 1%, according to AquaKIT manual (Saphymo GmbH, 2017).

• V_{sample} is the water sample volume (ml). All the measurements referred in this paper were performed with a sample volume of 100 ml.

• K is the Ostwald absorption coefficient which describes the ratio of the radon concentration in water to the radon concentration in air, at thermodynamic equilibrium. This coefficient has been computed using the following mathematical formula: $K = 0.105 + 0.405e^{-0.0502 \cdot T}$[°C] (Battino and Clever, 1965; Weigel, 1978).

As it was already mentioned above, radium is naturally occurring radioactive element in the Earth's crust and it is chemically similar to calcium and absorbed from soil by plants, passed up the food chain to humans. The radiation emitted by radium will affect the tissues in the bone marrow that produces red blood cells and also can cause bone cancer (Shivakumara et al., 2014). We would like to stress that radium (^{226}Ra) and its radioactive decay products are responsible for much of the internal dose that humans receive from natural radionuclides. In general radium (^{226}Ra) is a direct precursor of radon (^{222}Rn), and is in secular equilibrium with it. λ_{Ra} and λ_{Rn} (the radioactive decay constants of radium and radon) have been found to be appropriate for the number of radium and radon atoms N_{Ra} and N_{Rn} (Shivakumara et al., 2014). In the case of secular equilibrium, during $t << T_{1/2(Ra)}$, where $T_{1/2(Ra)}$ = 1620 years, the rate of disintegration of radium is actually constant, so it can be roughly said that $e^{-\lambda_{Rn} t} \approx 1$, which means $N_{Ra} = N_{Ra}(0)$ and the number of radon atoms is given by the equation:

$$N_{Rn} \approx N_{Ra}\frac{\lambda_{Ra}}{\lambda_{Rn}}\left(1 - e^{-\lambda_{Rn} t}\right).$$

In addition, even if the condition $t \geq T_{1/2\,(Rn)}$ is satisfied, where $T_{1/2\,(Rn)}$ = 3.82 days, then $e^{-\lambda_{Rn} t} \approx 0$, which leads to the equation:

$$N_{Rn} = N_{Ra}\frac{\lambda_{Ra}}{\lambda_{Rn}},$$

or that $\lambda_{Rn} \cdot N_{Rn} = \lambda_{Ra} \cdot N_{Ra}$, which actually means that the activities of the parent (^{226}Ra) and the "daughter/product" (^{222}Rn) become equal. In practice this means that the radon concentration is equal to the radium concentration, this occurs after a period of 30 days when radium can be counted in a secular balance with radon. For the analysis data processing was used Data View software by Bertin Instruments®.

RESULTS AND DISCUSSION

Our analyses of four samples (each sample was analyzed for radon and radium) taken consecutively showed the results as given in Table 1 and Table 2. Below, we present in more detail the results and comments related to radon and radium.

Radon

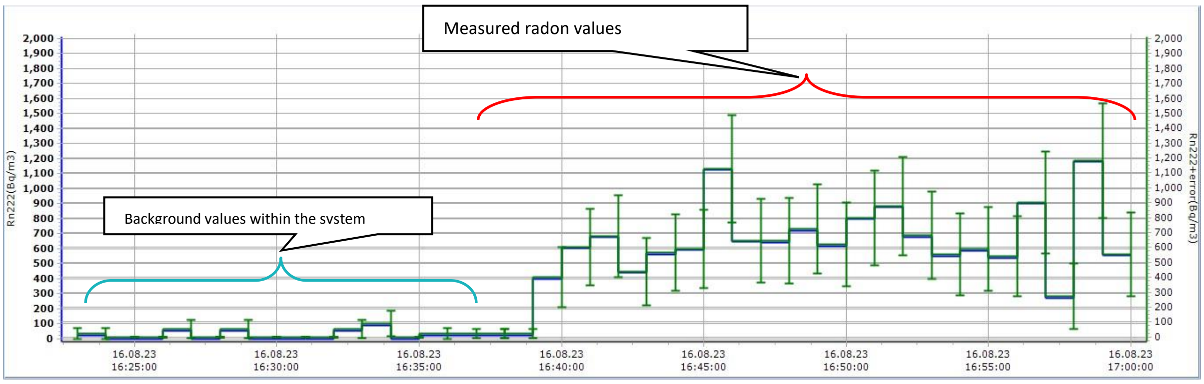
All the analyses of the radon in air within water samples from the analyzed samples (Fountain 1 to Fountain 4) showed minimal values within range from 1.83 to 20.68 Bq m^{-3}, maximal values within range from 1179.61 to 19174.00 Bq m^{-3}, average values ranged from 477.86 to 9142.37 Bq m^{-3}, while median values were within range from 558.98 to 14189.70 Bq m^{-3} (Table 1; Figure 4).

Calculation of radon in water measurements, for the Fountain 1 to Fountain 4 samples, ranged from 6.53 up to 157.73 Bq l^{-1} (Table 1; Figure 4).

