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Original scientific paper

RADON AND RADIUM CONCENTRATION IN SELF-BOTTLED MINERAL SPRING WATER FROM THE PUBLIC FOUNTAIN "ELIXIR" AT THE MOKLIŠTE AREA, REPUBLIC OF NORTH MACEDONIA

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A b s t r a c t: Within this paper is presented information about current study of radon and radium analysis in self-bottled drinking water from the public water fountain "Elixir" in the Moklište area, city of Kavadarci. Obtained results for the radon in water measurements, for the preventive method taken samples, ranged from 3.40 up to 3.69 Bq·l^{-1}, while values for the typical method taken samples ranged from 2.60 up to 3.62 Bq·l^{-1}. Radon concentration measured from samples obtained in *typical* way showed lower than the corresponding values obtained using the *preventive* sampling method, where comparison of respective samples P1-T1, P2-T2 and P3-T3 have shown lower values of 1.09 %, 17.62 % and 23.53 % for typical method. Obtained results for the radium in water, for the preventive method taken samples, ranged from 0.08 up to 0.19 Bq·l^{-1} while values for the typical method taken samples ranged from 0.11 up to 0.14 Bq·l^{-1}. Radium concentration measured from samples obtained in *typical* way showed lower than the corresponding values obtained using the *preventive* sampling method, where comparison of respective samples P1-T1, P2-T2 and P3-T3 have shown differences in respective values of of 8.33 %, 42.11 % and 42.86 % for typical method. The committed effective dose for the population consuming the self-bottled water from the Moklište public drinking water fountain of the region was estimated using the concentration of ^{222}Rn and ^{226}Ra in water samples, which ranges from 21.09 to 33.43 μSv y^{-1} for preventive method and from 22.79 to 26.01 μSv y^{-1} for traditional method.

Key words: radon; radium; water; self-bottled; effective dose; Moklište; Kavadarci

INTRODUCTION

Radiation from a variety of sources (natural and anthropogenic) has always been a potential danger to humans. 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).

As it is already well known, surface and underground waters contain radionuclides as natural components in various concentrations depending on their origin. The radionuclides are part of the terrestrial composition where they could be found in different concentrations. The radionuclides from radiactive series of ^{238}U, ^{235}U, and ^{232}Th are 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). Also, radon in water may originate from dissolution of airborne radon into water and other higher radon bearing water in-flows in the catchment area. Also, we would like to stress that 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). Recently radon and radium concentration in ground water and its variability with time and space have been studied (Alshamsi et al., 2013; Eröss et al., 2015). Radium is 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, too. 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).

Up to date national and international regulations on water intended for human consumption exclude bottled mineral waters due to fact that they have always been regarded as a voluptuary good. However, in our modern era of living 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 liter for day (Statista, 2016). This is very similar to the average individual consumption of bottled mineral water is 0.36 liters for day in Europe (Di Carlo et al, 2019). Population exposure to radon concentration in such waters is usually low because radon half-life (3.8 days) 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). Oposite 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).

Recently, under the influence of certain respectable medical individuals in the Republic of Northern Macedonia, significant number of inhabitants of the town of Kavadarci and the surrounding settlements started to self-bottle water for individual use from the public fountain in the locality Moklište, approximately 6 km from the city center. This water is believed to have positive effects to human's health, so self-bottling is becoming more common lately.

STUDY AREA

Radon and radium activity concentration measurements in the public fountain water was carried out on 6 samples from the Moklište location in the Kavadarci city. Sampled water 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, within this part, we are giving brief preview of the local geology.

Geological characteristics of the Tikveš area

The geological characteristics of the Tikveš area up to date have been studied by numerous geologists, but the most complete description can be found in the works of Maksimović et al. (1954); Hristov et al. (1973), and lately in Stojanova and Petrov (2012, 2014). Based on the regional and detailed geological explorations for the necessities of the Basic Geological Map of the Republic of North Macedonia, the geological setting and litho-stratigraphic sequence in Tikveš area were defined (Figures 1 and 2).

The oldest formations have northwest–southeast direction delineation (NW-SE) and belong to the inner part of the Vardar zone. The lowest Paleozoic (Pz) metamorphic complex is represented by two series as follows: a series of amphibole and amphibole-chlorite schists with layers of marbles and a series of quartz-schist with quartz-sericite interlayers of marble and phyllite. Along the rupture structures in the Vardar zone in the form of elongated stripes and intersected lenses of serpentinite appear, too. The furthest south-west of the area Tikveš is represented with marbles and dolomites, which are probably of Devonian age. Through a series of Paleozoic metamorphic rocks developed the Mesozoic (Mz) formations, mainly from the Late

Cretaceous age. The Turonian (K_2) sandstones, massive conglomerates and limestone extend to the southwest and the west of the Tikveš area. The diabase and the submarines outbursts of spilite are common in the lower parts of the sequence, where also smaller masses of gabbro appear. The Paleozoic and Mesozoic rocks cover nearly 39 km^2 in the southwest and west part of the Tikveš area.

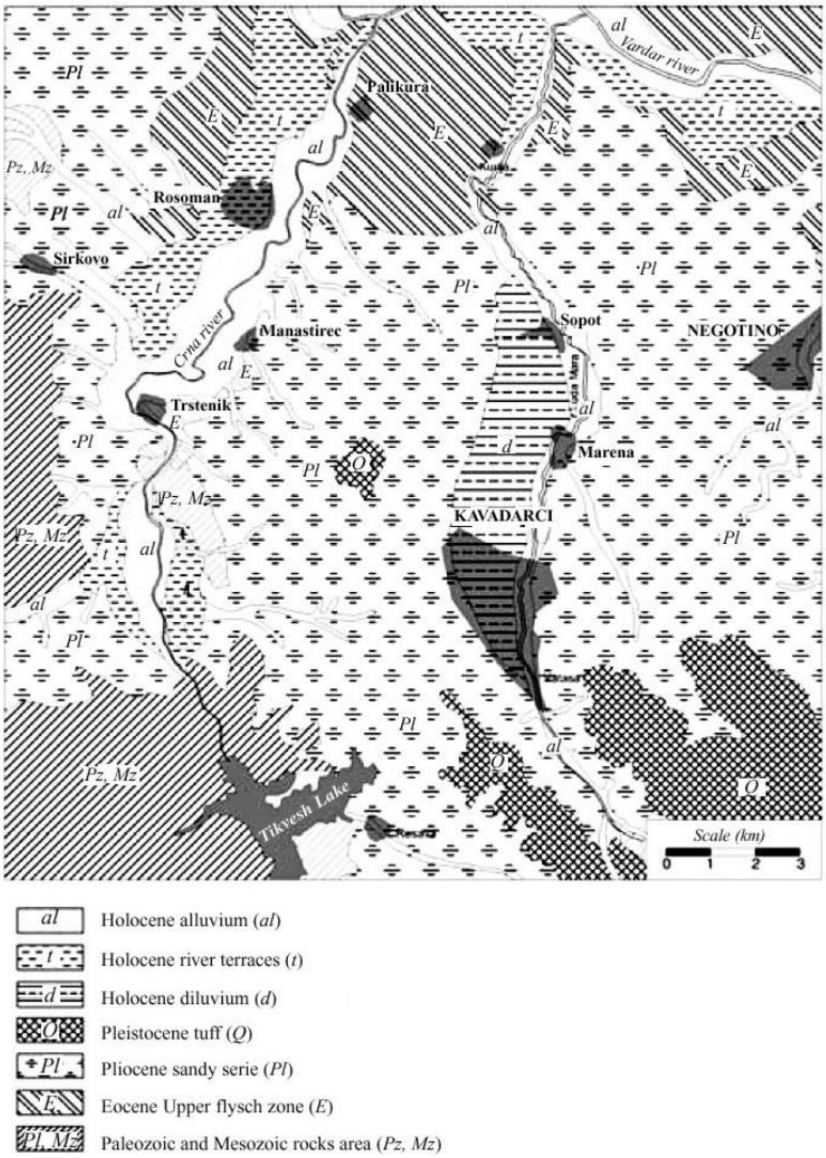


Fig. 1. Sketch of the Tikveš area geological map
(Excerpt from the Basic Geological Map of N. Macedonia modified by Stojanova and Petrov, 2014)

The complex of Tertiary and Quaternary sediments covers most of the Tikveš area. The Upper Eocene ($^4E_3$) flysch sediments and yellow sandstones occur along the valleys of the Vardar, Crna Reka and Luda Mara rivers, as well as in a fraction of the Tikveš basin. These sediments with depth to 3500 m cover about 34 km^2 mainly in the northern part of the Tikveš area. The Tikveš basin is filled with Pliocene (Pl) sediments, bordering with the Vardar river in the north and the Paleozoic-Mesozoic formation which covers the northwest-southeast. This area is mainly represented by sandy series of different sands. These series are homogeneous, containing mostly yellow sands with low content of coarse sandy clay (pebble sandy clay) and fine-bean gray sandstone, poor in fossil remains. The Pliocene (Pl) sediments cover most (about 182 km^2) of the central part of the Tikveš area. Southeast of Kavadarci there are Quaternary (Q) pyroclastic volcanite with tuffs, breccia and agglomerate, which covered around 25 km^2. The Quaternary period is represented by diluvium (d), river terraces (t) and alluvium (al). The diluvial sediments (12 km^2) contain coarse material from the surrounding rocks, mixed with sand and clay material. Along the Vardar, Crna and Luda Mara rivers terrace sediments are formed (23 km^2). The terraces contain gravel, sand and clay. Alluvial sediments (40 km^2) cover the flooding plains of the rivers of Vardar, Crna and Luda Mara and consist mainly of sand and clay. The city of Kavadarci is located in the Tikveš basin, in the SW part of the Republic of North Macedonia. This particular basin is composed of the peripherally positioned Paleogene sediments (basal lithozone, lower flysch lithozone, lithozone of yellow sandstones and upper flysch lithozone) that are extending in the NW-SE direction and occupy more than 20% of the area and their thickness that reaches 3000–3500 m while the central parts of the basin are covered by Neogene and Quaternary deposits (Stojanova and Petrov, 2014).

