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Original scientific paper

SEASONAL MONITORING OF RADON AND RADIUM IN "HEALING WATER" FROM THE SMRDLIVA VODA LOCALITY, REPUBLIC OF NORTH MACEDONIA

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A b s t r a c t: Our current study focused on seasonal measurements of radon and radium in drinking water from the public water fountain known as Smrdliva Voda, which is believed to help with certain health problems in humans. Results of the radon in water measurements, for all 4 seasons, ranged from 3.94 up to 7.15 Bq l^{-1}. Obtained results for the radium in water, for all 4 seasons as well, ranged from 0.25 up to 0.53 Bq l^{-1}. Both, radon and radium measurements, in water samples from this certain fountain have shown values below the strictest standards given by the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO), respectively. The committed effective dose for the population consuming the water directly from the fountain or as self-bottled waters from the Smrdliva Voda area was estimated using the concentration of ^{222}Rn and ^{226}Ra in water samples, ranges from 40.51 μSv y^{-1} to 75.81 μSv y^{-1}, which once again for all 4 seasons is below than the WHO recommended values of maximum 100 μSv y^{-1}.

Key words: radon; radium; water; public fountain; effective dose; Smrdliva Voda

INTRODUCTION

The average World annual personal dose is about 2.4 mSv, so although it is inevitable, its continuous control is necessary (UNSCEAR, 1993; WHO, 2011, 2018). 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). 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). Radionuclides from the radioactive series ^{238}U, ^{235}U, and ^{232}Th are continuously present in the human body and contribute to internal radiation emitting alpha and beta particles. Here we would like to stress that the radium (^{226}Ra, with half-life T½ = 1620 years) and radon (^{222}Rn, with half-life T½ = 3.8 days) are two of the most common naturally occurring radionuclides found in ground water. 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 (Ilani et al., 2006; Sannappa et al., 2006; Moreno et al., 2014; Fonollosa et al., 2016). 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). 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 200–300 Bq·l^{-1}; Najeeb et al., 2014) than the usual drinking water (Moldovan et al., 2009). Therefore drinking ground waters should be expeditiously and accurately analyzed for the evaluation and prevention of eventual high radiation exposure. Up to date studies classified the radon as a human lung carcinogen, placing it as the second most significant cause of lung cancer after smoking (USEPA, 1999; WHO, 2008). Radium in water causes two main problems in terms of radiological protection: direct ingestion of ^{226}Ra during water consumption (due to its similar physico-chemical properties to calcium it may accumulate in bones and pose a potential cause of bone marrow cancer) and secondly radium continuously produces radon. Due to the fact that radium and radon are components of the decay sequence of the uranium (^{238}U) their activity in ground water is closely related to his content in aquifer material (Ródenas et al., 2008). Due to the fact that water is necessary for life and it cannot be replaced, control and ensuring its quality, also due to the content of radioactive substances, is extremely important (Rusconi et al., 2004). So, determination of radon and radium in water is important from the standpoint of radiation and environmental protection (Roba et al, 2012; Chmielewska et al., 2020; Thakur et al., 2021).

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). In non-industrially bottled mineral waters, radon exposure can not be negligible when consumers fill bottles and containers directly from public fountains thus reducing significantly the time elapsing between mineral water bottling and subsequent consumption (Kralik et al., 2003; Di Carlo et al, 2019; Statista, 2021). 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 some settlements in the Republic of Northern Macedonia to self-bottled 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 or even more to have positive medicinal effects to people's health. However, scientific approach and analyses of such waters are quite scarce. In fact, concentrations of both radium and radon were observed in the water from a public water fountain Smrdliva Voda in this study.

STUDY AREA

The locality Smrdliva Voda (in English "Smelling Water") is located at an altitude of 712 meters, and it is 24 kilometers away from the city of Gevgelija in the southern parts of the Republic of North Macedonia. It occupies the space between the mountain peaks of Flora, Adjibarica, Belezi and the Konjsko village. Mineral water spring got the name "Smrdliva Voda" due to fact that the water, when fresh, have an unpleasant "rotten egg" smell. According to its chemical composition, it is hydrocarbonate, mineralized, mildly acidic water (Stojmilov, 1979). It is believed that when this water is used by drinking helps or facilitates treatment of stomach diseases, kidney stones, urinary tract stones and sands, inflammation of the urinary system, etc. Radon and radium activity concentration measurements in the public fountain water of the Smrdliva Voda locality were carried or covered four three monthly seasons (autumn, winter, spring, and summer). Sampled water is regularly used for direct human consumption through the process known as self-bottling. 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 sediments into which the water body is situated and the recharge rate of the bedrock fractures or the sand and gravel aquifer. In that regard, within this part, we are giving a brief preview of the local geology.