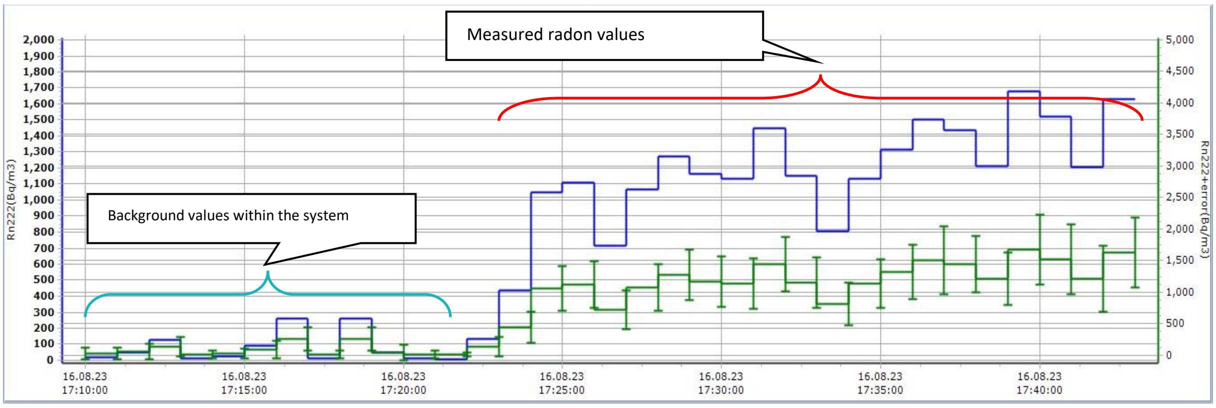
Table 1

Radon concentration in air and water within water samples from the public water fountains in the Moklište area

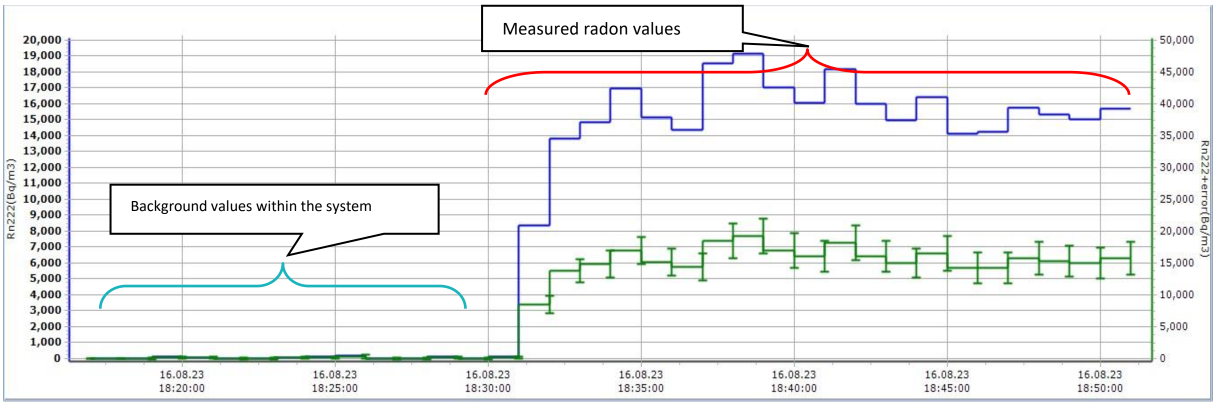
Sample	N (number of measurements)	MinAir (Bq m^{-3})	MaxAir (Bq m^{-3})	AverageAir (Bq m^{-3})	MedianAir (Bq m^{-3})	Water (Bq l^{-1})
F1	37	20.68	1179.61	477.86	558.98	6.53
F2	33	7.99	1678.10	758.69	1048.22	11.52
F3	34	1.83	19174.00	9142.37	14189.70	157.73
F4	36	8.30	7151.12	3854.81	5576.53	60.23