Paleogene sediments comprise of four lithostratigraphic units: basal lithozone, lower flysch lithozone, lithozone of yellow sandstones, and upper flysch lithozone (Figure 2).

The basal zone (thickness varies from 350–700 m) of the Paleogene sediments within the Tikveš basin is represented by conglomerates and sandstones that alternately change into clayey soil and sandy marls, and pelitomorphic limestone. The lower flysch lithozone (thickness is 300 m) differs from other units by rhythmic occurrence and prevalence of sandstones over conglomerates, and by rare inner layers of clayey soil, marls, and aleurolites. The lower flysch lithozone is composed of yellow sandstones with layers and inner layers of clayey soil and marls. The lower and upper borders of the lithozone of yellow sandstones (thickness from 100 to 400 m) are continuous and clear, which separates this unit from the lower and upper flysch lithozone. The upper flysch lithozone (thickness of this lithozone ranges from 2000 to 2500 m) is isolated as being a separate lithostratigraphic unit because of the rhythmic occurrence and prevalence of clayey soil and sandstones with the presence of thin inner layers of marls, aleurolites and limestones (Maksimovič et al., 1954; Stojanova and Petrof, 2014).

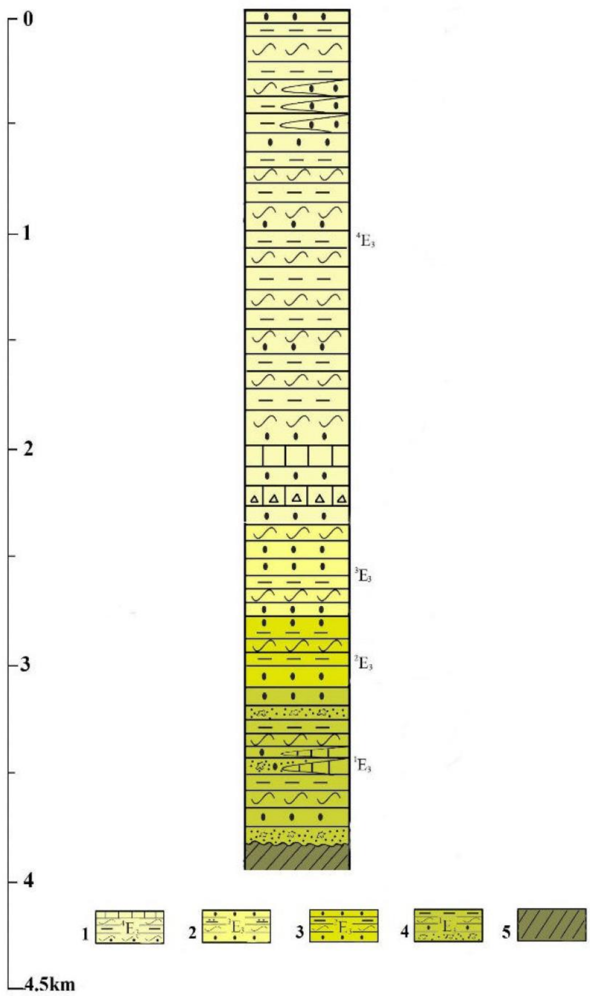


Fig. 2. Geological column of the Tikveš basin (Stojanova and Petrov, 2014)
1 – basal lithozone, 2 – lower flysch lithozone,
3 – lithozone of yellow sandstones,
4 – upper flysch lithozone, 5 – paleorelief

METHODOLOGY

Within this part of the paper, we explain the water sampling, measurement system and analysis process itself.

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 fountain is higher than in any other scenario interesting the same source. 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 inside the plant allows to know and minimize the time elapsing between the collection and the first opening of the bottle.

For the necessities of 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 3).

Preventive way usually is obtained by inclining the bottle and supposedly reducing the water flow rate at the minimum value (Di Carlo et al., 2019).

The remaining three samples were collected in *typical way*, with a medium water flux and by simply placing the bottle in vertical position during filling operation, as a common user would have done (Figure 3c).

For the drinking water public fountain of interest, three samplings were carried out in the so-called *preventive way*. As it is supposed such filling method aims to obtain a near laminar water flux that avoids spontaneous degassing of dissolved gases during filling the sampling bottle (Figure 3b).

a)

b)

c)

Fig. 3. a) Star denotes position of the sampling area – the public water fountain in the Moklište area, Kavadarci, North Macedonia; **b)** Sampling the preventive way; **c)** Sampling the typical way.

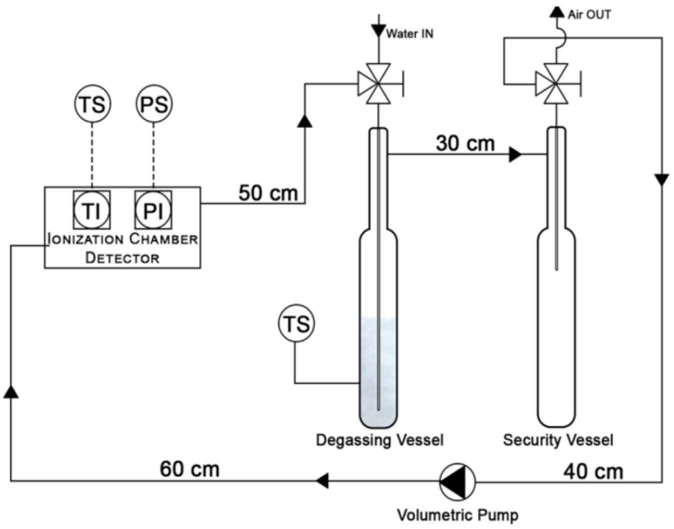
The sealed samples were then transported to the University "Goce Delcev" Teaching Center in Kavadarci where the radon concentration measurements were performed. The time delay between the sample collection and measurements was kept below 6 h in order to increase measurements precision and to reduce radon loss due to diffusion through PET.

Measurement system and procedure

The 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 a relative accuracy of 1% for the other two parameters.

The measurements were carried out by means of AlphaGUARD DF2000 (Bertin Instruments®) to measure radon concentration, and AquaKIT (Bertin Instruments®) accessory for samples degassing (Figures 4a, 4b). 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%.

The measuring set-up (Figure 4), 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″).



a)

b)

Fig. 4. 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)

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 overcomes 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:

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

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 (Genitron Instrument GmbH, 2012; 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: $K = 0.105 + 0.405e^{-0.0502.T}$[°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 (^{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 << T1/2(Ra), where T1/2 (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 $N_{Rn} = N_{Ra}$ (0) and the number of radon atoms is given by the equation:

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

In addition, even if the condition $t \geq$T1/2 (Rn) is satisfied, where T1/2 (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

Ours analyses of six samples (three by preventive method and three by typical method) taken consecutively showed the results as given in Table 1 and Table 2. In addition, 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 preventive method showed minimal value of 7.00 Bq·m^{-3}, maximal value of 844.88 Bq·m^{-3}, average value of 469.98 Bq·m^{-3} and median value of 490.81 Bq·m^{-3} (Table 1; Figure 5).