Geological and hydrogeological features of the studied area

Several stratigraphic complexes compose the geology of the wider terrain around the locality of interest: Precambrian metamorphic rocks (fine-grained amphibole-muscovite gneiss, marble, and cipoline), the Early Paleozoic complex (represented by rocks of lower degree of crystallinity (phyllite, various schist types, cipoline, argilloschist, marble, and metamorphosed limestone as well as metamorphosed quartz-porphyry), as well as the Mesozoic rocks (Triassic sediments, gabbro, diabase, quartz-keratophyre and various clayey schist, quartzite, and sandstone) Tertiary complex (andesite and andesite tuffs), followed by spring tufa, gravel, alluvial terrace sediments, diluvial and alluvial-fluvial sediments (Figure 1). According to the tectonic regional setting of the Macedonia the terrain belongs to the Vardar zone (Arsovski, 1997).

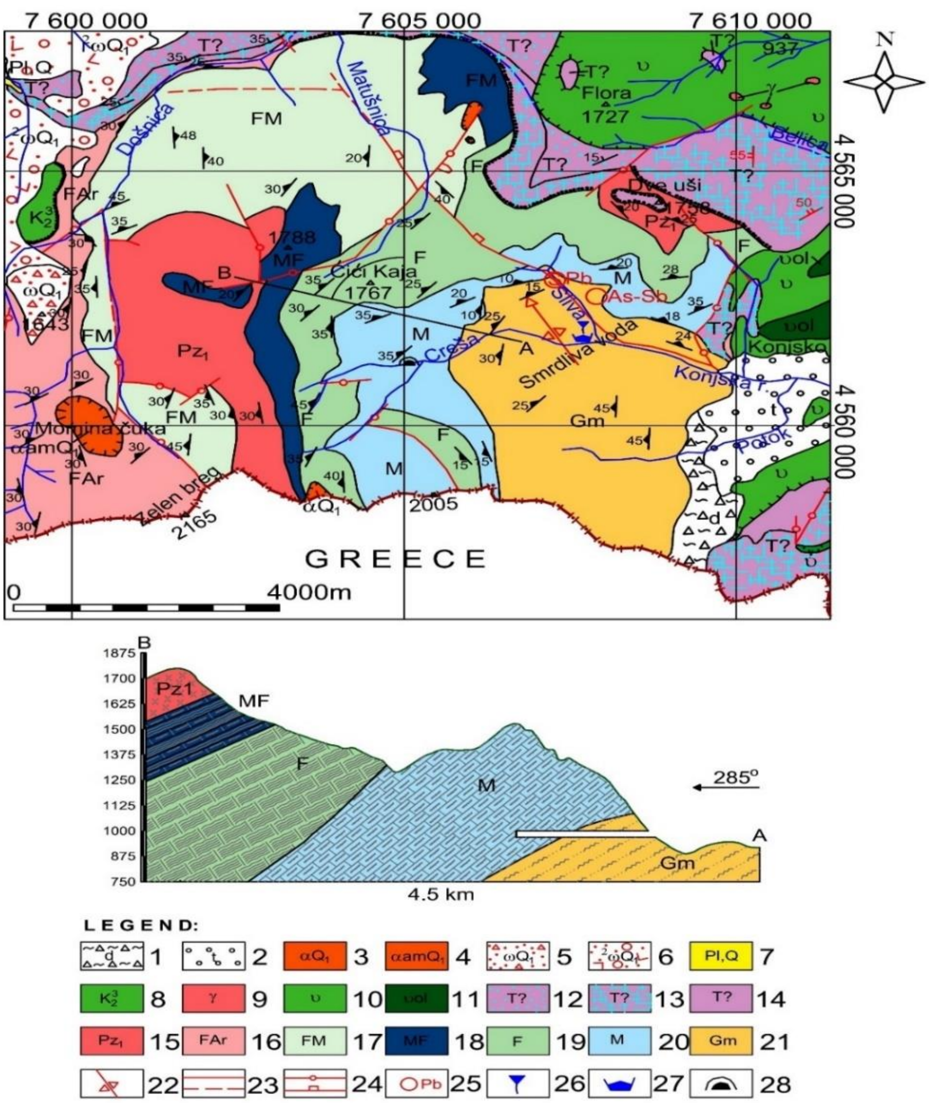


Fig. 1. Simplified geological map and cross-section of the catchment gallery in muscovite gneisses and marbles and cipolines on the Cici hill near Smrdliva Voda (according: Kekić and Mirčovski, 2004)
A) Star denotes position of the sampling area; Pz1– Quartz-porphyry; MF – Cipoline and schist; F – Phillite and philitic schists; Gm – Muscovite gneiss; M – Marble and cipoline