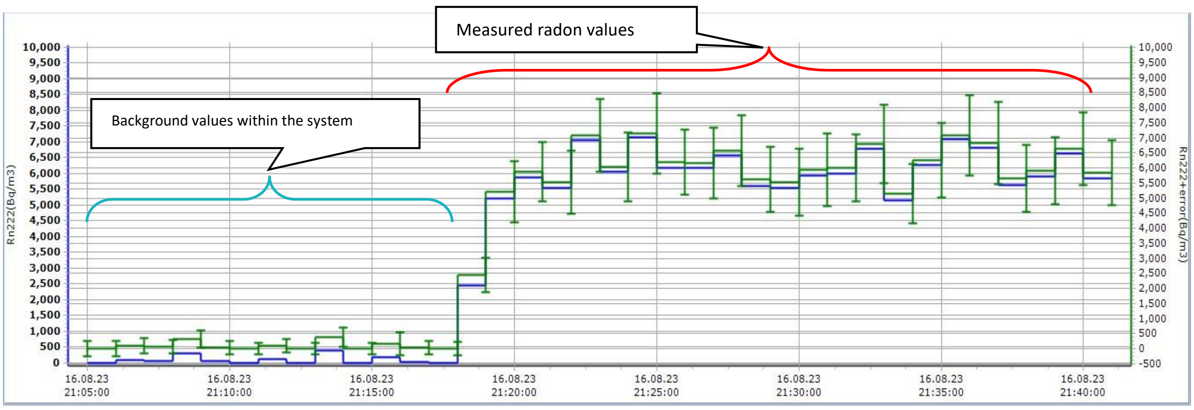
F1



F2



F3



F4

Fig. 4. Radon measurements, in all 4 public water fountains samples (F1–F4)

Results of radon analyses in the respective public fountains water samples were compared with Macedonian national reference value (MDK; 1000 Bq l^{-1}), World Health Organization reference value of 100 Bq l^{-1} (WHO, 2011; WHO 2018) and the strictest one given by United States Environmental Protection Agency or US-EPA (US-EPA, 1999), which is set at 11.1 Bq l^{-1} (Di Carlo et al. (2019). As can be seen from Table 1 and Figure 5, the concentrations of radon in three of four analyzed water samples (F2, F3 and F4) in the Kratovo-Zletovo volcanic area were above the maximum allowed values accoding to the US-EPA (US-EPA, 1999).

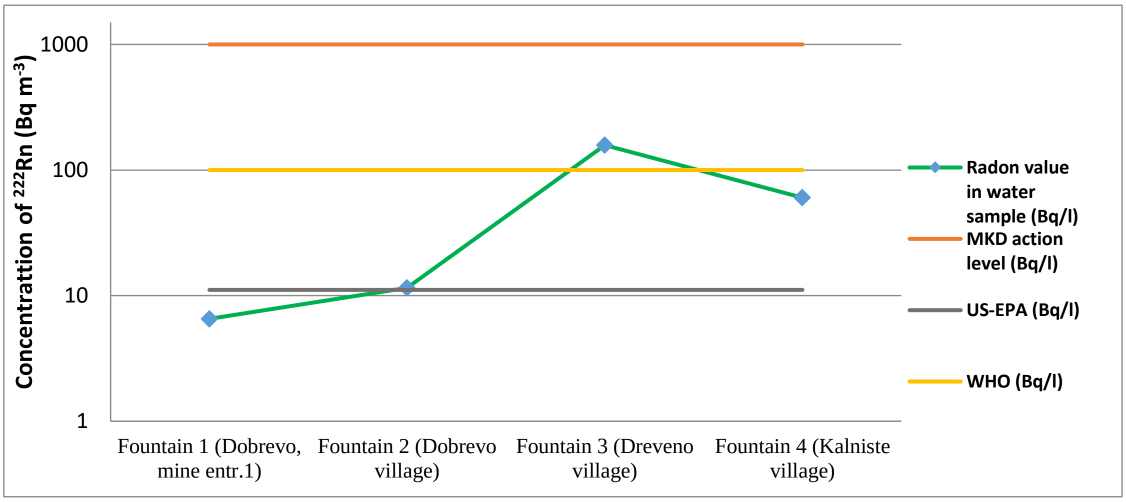


Fig. 5. Concentration of radon in waters from public fountains within Kratovo-Zletovo volcanic area compared to maximum allowed values according to the MDK action levels, World Health Organization (WHO) and United States Environmental Protection Agency (EPA)

Also, we must not ignore the fact that the obtained values for the concentration of radon in these consumable waters, are several times (4–50 times) higher than the values obtained when measuring tap water from homes in the Macedonian city (Tasev et al., 2021).

Radium

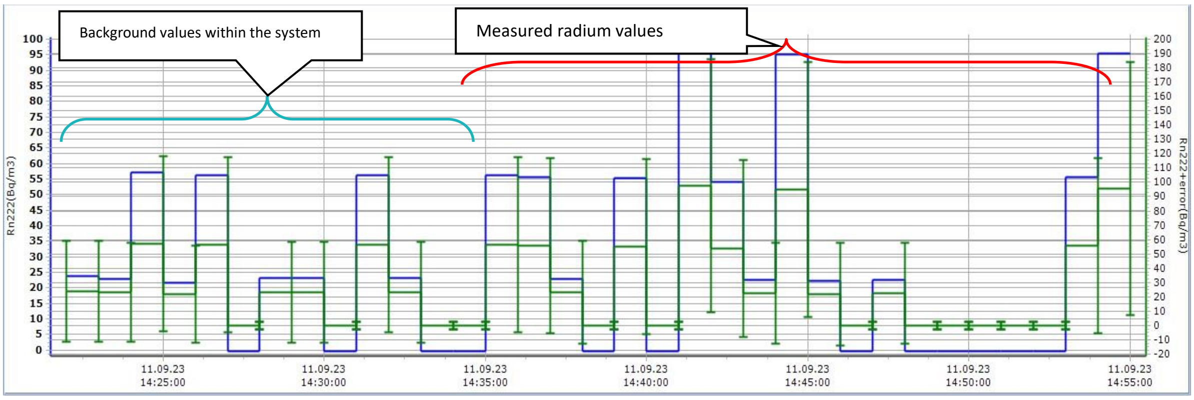
As we already mentioned above, after the 30 days period after the initial water sampling, once again we measured the radon in water within the duplicate samples. In practice this means that the radon concentration is equal to the radium concentration due to fact that after a period of 30 days radium can be counted in a secular balance with radon. Our analyses of four samples (Fountain 1 to Fountain 4) taken consecutively showed the results as given in Table 2.