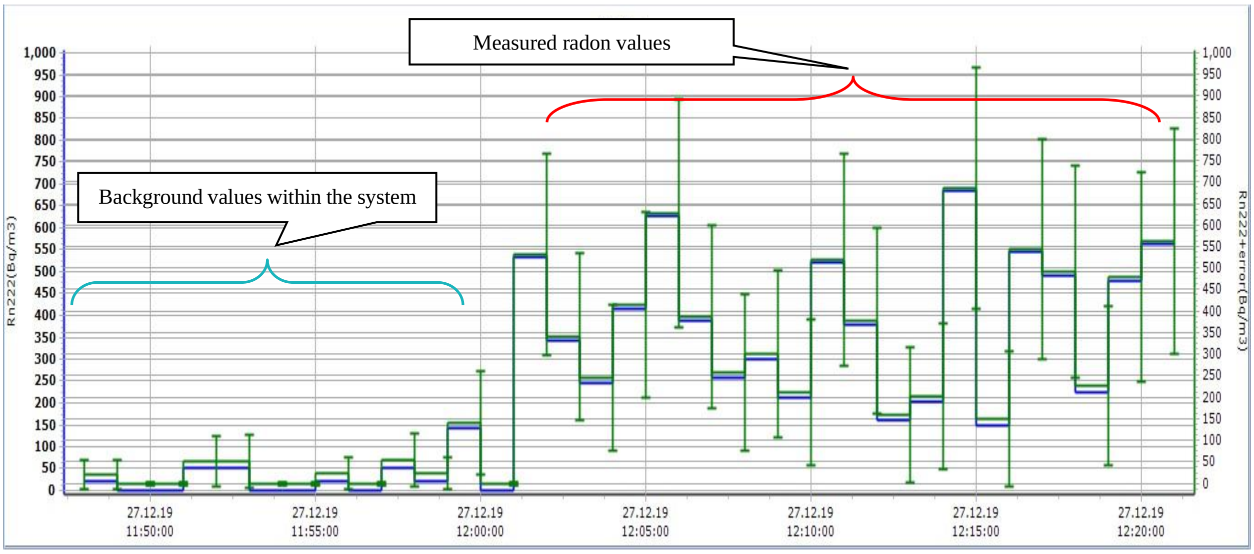
T a b l e 1

Radon concentration in air and water within water samples from the public water fountain in the Mokliště area

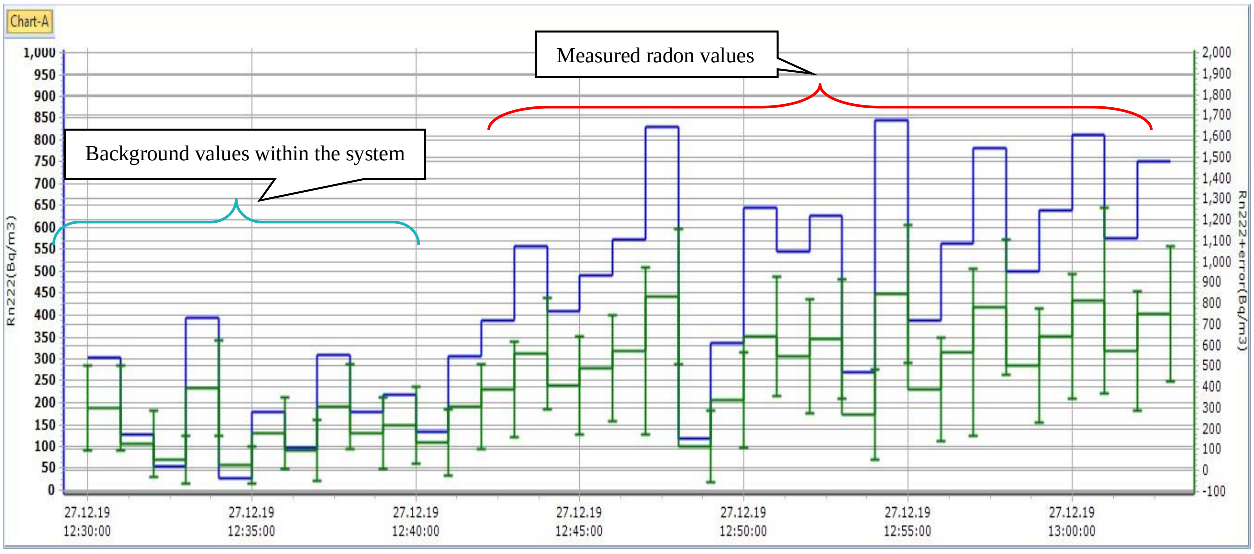
Sample	N (number of measurements)	Min$_{Air}$ (Bq·m^{-3})	Max$_{Air}$ (Bq·m^{-3})	Average$_{Air}$ (Bq·m^{-3})	Median$_{Air}$ (Bq·m^{-3})	Water (Bq·l^{-1})
P_1	21	7.00	684.39	367.95	378.30	3.66
P_2	22	117.36	844.88	543.20	561.35	3.69
P_3	21	176.20	825.70	495.31	512.07	3.40
T_1	21	267.77	1341.00	577.31	515.31	3.62
T_2	24	82.25	681.66	384.87	379.06	3.04
T_3	21	27.82	602.59	309.29	275.08	2.60
			Average P_1–P_3			3.58
			Average T_1–T_3			
			AVERAGE all samples (P and T)			3.34

Calculation of radon in water measurements, for the preventive method taken samples, ranged from 3.40 up to 3.69 Bq·l^{-1}, while values for the typical method taken samples ranged from 2.60 up to 3.62 Bq·l^{-1} (Table 1; Figure 5). Results of the analyses of radon in air within water samples from the typical method showed minimal value of 27.82 Bq·m^{-3}, maximal value of 1341.00 Bq·m^{-3}, average value of 422.05 Bq ·m^{-3} and median value of 408.76 Bq·m^{-3} (Table 1; Figure 6). Radon concentration measured from samples obtained in *typical* way showed lower than the corresponding values obtained using the *preventive* sampling method. Comparison of respective samples P1-T1, P2-T2 and P3-T3 have shown lower values of 1.09 %, 17.62 % and 23.53 % for typical method. An average P1-P3 values compared to average T1-T3 values showed lower value of 13.69% for those obtained by typical sampling method, which is quite similar to the findings of Di Carlo et al. (2019) for numerous Italian self-bottled mineral spring waters. We may conclude that the *typical* way of sampling leads to a not too large radon loss opposite to a more careful sampling procedure (preventive method) and since it represents the typical consumer's handling during self-bottling process of the water from the public fountains, it can be considered more representative (in regards to real radon levels) than the other alternative bottling approach.

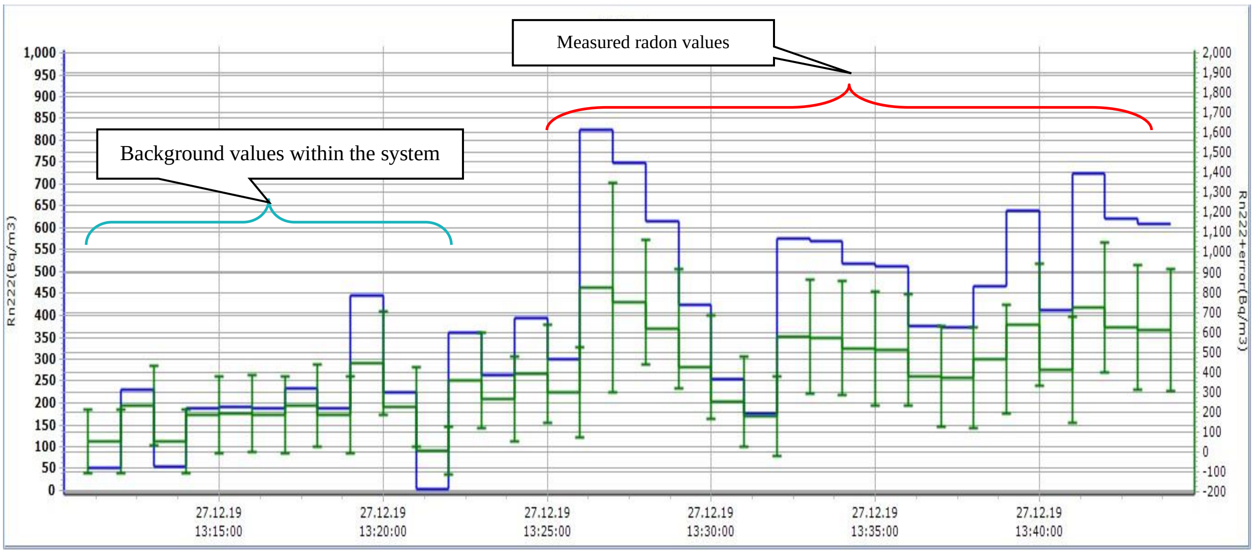
As can be seen from Table 1 and Figure 7a, the concentrations of radon in all analyzed water samples (P1-P3 and T1-T3) from the public water fountain in the Mokliště locality, city of Kavadarci, are below the maximum allowed values according to the MDK action level and the values recommended by the World Health Organization (WHO, 2008). However, even more important is the fact that the concentrations of radon in all these samples (P1-P3 and T1-T3), which go directly to consumers and are consumed, are below the strictest, maximum allowed values, by the United States Environmental Protection Agency (US-EPA, 1999).