The structural type of porosity in Mt. Kožuf made possible the formation of several types of aquifers: phreatic, complex, fracture and karst ones (Radovanović, 1929; Kekić and Mirčovski, 2004). Within the Smrdliva Voda locality rocks of fracture porosity are the most common and heterogenous. As its name suggests they are highly fractured and located at great depth, as well. These rocks are source of numerous natural springs along the Konjska River and Smrdliva Voda localities. Yield of those springs seldomly exceeds 1 $l \cdot s^{-1}$. Based on their yield the terrains of fracture type aquifers in this area belong to: low (0.1 – 1.0 $l \cdot s^{-1}$) and good water yielding terrains (1.0 – 10.0 $l \cdot s^{-1}$).

METHODOLOGY

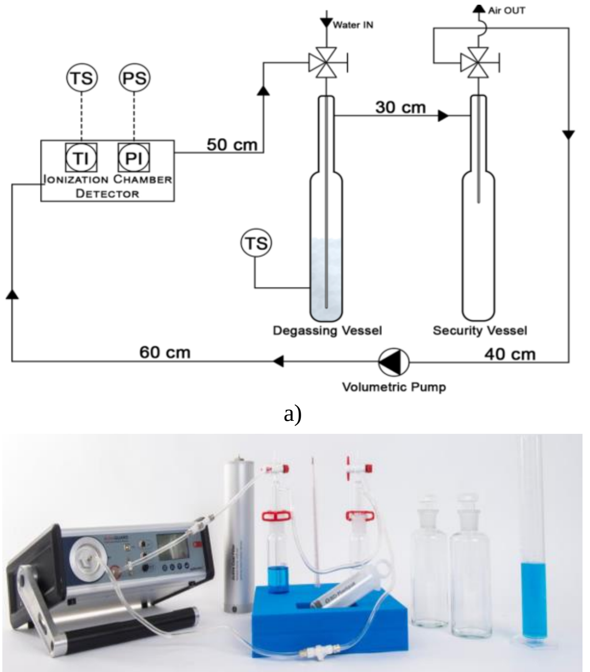
Methodology consisted of three steps: public fountain water sampling, measurement system, and the process of radon and radium analysis.

Water sampling procedure. The radon concentration is evaluated at the point where the drinking water is put into bottles for direct consumption, in a matter of an hours elapsing between the collection and the first opening of the bottle and water consumption (Figure 2).

Fig. 2. a–b) Autumn sampling; c–d) Winter sampling; e–f) Spring sampling; g–h) Summer sampling of the Smrdliva Voda public water fountain

Due to fact that polyethylene terephthalate (PET) bottles have 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), such PET bottles were used for our water sampling process. Four seasonal 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 (Figure 2b). Sealed water samples were then transported to the "Goce Delčev" University, Faculty of Natural and Technical Sciences in Štip, where the radon/radium 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. Water quality parameters such are pH, electrical conductivity, and total dissolved solids (TDS) were measured 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. Radiometric measurements were carried out by Alpha GUARD DF2000 (Bertin Instruments®) to measure radon/ radium concentrations, and AquaKIT (Bertin Instruments®) accessory for water samples degassing (Figure 3a, b).



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)

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 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; (i*v*) 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 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:

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

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 liters 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_{sys} 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: $k = 0.105 + 0.405e^{-0.0502 \cdot T}$ (°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 (^{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. λRa and λRn (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 $N_{Ra} = N_{Ra}(0)$ and the number of radon atoms is given by the equation:

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

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:

$$N_{\mathrm{Rn}} = N_{\mathrm{Ra}} \frac{\lambda_{\mathrm{Ra}}}{\lambda_{\mathrm{Rn}}}.$$

Or that $\lambda_{\mathrm{Rn}} \cdot N_{\mathrm{Rn}} = \lambda_{\mathrm{Ra}} \cdot N_{\mathrm{Ra}}$, 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 (autumn, winter, spring and summer) showed minimal values within range from 72.74 to 123.90 Bq m^{-3}, maximal values within range from 930.41 to 1272.67 Bq m^{-3}, average values within range from 412.36 to 713.72 Bq m^{-3} and median values within range from 417.23 to 718.78 Bq m^{-3} (Table 1; Figure 4).