All the analyses of radium in air within water samples from the preventive method showed the lowest minimal value of 18.04 Bq m^{-3}, the highest maximal value of 382.85 Bq m^{-3}, while average values ranged 45.85 to 94.01 Bq m^{-3} and median values from 23.11 Bq m^{-3} to 64.47 Bq m^{-3} (Table 2; Figure 6).

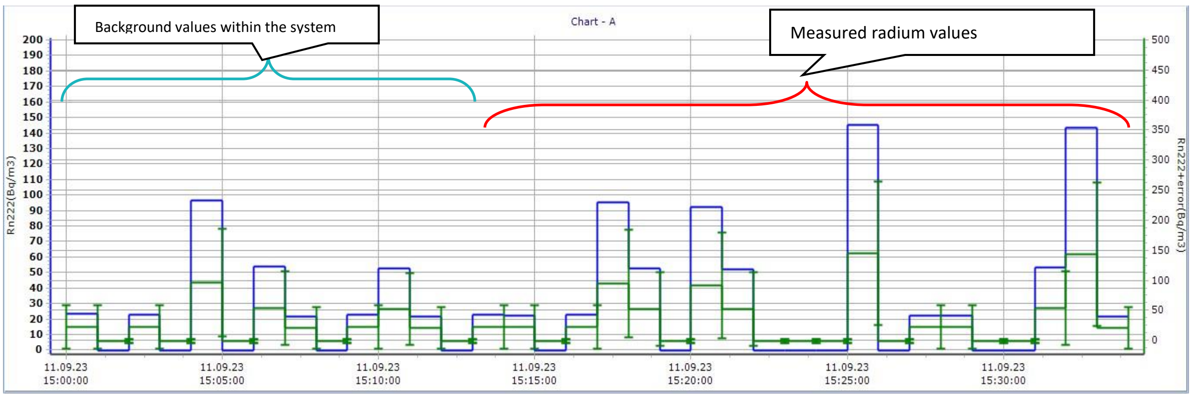
Table 2

Radium concentration in air and water within water samples from the public water fountains in the Kratovo-Zletovo volcanic area

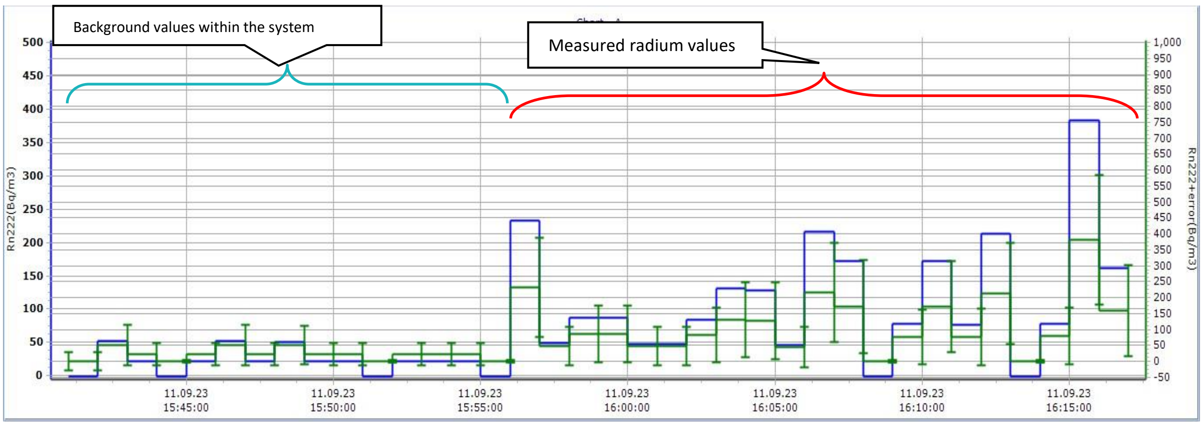
Sample	*N* (number of measurements)	MinAir (Bq m^{-3})	MaxAir (Bq m^{-3})	AverageAir (Bq m^{-3})	MedianAir (Bq m^{-3})	Water (Bq l^{-1})
F1	34	21.75	97.44	45.85	54.10	0.20
F2	35	21.49	145.01	51.45	23.11	0.26
F3	36	21.47	382.85	94.01	64.47	1.08
F4	35	18.04	176.81	57.13	44.23	0.60