P1

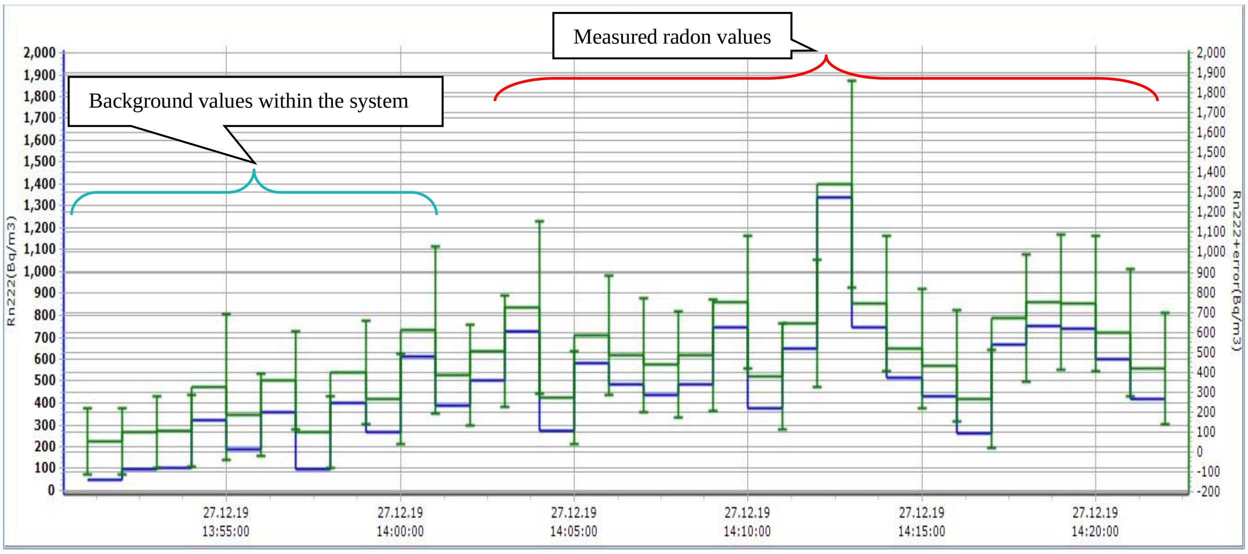


P2

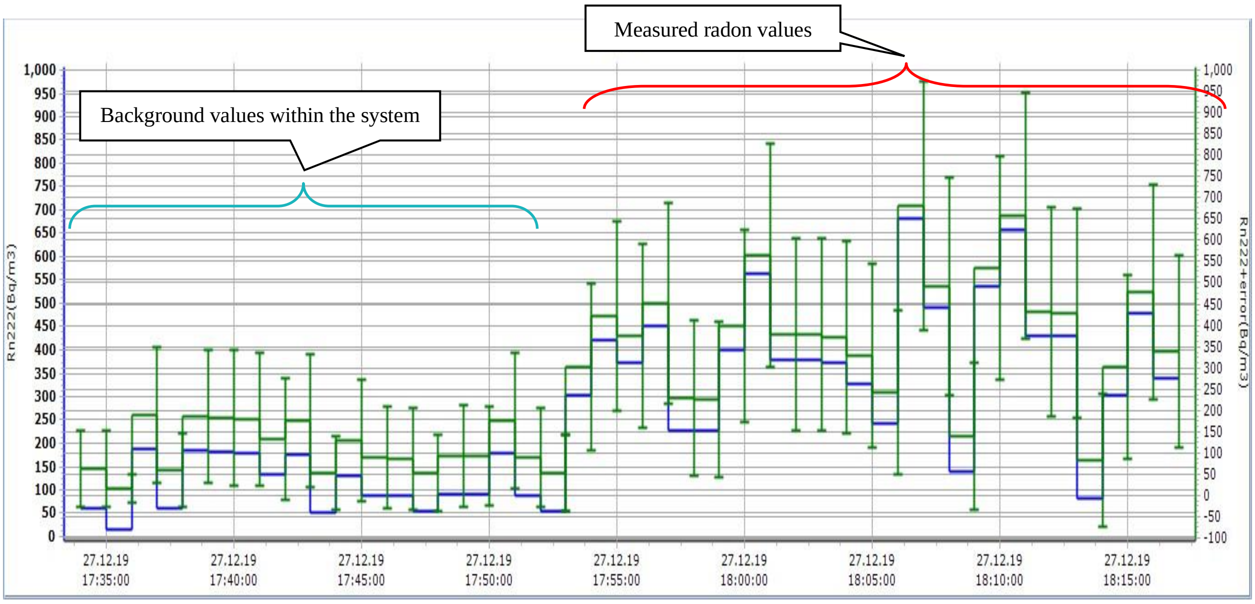


P3

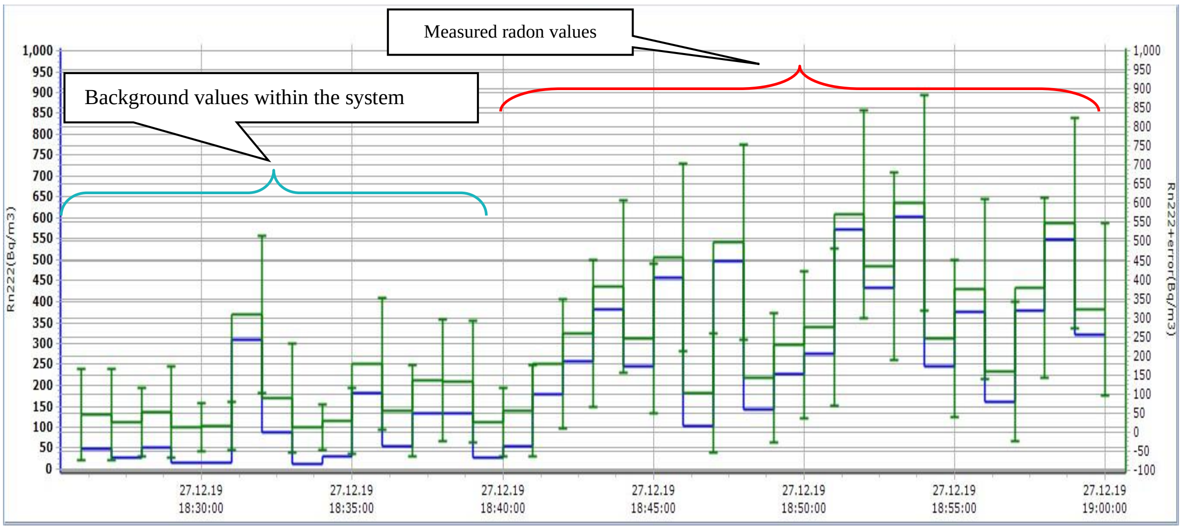
Fig. 5. Radon measurements, in all 3 samples of the preventive method (P1-P3)