Calculation of radon in water measurements, for the 4 seasons of interest, ranged from 3.94 (during spring) up to 7.15 Bq l^{-1} (during autumn) as can be seen from the Table 1 and Figure 4. 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, 2018) and the strictest one given by United States Environmental Protection Agency or USEPA (USEPA, 1999), which is 11.1 Bq l^{-1} (Di Carlo et al. (2019).

Table 1

Radon 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})
Autumn	38	89.32	1272.67	713.72	718.78	7.15
Winter	38	123.90	930.41	568.10	522.35	5.70
Spring	36	72.74	987.54	412.36	417.23	3.94
Summer	34	117.05	934.65	570.64	550.14	5.28

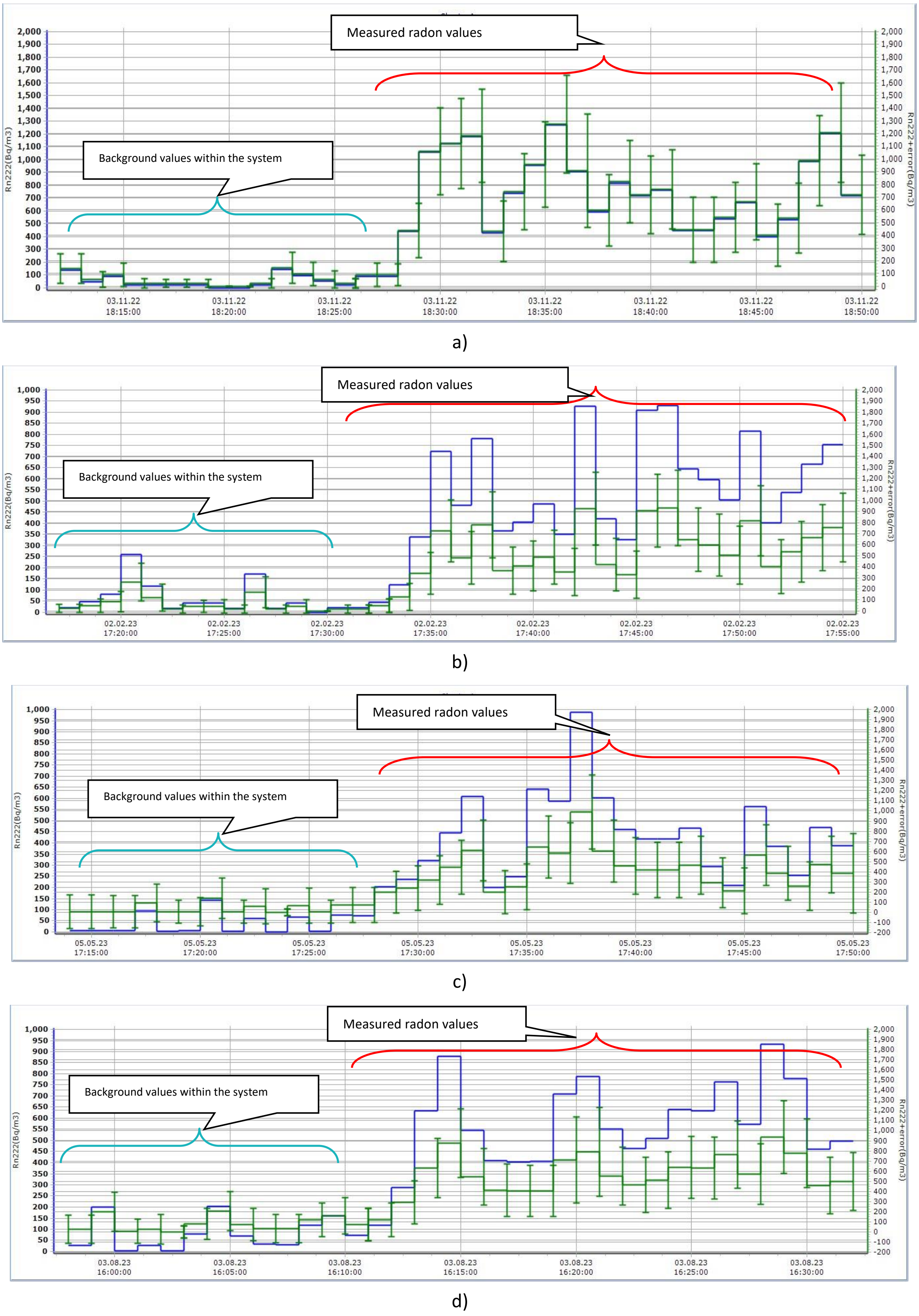


Fig. 4. Radon measurements. Smrdliva Voda water fountain during each of four seasons:
a) autumn; b) winter; c) spring; d) summer