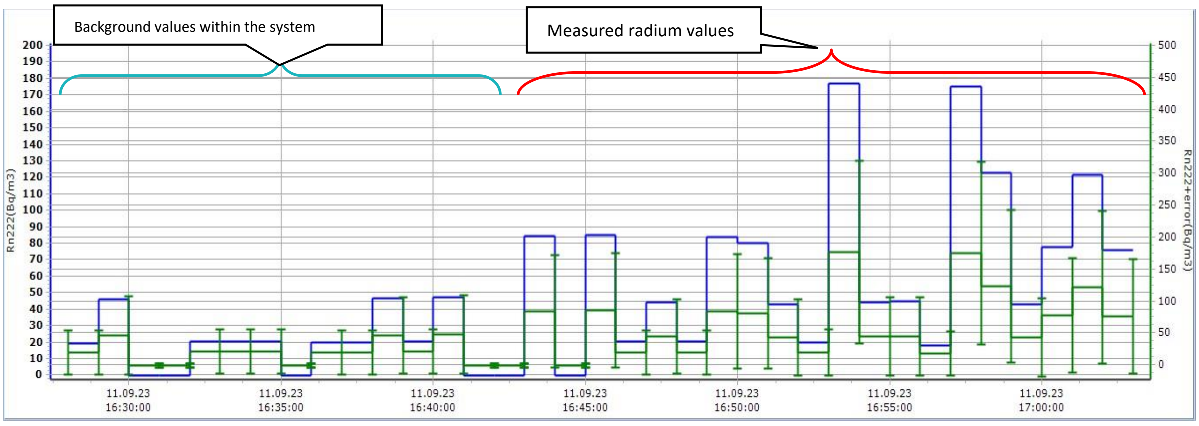
F1



F2



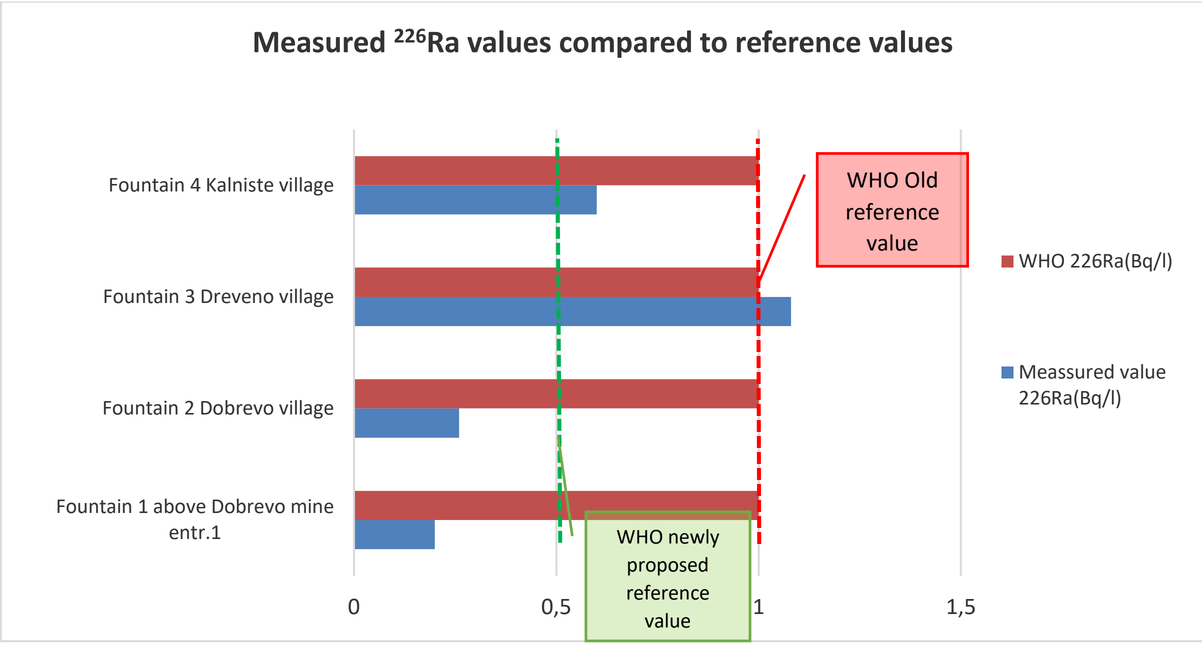
F3



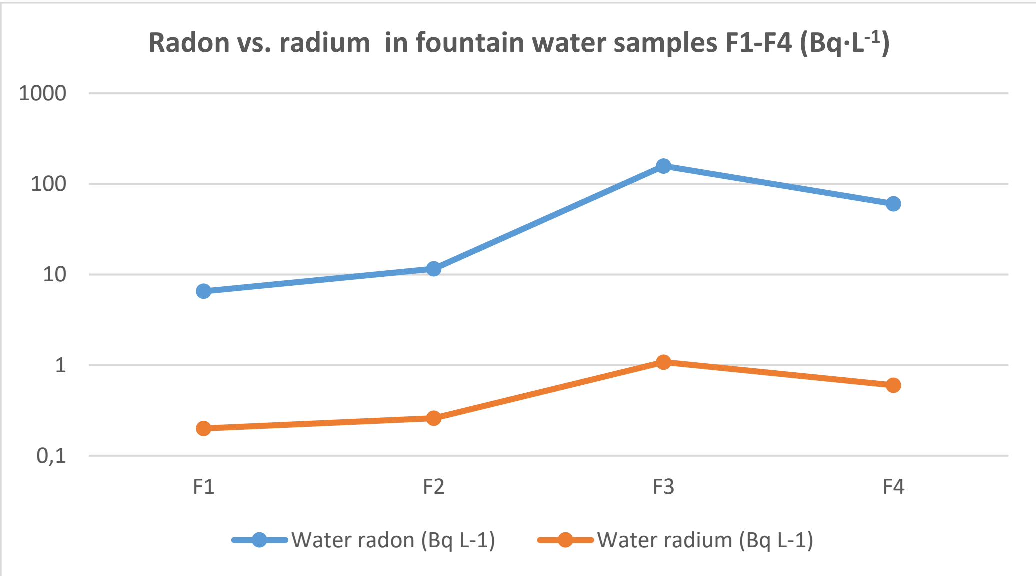
F4

Fig. 6. Radium measurements, in all 4 water fountain samples (F1-F4)

One of the analyzed four samples of drinking waters from public fountains within the Kratovo-Zletovo volcanic area, was above the reference value for radium given by the World Health Organization (WHO) in the amount of 1 Bq·l^{-1} (Fountain 3)), while two analyzed samples (Fountain 3 and Fountain 4) have shown concentrations exceeding the newly proposed value of 0.5 Bq·l^{-1} (Figure 7a).



a)



b)

Fig. 7. a) Radium concentration in drinking waters from the Kratovo-Zletovo volcanic area public fountains; **b)** Correlation of radon vs. radium in drinking waters from the Kratovo-Zletovo volcanic area public fountains

As we initially supposed the relation between the radon and radium was strong, as it was confirmed by positive correlation factor of 0.994876, which confirmed strong dependency between the predecessor (^{226}Ra) and successor (^{222}Rn) elements in the uranium decay chain.

Increased values of radon and radium in the studied area can be explained with the fact that rocks of the Kratovo-Zletovo area are mainly of volcanic origin (andesite, trachy-andesite, dacite and rhyolite; Serafimovski, 1990, 1993), with a significant concentration of natural radionuclides, includeing radium which decays into radon (Bochicchio et al, 1999),

Dose due to ^{222}Rn and ^{226}Ra concentration in water