T1

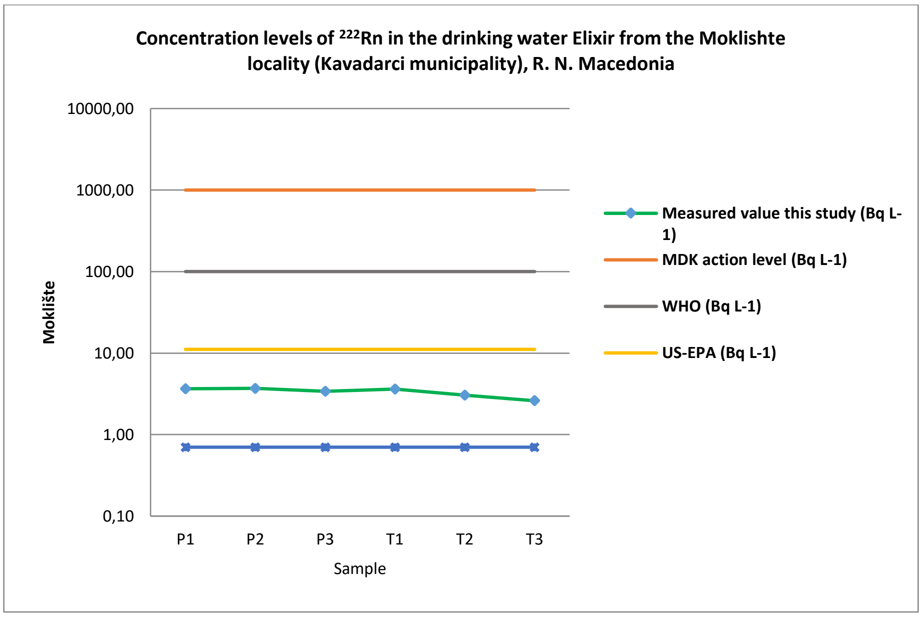


T2

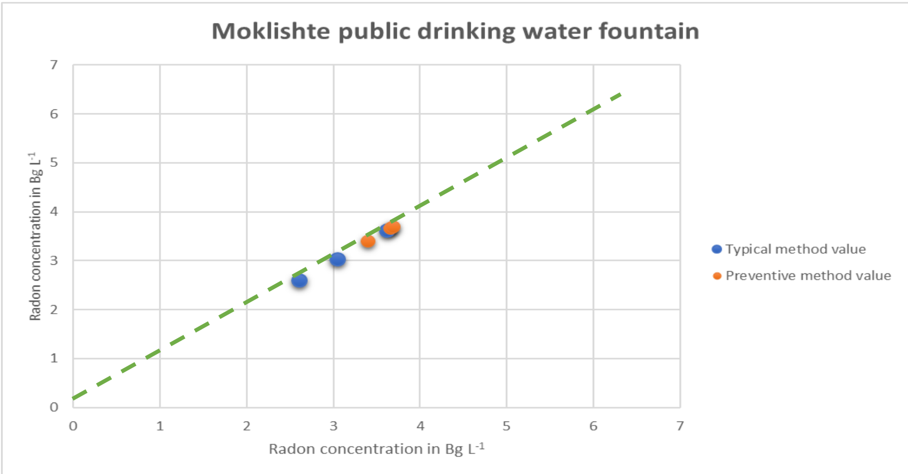


T3

Fig. 6. Radon measurements, in all 3 samples for the typical method (T1-T3)



a)



b)

Fig. 7. a) Radon concentration in drinking water from the Elixir public water fountain compared to maximum allowed values according to the MDK action levels, World Health Organization (WHO) and United States-Environmental Protection Agency (EPA). **b)** Radon in water concentrations obtained through *typical* vs. *preventive* sampling. The green dashed line denotes the equality of the two variables (i.e., $y = x$). The dashed line denotes a situation where y variable is maximaly 13% lower than x variable (i.e., $y = 0.87x$).

However, we must not ignore the fact that the obtained values for the concentration of radon in these self-bottled waters, are several times (4–5 times) higher than the values obtained when measuring tap water from homes in the city of Kavadarci (Tasev et al., 2021).

RADIUM

As we already mentioned above, after the 30 days period after the initial water sampling and radon in sampled water analysis, 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 when radium can be counted in a secular balance with radon.

Ours analyses of six samples (three by preventive method and three by typical method) taken consecutively showed the results as given in Table 2.

Table 2

Radium concentration in air and water within water samples from the public water fountain in the Moklište area

Sample	N (number of measurements)	Min_{Air} (Bq·m^{-3})	Max_{Air} (Bq·m^{-3})	$Average_{Air}$ (Bq·m^{-3})	$Median_{Air}$ (Bq·m^{-3})	Water (Bq·l^{-1})
P_1	16	21.19	135.24	46.53	21.90	0.11
P_2	15	19.88	133.20	44.79	21.74	0.19
P_3	9	20.49	92.01	41.83	21.90	0.08
T_1	13	21.19	191.50	50.60	49.66	0.12
T_2	17	20.31	191.50	51.36	48.59	0.11
T_3	15	20.40	135.02	47.00	47.76	0.14
				Average P1-P3		0.12667
				Average T1-T3		0.12333
				AVERAGE all samples (P and T)		0.125

All the analyses of the radium in air within water samples from the preventive method showed minimal value of 19.88 Bq·m^{-3}, maximal value of 135.24 Bq·m^{-3}, average value of 44.82 Bq·m^{-3} and median value of 21.90·Bq m^{-3} (Table 2; Figure 8). Results of the analyses of radium in air within water samples from the typical method showed minimal value of 20.31 Bq·m^{-3}, maximal value of 191.50 Bq· m^{-3}, average value of 49.69 Bq·m^{-3} and median value of 48.22 Bq·m^{-3} (Table 2; Figure 9). Calculated radium in water measurements, for the preventive method taken samples, ranged from 0.08 up to 0.19 Bq·l^{-1} while values for the typical method taken samples ranged from 0.11 up to 0.14 Bq·l^{-1}. Radium concentrations measured from samples obtained in *typical* way showed lower than the corresponding values obtained using the *preventive* sampling method. Comparison of respective samples P1-T1, P2-T2 and P3-T3 have shown differences in respective values of of 8.33 %, 42.11 % and 42.86 % for typical method. An average P1-P3 values compared to average T1-T3 values showed difference of 2.63% in favour of those obtained by typical sampling method. Similarly as it was case for the radon values, we may conclude that the *typical* way of sampling leads represents the typical consumer's handling during self-bottling process of the water from the public fountains, and it can be considered more representative (in regards to real radium levels in this case) than the other alternative bottling approach.

None of the analyzed samples of drinking water from the public fountain Elixir in the Moklište locality in the vicinity of Kavadarci, were above the reference value for radium given by the World Health Organization (WHO) in the amount of 1 Bq·l^{-1} nor the newly proposed value of 0.5 Bq·l^{-1} was not exceeded (Figure 10a).

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 Moklište public drinking water fountain 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).

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

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

$$Ingestion\ \text{dose}\ ^{226}\text{Ra}\ (\mu\text{Sv}) = {}^{226}\ R\text{a conc}\ (\text{Bq}\cdot \text{l}^{-1}) \times 365\ \text{l}\cdot \text{y}^{-1} \times 0.28\ \mu\text{Sv}\ \text{Bq}^{-1} \times 10^{-3}$$

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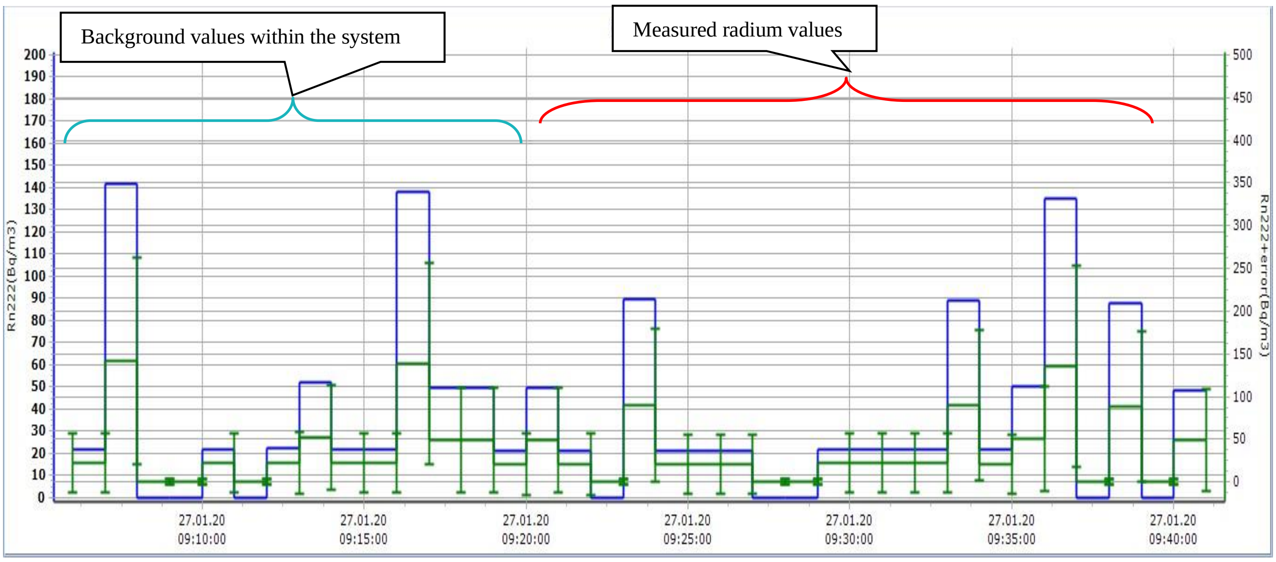
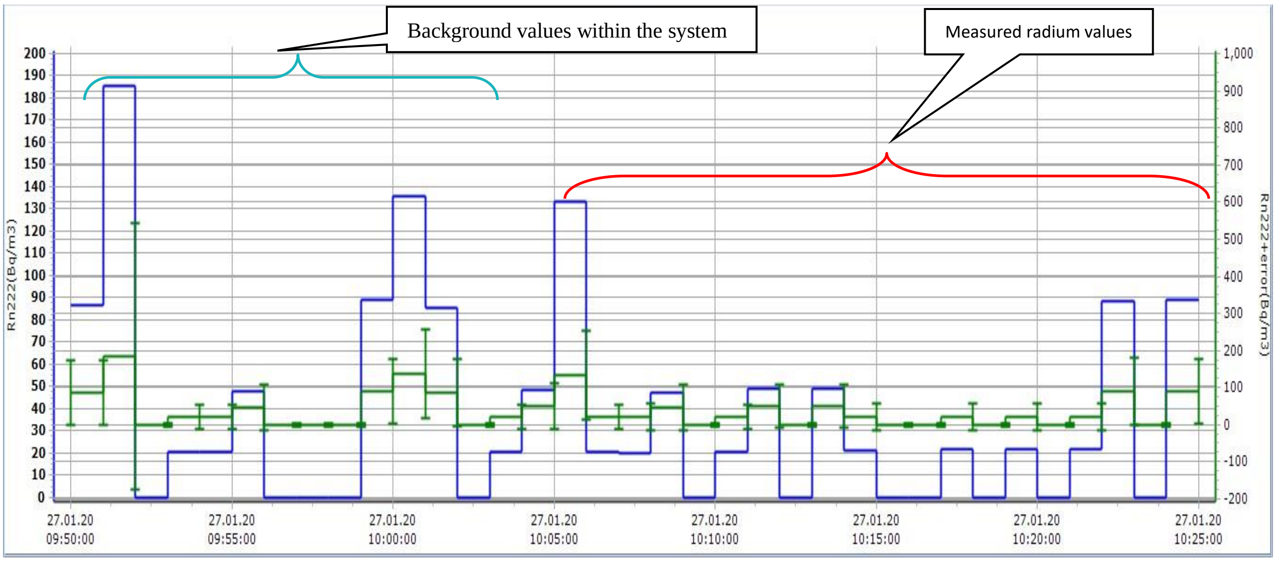
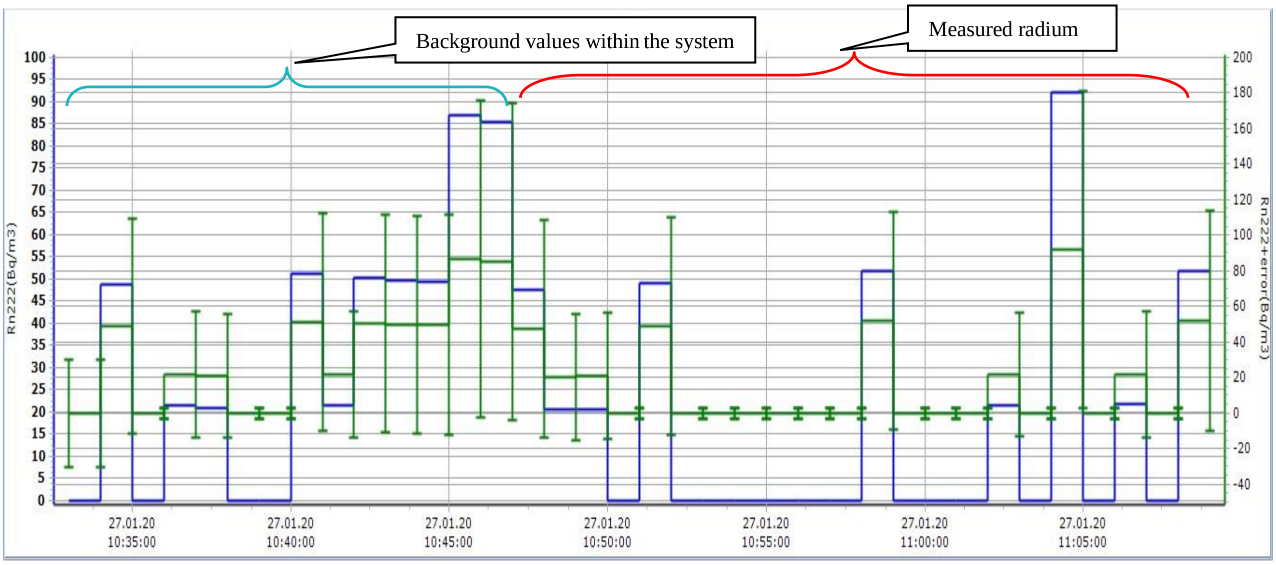


P1



P2



P3

Fig. 8. Radium measurements, in all 3 samples of the preventive method (P1-P3)

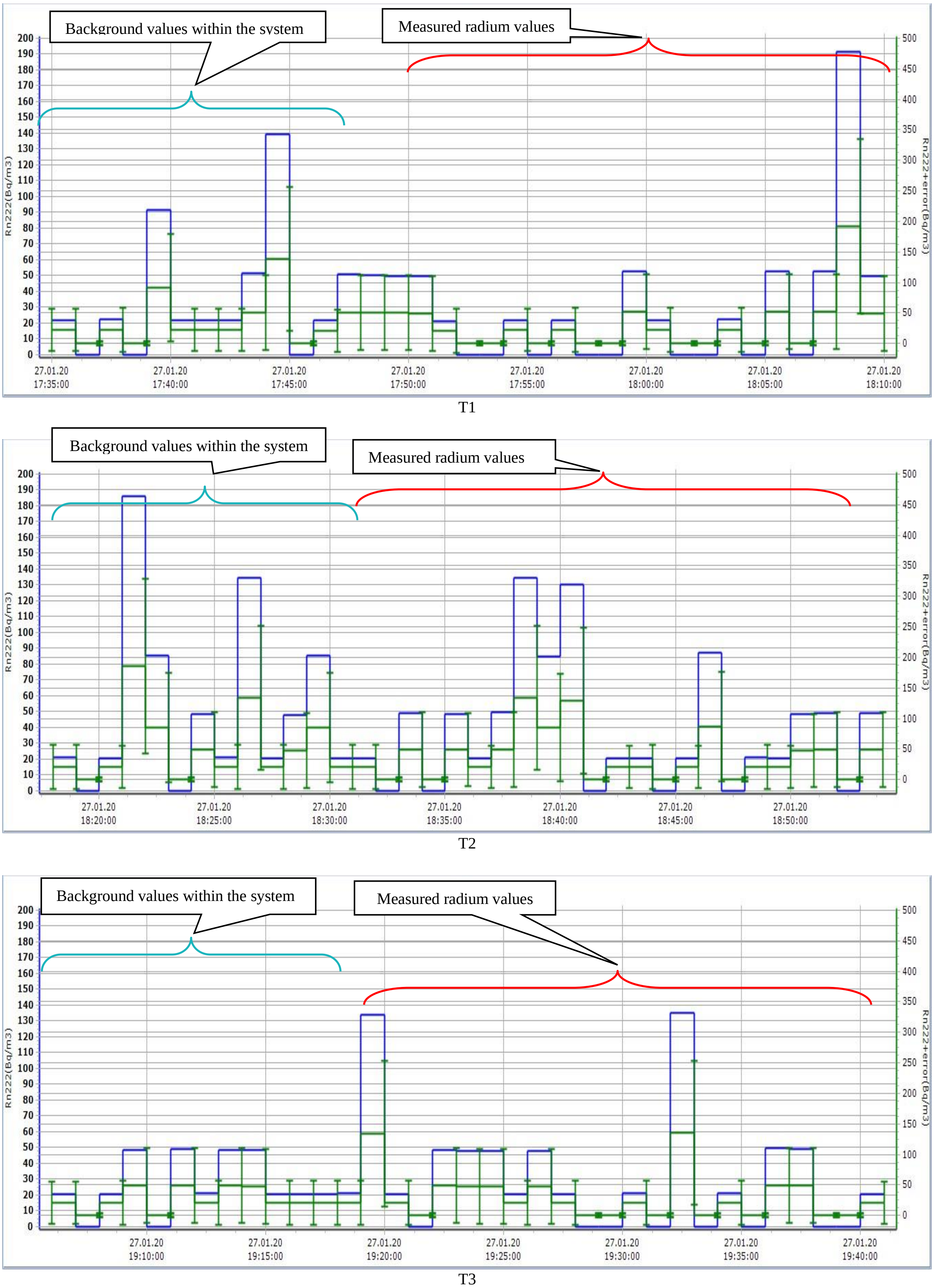
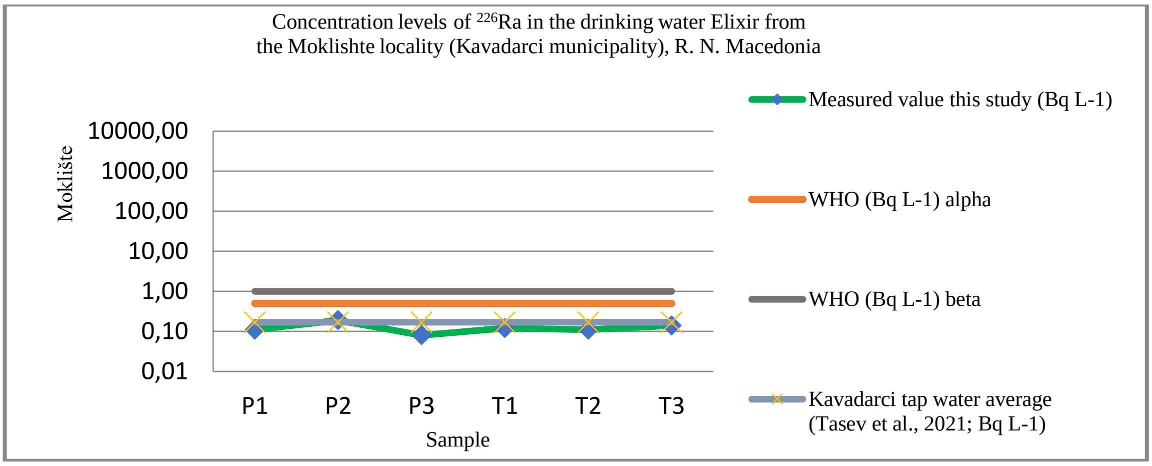
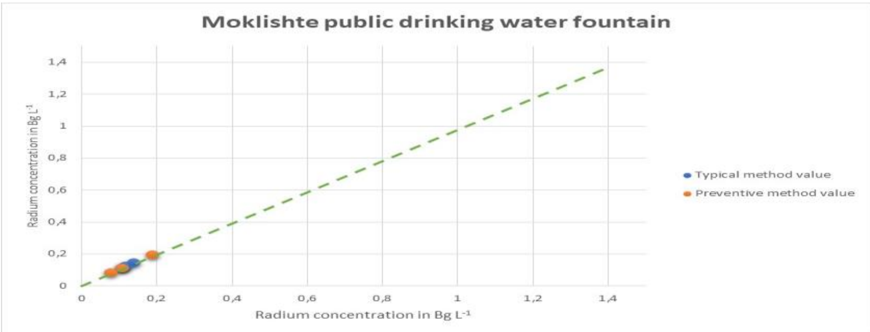