The committed effective dose for the population consuming the self-bottled water from the Krtovo-Zletovo volcanic area public drinking water fountains (Fountain 1 to Fountain 4) of the region was estimated using the concentration of ^{222}Rn and ^{226}Ra in water samples and directions given in UNSCEAR (2000), WHO (2011), Shivakumara et al. (2014). The parameters for the inhalation pathway were ^{222}Rn concentration in water, air water concentration ratio of 10^{-4}, indoor occupancy of 7000 h per year, equilibrium factor 0.4 and inhalation dose conversion coefficient 9 nSv (Bq h m^{-3})$^{-1}$. The effective dose to the ingestion mainly depends upon the amount of water consumed by a human being in a day (in our case 1 l day^{-1}). The dose due to inhalation and ingestion are calculated by the equations given in UNSCEAR (2000):

$$\textit{Inhalation dose } {}^{222}\mathrm{Rn}\ (\mu\mathrm{Sv}) = {}^{222}\mathrm{Rn}_{\mathrm{conc.}})\ \mathrm{Bq}\cdot l^{-1}) \times 10^{-4} \times 7000\ \mathrm{h} \times 0.4 \times 9\ \mathrm{nSv}\ (\mathrm{Bq}\cdot\mathrm{h}\cdot\mathrm{m}^{-3})^{-1}$$

$$\textit{Ingestion dose } {}^{222}\mathrm{Rn}\ (\mu\mathrm{Sv}) = {}^{222}\mathrm{Rn}_{\mathrm{conc.}}\ (\mathrm{Bq}\cdot l^{-1})\ 365\ l\ \mathrm{y}^{-1} \times 3.5\ \mathrm{nSv\ Bq}^{-1} \times 10^{-3}$$

$$\textit{Ingestion dose } {}^{226}\mathrm{Rn}\ (\mu\mathrm{Sv}) = {}^{226}\mathrm{Rn}_{\mathrm{conc.}}\ (\mathrm{Bq}\cdot l^{-1})\ 365\ l\ \mathrm{y}^{-1} \times 0.28\ \mathrm{nSv\ Bq}^{-1} \times 10^{-3}$$

Calculated values for the exposure during inhalation of radon and ingestion of radon and radium within water samples from the public water fountains in the central parts of the Kratovo-ZLetovo volcanic area are given in Table 3.