Fig. 9. Radium measurements, in all 3 samples of the typical method (P1-P3)



a)



b)

Fig. 10. a) Radium concentration in drinking water from the Elixir public water fountain. **b)** Radium in water concentrations obtained through *typical* versus *preventive* sampling. The green dashed line denotes the equality of the two variables (i.e., $y = x$). The dashed line denotes a situation where y variable is maximaly 2.63% lower than x variable (i.e., $y = 0.9737x$).

Table 3

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

	Moklište					
Sampling location	P1	P2	P3	T1	T2	T3
Number of measurements	21+16	22+15	21+9	21+13	24+17	21+15
pH	6.1	6.2	5.8	5.8	5.6	5.6
TDS (Rn_{meas}/$Ra_{meas.}$)	200/210	200/200	200/200	200/210	200/200	200/210
EC (μS cm^{-1}), (Rn_{meas}/$Ra_{meas.}$)	420/440	420/410	410/410	410/430	420/410	410/410
^{222}Rn (Bg l^{-1})	3.66	3.69	3.4	3.62	3.04	2.6
^{226}Ra (mBg l^{-1})	110.00	190.00	80.00	120.00	110.00	140.00
Inhalation dose ^{222}Rn (μSv y^{-1})	9.22	9.30	8.57	9.12	7.66	6.55
Ingestion dose ^{222}Rn (μSv y^{-1})	4.68	4.71	4.34	4.62	3.88	3.32
Ingestion dose ^{226}Ra (μSv y^{-1})	11.24	19.42	8.18	12.26	11.24	14.31
TOTAL dose (μSv y^{-1})	25.14	33.43	21.09	26.01	22.79	24.18
TOTAL dose (μSv y^{-1})	0.02514085	0.033430775	0.0210875	0.02601095	0.0227864	0.0241815
TOTAL ingestion dose (μSv y^{-1})	0.01591765	0.024131975	0.0125195	0.01688855	0.0151256	0.0176295
TOTAL inhalation and ingestion ^{222}Rn (μSv y^{-1})	13.90	14.01	12.91	13.75	11.54	9.87

Calculated values for the exposure during inhalation of radon and ingestion of radon and radium within water samples from the public water fountain Elixir in the Moklište locality, city of Kavadarci is given in Table 3.

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.

Computing from the radium and radon activity concentrations in public fountain water samples, the total dose due to ingestion and inhalation varies from 21.09 to 33.43 μSv y^{-1} with a geometric mean of 65.94 μSv y^{-1}, which is below the prescribed dose limit of 100 μSv y^{-1} by WHO (2011), see Figure 11 below. These values quite on the opposite side 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).

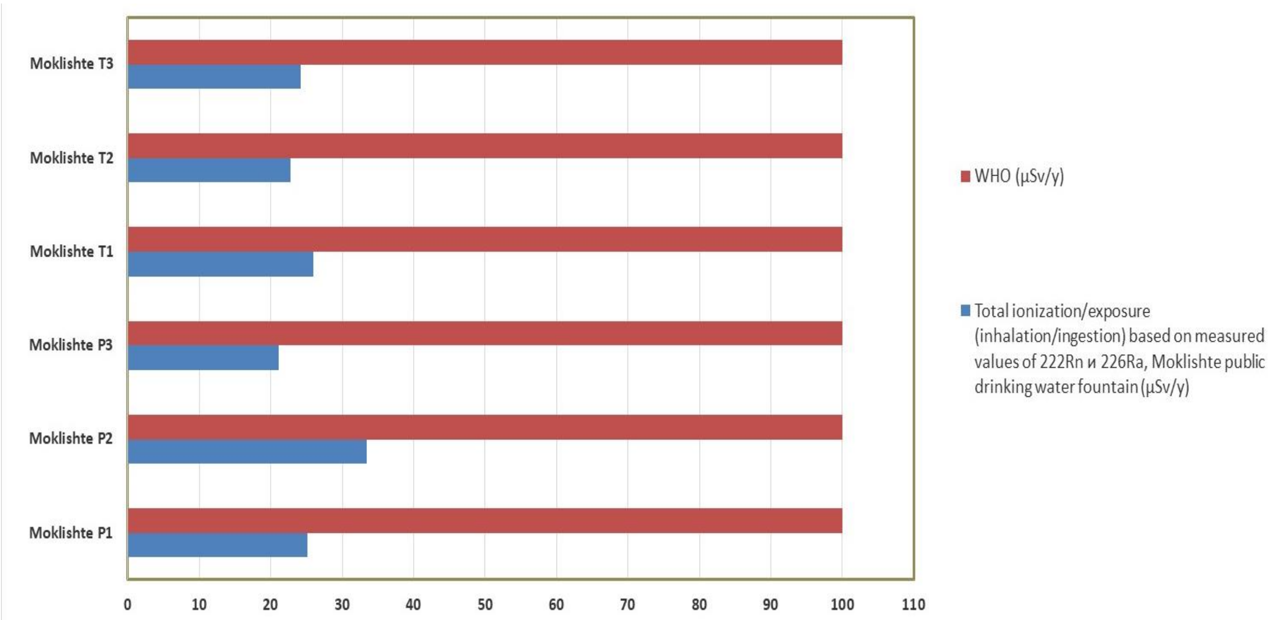


Fig. 11. Total exposure dose for both ^{222}Rn and ^{226}Ra and both methods of sampling (*preventive* and *typical*) in water from the Elixir public water fountain in the Mokliště locality, Kavadarci

Discharging water of the local Mokliště fountain spring flow system is characterized by elevated total dissolved solid content (TDS), temperature and by reducing conditions, and therefore with negligible uranium content, whereas some regional water flow systems have lower TDS and temperature, represent oxidizing environments, and therefore their radium content is probably low (Tasev et al, 2021).

CONCLUSIONS

A systematic survey of natural mineral spring water located in Mokliště (Tikveš region, Republic of North Macedonia) was carried out in order to evaluate if radon and radium levels in this mineral spring water may be of public health concern due to human consumption.

The measurements and analysis of the samples allowed us to determine the concentration of radon and radium in the mineral spring water that the consumers self-bottled directly from the public fountain located in Mokliște, which is a common habit lately in this particular region. Namely, the radon concentrations were in the range from 3.40 to 3.69 Bq·l^{-1} for the preventive method and in the range from 2.60 to 3.62 Bq·l^{-1} for the traditional method and did not exceed even the strictest US-EPA standards for drinking water of 11.1 Bq·l^{-1}. Similar to radon and radium measurements showed a range of concentrations from 0.08 to 0.19 Bq·l^{-1} in the preventive method and 0.11 to 0.14 Bq·l^{-1} in the traditional method, which in this case did not exceed the existing (1.0 Bq·l^{-1}) and suggested (0.5 Bq·l^{-1}) values according to the World Health Organization. In that direction were calculated effective doses due to inhalation of radon and ingestion of radon and radium, in the range from 21.09 to 33.43 μSv y^{-1} for the preventive method and 22.79 to 26.01 μSv y^{-1} for the traditional method, which in neither one case did not exceed the maximum permissible values of 100 μSv y^{-1}.