As already mentioned elsewhere (Tasev et al., 2022), the dose due to ^{222}Rn is divided into two parts, namely the dose from ingestion and the dose from inhalation. For the ingestion and inhalation part, ^{222}Rn and its progeny in water impart a radiation dose to the stomach and lung, respectively.

Table 3

Exposure dose due to inhalation of radon and ingestion of radon and radium within sampled water samples in this study

Sampling location	Fountain 1 (above Dobrevo Pb-Zn mine entrance)	Fountain 2 (near Dobrevo village)	Fountain 3 (Dreveno village)	Fountain 4 (Kalnište village)
Number of measurements	37+34	33+35	34+36	36+35
pH	7.1	7	6.2	6.2
TDS (Rn_{meas}/$Ra_{meas.}$)	460	410	580	630
EC (µS cm^{-1}) (Rn_{meas}/$Ra_{meas.}$)	930	830	1190	1290
^{222}Rn (Bg l^{-1})	6.59	11.52	157.73	60.23
^{226}Ra (mBg l^{-1})	200.00	260.00	1080.00	600.00
Inhalation dose ^{222}Rn (µSv y^{-1})	16.61	29.03	397.48	151.78
Ingestion dose ^{222}Rn (µSv y^{-1})	8.42	14.72	201.50	76.94
Ingestion dose ^{226}Ra (µSv y^{-1})	20.44	26.57	110.38	61.32
TOTAL dose (µSv y^{-1})	**45.47**	**70.32**	**709.36**	**290.04**
TOTAL dose (mSv y^{-1})	0.045465525	0.0703192	0.709355675	0.290043425
TOTAL ingestion dose (mSv y^{-1})	0.028858725	0.0412888	0.311876075	0.138263825
TOTAL inhalation and ingestion ^{222}Rn (µSv y^{-1})	25.03	43.75	598.98	228.72

Computing from the radium and radon activity concentrations in public fountains water samples, the total dose due to ingestion and inhalation varies from 45.47 to 709.36 mSv y^{-1}, which is below the prescribed dose limit of 100 μSv y^{-1} by WHO (2011) for the first two public fountains, while the Fountain 3 and 4 exhibited 7 and 2 times fold higher values than the one given by WHO, see Figure 8 below. These values were quite compatible when compared to certain values measured around the World, such as those at Malavalli, Mandya and Yettaganahalli in India where the total dose is above maximally allowed 100 μSv y^{-1} due to higher concentration of radium and radon in borewell water (Eckerman et al., 2012; Shivakumara et al, 2014).

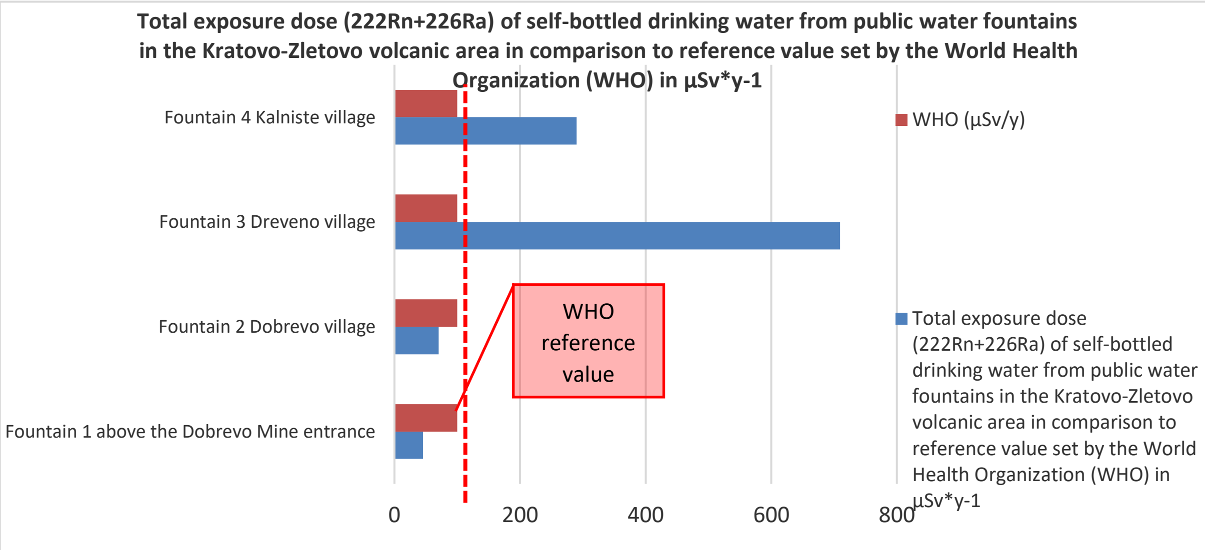


Fig. 8. Total exposure dose for both, ^{222}Rn and ^{226}Ra, in water from the public water fountains at the Kratovo-Zletovo volcanic area (Fountain 1 to Fountain 4)

Also, as indicated by the high correlation ratio ^{222}Rn vs. ^{226}Ra (0.994876), some other intertwined parameters related to the dose due to these two elements showed high correlation factors. Ingestion dose due to ^{226}Ra vs. concentrattion of ^{222}Rn showed the same exact correlation factor as it was for ^{222}Rn vs ^{226}Ra, while total dose due to ingestion of ^{222}Rn and ^{226}Ra and inhalation of ^{222}Rn vs. ^{226}Rn have shown even higher correlation factor of 0.999908. Discharging waters of the Kratovo-Zletovo volcanic area fountains were characterized by elevated total dissolved solid content (TDS), temperature and by oxidizing conditions, and therefore with certain uranium content and therefore their radium content is probably higher (Tasev et al, 2021). All the measured can be explained.

CONCLUSIONS

A systematic survey of natural mineral spring waters originating from four water fountains within the Kratovo-Zletovo volcanic area (Fountain 1 to Fountain 4) Republic of North Macedonia was carried out in order to evaluate if contained radon and radium levels may be of public health concern due to regular consumption by local inhabitants. The presence of radon in fountain waters compared to the parametric value was previously not analyzed in the subject region.

These particular measurements and analysis of the samples allowed us to determine the concentration of radon and radium in the self-bottled water from the four public fountains located at the Kratovo-Zletovo volcanic area that the consumers directly use them on daily basis, which is a common habit in this region. Namely, the radon concentrations were in the range 6.59 to 157.73 Bq l^{-1}, which for Fountain 3 and Fountain 4 significantly exceeded the strictest US-EPA standards for drinking water of 11.1 Bq l^{-1}. Similar as it was case with radon, radium measurements showed a range of concentrations from 0.20 to 1.08 Bq l^{-1}, which in this case exceeded the existing (1.0 Bq l^{-1}) and suggested (0.5 Bq l^{-1}) values according to the World Health Organization for the waters from Fountain 3 and Fountain 4. Also, in that direction were calculated effective doses due to inhalation of radon and ingestion of radon and radium, in the range from 45.47 to 709.36 mSv y^{-1}, which for waters from Fountain 3 and Fountain 4 exceeded the maximum permissible values of 100 mSv y^{-1}. Results as these are can be explained with the fact that rocks of the Kratovo-Zletovo area are mainly of volcanic origin (andesite, trachy-andesite, dacite and rhyolite; Serafimovski, 1990, 1993), with a significant concentration of natural radionuclides, including radium which decays into radon (Bochicchio et al, 1999). If the results of this particular survey will be confirmed by further and more detailed studies in other adjacent zones, requirements regarding radon as well as radium, some sort of control in mineral waters should probably be considered for the future, especially for habitants where consumption of such waters cannot be considered negligible.

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Р е з и м е

КОНЦЕНТРАЦИЈА НА РАДОН И РАДИУМ ВО ВОДА ОД ЈАВНИ ЧЕШМИ ВО ЦЕНТРАЛНИТЕ ДЕЛОВИ НА ВУЛКАНСКОТО ПОДРАЧЈЕ КРАТОВО-ЗЛЕТОВО, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: радон; радиум; вода; чешми; ефективна доза; Кратово; Злетово

Во трудот се претставени информации од нашите најнови испитувања на радонот и радиумот во водата за пиење од јавните чешми во централните делови на кратовско-злетовската вулканска област. Резултатите од мерењата на радонот во испитуваната вода, примероците од чешма 1 до чешма 4, се движеа од 6,63 до 157,73 Bq l^{-1}. Добиените резултати за радиумот во водата, примероците од чешма 1 до чешма 4, се движеа од 0,20 до 1,08 Bq l^{-1}. Мерењата и на радонот и на радиумот во примероците вода од дадените чешми покажаа значително повисоки вредности од најстрогите стандарди дадени од Агенцијата за заштита на животната средина на Соединетите Држави (USEPA) и Светската здравствена организација (СЗО). Нивната ефективна доза што ја прима населението кое ја консумира водата од вулканската област Кратово-Злетово директно од чешмите или како само-флаширана, беше проценета мерејќи ја концентрацијата на ^{222}Rn и ^{226}Ra во примероците вода, а која се движи од 45,47 μSv y^{-1} до 709,36 μSv y^{-1}, што повторно покажа дека концентрацијата на овие елементи во некои јавни чешми е повисока од препорачаната од СЗО, односно од максималните 100 μSv y^{-1}.