REFERENCES

Alshamsi, D. M., Murad, A. A,, Aldahan, A., Hou, X. (2013): Uranium isotopes in carbonate aquifers of arid region setting. *J Radioanal Nucl Chem* **298**, pp. 1899–1905.

Battino, R., Clever, H. L. (1965): The solubility of gases in liquids. *Chem. Rev*. **66**, pp. 395–463.

Di Carlo, C., Lepore, L., Venoso, G., Ampollini, M., Carpentieri, C., Tannino, A., Ragno, E., Magliano, A., D'Amario, C., Remetti, R., Bochicchio, F. (2019): *Radon concentration in self bottled mineral spring waters as possible health issue*. Scientific Reports (Natureresearch), 9 (1).

Eckerman, K., Harrison, J., Menzel, H. G., Clement, C. H. (2012): ICRP Publication 119: Compendium of dose coefficients based on ICRP Publication 60, Annals of the ICRP, 41 (Suppl.1), pp. 1–130.

Eröss, A., Surbeck, H., Csondor, K., Horváth, Á., Mádl-Szönyi, J. and Lénárt, L. (2015): Radionuclides in the waters of the Bükk region, Hungary. *J Radioanal Nucl Chem* **303**, pp. 2529–2533.

Fonollosa, E., Peňalver, A., Borrull, F., Aguilar, C. (2016): Radon in spring waters in the south of Catalonia. *J. Environ. Radioact*. **151**, 275–281.

Hristov, S., Karajovanović, M. and Stračkov, M. (1973): *Manual for the Basic Geological Map of SFRJ, 1 : 100 000,* Sheet Kavadarci, Geological Survey, Skopje [in Macedonian].

Ilani, S., Minster, T., Kronfeld, J., & Even, O. (2006): The source of anomalous radioactivity in the springs bordering the Sea of Galilee, Israel. *Journal of Environmental Radioactivity*, **85**, pp. 137–146.

ISO – International Standard Organization (2013a): *Water quality – Radon*-222, Part 1: *General principles*.

ISO – International Standard Organization (2013b): *Water quality – Radon-222,* Part 3: *Test method using emanometry*.

Jobbágy, V., Altzitzoglou, T., Malo, P., Tanner, V. and Hult, M., (2017): A brief overview on radon measurements in drinking water. *J. Environ. Radioact*. **173**, pp. 18–24.

Kralik, C., Friedrich, M. and Vojir, F. (2003): Natural radionuclides in bottled water in Austria. *J. Environ. Radioact*. **65**, pp. 233–241.

Leaney, F. W., Herczeg, A. L., Land, C., Osmond, G. A. (2006): Rapid field extraction method for determination of radon-222 in natural waters by liquid scintillation counting. *Limnol. Oceanogr. Methods*, pp. 254–259.

Lubin, J. H., Boice, J. D., Edling, C., Hornung, R. W., Howe, G. R., Kunz, E., et al. (1995): Lung cancer in radon-exposed miners and estimation of risk from indoor exposure. *Journal of the National Cancer Institute*, **87**, pp. 817–827.

Lucchetti, C., De Simone, G., Galli, G., Tuccimei, P. (2016): Evaluating radon loss from water during storage in standard PET, bio-based PET, and PLA bottles. *Radiat. Meas*. **84**, pp. 1–8.

Maksimović, B., Sikošek, B., Marković, O., Veselinović, M. (1954). Geološki sastav i tektonska struktura jednog dela Ovčeg Polja i Tikveša sa paleontološkom dokumentacijom. *Trudovi na Geološki zavod na NRM*, **4**, Skopje, 1–177 (in Macedonian).

Moldovan, M., Cosma, C., Encian, I., Dicu, T. (2009): Radium-226 concentration in Romanian bottled mineral waters. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. **279**, No. 2, pp. 487–491.

Moreno, V., Bach, J., Baixeras, C., Font, L. (2014): Radon levels in groundwaters and natural radioactivity in soils of the volcanic region of La Garrotxa, Spain. *J. Environ. Radioact*. **128**, 1–8.

Najeeb, N. K., Vinayachandran, N., Jose, B.,, Vashistha, R. (2014): Radon in groundwater in Tumkur district of Karnataka with special reference to sampling sensitivity. *Journal of the Geological Society of India*, **83**, pp. 665–668.

Sannappa, J., Chandrashekara, M. S., Paramesh, L. (2006): Spatial distribution of radon and thoron concentrations indoors and their concentrations in different rooms of buildings. *Indoor and Built Environment*, **15** (3), pp. 283–288.

Saphymo GmbH (2017): *Alpha Guard Professional Radon Monitor Types D50, D2000, DF2000.* User Manual **12**, 73 pp.

Shivakumara, B. C., Chandrashekara, M. S., Kavitha, E., Paramesh, L. (2014): Studies on ^{226}Ra and ^{222}Rn concentration in drinking water of Mandya region, Karnataka State, India. *Journal of Radiation Research and Applied Sciences*, Vol. **7**, pp. 491–498.

Statista (2016): The Statistics Portal. Per capita consumption of bottled water in Europe in 2016, by country.

Stojanova, V., Petrov V. (2012): Foraminifers and nannofossils from upper flysch lithozone in the Tikveš basin, Republic of Macedonia. *Geologica Macedonica*, **26**, 1, 87–98.

Stojanova, V., Petrov, G. (2014): Litostratigraphic characteristics of Paleogene basins in the Republic of Macedonia. *Geologica Macedonica*, **28** (2). pp. 175–183. ISSN 0352–1206

Tasev, G., Serafimovski, T., Serafimovski, D. (2021): Radon and radium in tap drinking waters in the city of Kavadarci. *Geologica Macedonica*, **35** (1). pp. 15–26. ISSN 0352-1206.

UNSCEAR (1993): United Nations Scientific Committee on the Effects of Atomic Radiation. *Sources and Effects of Ionizing Radiation*. I.

UNSCEAR (2000): *Report to the General Assembly* with scientific annexes (pp. 97–108). New York: United Nations. Annex B.

UNSCEAR (2006): *Report to the General Assembly,* with scientific annexes. In *Effects of Ionizing Radiation* (Vol. **II**).

US-EPA (1999): *Radon in Drinking Water: Health Risk Reduction and Cost Analysis*. Federal Register 64, Washington.

Weigel, F. (1978): Radon. *Chem. Zeitung* **102**, 287–299.

WHO (World Health Organization) (2011): *Guidelines for Drinking-Water Quality* – Second Edition, https://doi.org/10.1017/CBO9781107415324.004.

WHO (World Health Organization) (2018): *Management of Radioactivity in Drinking Water*.

WHO (2008): World Health Organization guidelines for drinking water quality. In: *Incorporating First and Second Addenda*, 3rd. ed., WHO Press, Geneva Switzerland.

Р е з и м е

КОНЦЕНТРАЦИЈА НА РАДОН И РАДИУМ ВО САМОФЛАШИРАНА МИНЕРАЛНА ИЗВОРСКА ВОДА ОД ЈАВНАТА ЧЕШМА „ЕЛИКСИР“ ВО МОКЛИШТЕ, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: радон, радиум, вода, самофлаширана, ефективна доза, Моклиште, Кавадарци

Во овој труд се презентирани информации за тековните проучувања на радон и радиум во самофлашираните води за пиење од јавната чешма Еликсир во областа Моклиште, град Кавадарци. Добиените резултати за радонот при мерењата на водата, за примероците земени по превентивниот метод, се движеа од 3,40 до 3,69 Bq·l^{-1}, додека вредностите за примероците земени по типичниот метод се движеа од 2,60 до 3,62 Bq·l^{-1}. Концентрацијата на радонот измерена во примероците земени на типичен начин покажала пониски вредности од соодветните вредности добиени со превентивниот метод на земање примероци, каде споредбата на соодветните примероци P1-T1, P2-T2 и P3-T3 покажала пониски вредности од 1,09%, 17,62% и 23,53 % за типичниот метод. Добиените резултати за радиумот во водата, за примероците земени со превентивниот метод, се движеа од 0,08 до 0,19 Bq·l^{-1}, додека вредностите во примероците земени според типичниот метод се движеа од 0,11 до 0,14 Bq·l^{-1}. Концентрацијата на радиумот измерена во примероците добиени на типичен начин беше пониска од соодветните вредности добиени со превентивниот метод на земање примероци, каде што споредбата на соодветните примероци P1-T1, P2-T2 и P3-T3 покажала разлики во соодветните вредности од 8,33%, 42,11 % и 42,86 % за типичниот метод. Потврдената ефективна доза за населението што ја консумира самофлашираната вода од јавната чешма во регионот Моклиште беше проценета со употреба на концентрацијата на ^{222}Rn и ^{226}Ra во примероците на вода, и се движи од 21,09 до 33,43 μSv y^{-1} за примероците земени со превентивниот метод и од 22.79 до 26.01 μSv y^{-1} за традиционалниот метод.