As can be seen from Table 1 and Figure 5, the concentrations of radon in the four analyzed water samples (four seasons) from the public water fountain Smrdliva Voda were below the maximum allowed value according to the USEPA (USEPA, 1999), which is the strictest one.

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

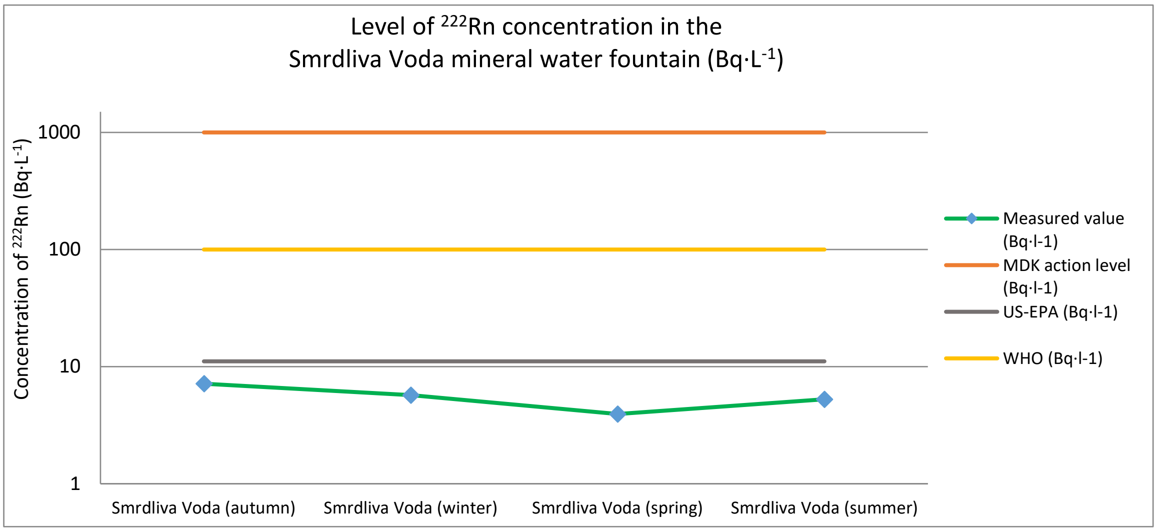


Fig. 5. Concentration of radon in water from the public fountain Smrdliva Voda during four seasons and compared to maximum allowed values according to the MDK action levels, World Health Organization (WHO) and United States Environmental Protection Agency (EPA)

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 (autumn, winter, spring, and summer) taken consecutively showed the results as given in Table 2.

All the analyses of the radium in air within water samples from the preventive method showed the lowest minimal value of 12.73 Bq m^{-3}, the highest maximal value of 420.69 Bq m^{-3}, while average values ranged from 45.30 to 117.27 Bq m^{-3}, and median values from 35.49 Bq m^{-3} to 55.19 Bq m^{-3} (Table 2; Figure 6).

Table 2

Radium concentration in air and water within water samples from the public water fountain Smrdliva Voda 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})
Autumn	37	18.95	138.24	55.51	47.61	0.37
Winter	41	12.73	420.69	117.27	55.19	0.53
Spring	36	21.14	193.55	74.54	51.72	0.25
Summer	35	19.59	90.51	45.30	35.49	0.26

Fig. 6. Radium measurements in Smrdliva Voda water fountain during each of four seasons:
a) autumn; b) winter; c) spring; d) summer

None of the analyzed four seasonal samples of drinking waters from the public water fountain of Smrdliva Voda (0.25–0.53 Bq·l^{-1}), were above the reference value for radium given by the World Health Organization (WHO, 2008, 2011) in the amount of 1 Bq·l^{-1}, while only winter sample have shown concentrations slightly exceeding the newly proposed value of 0.5 Bq·l^{-1} (Figure 7).

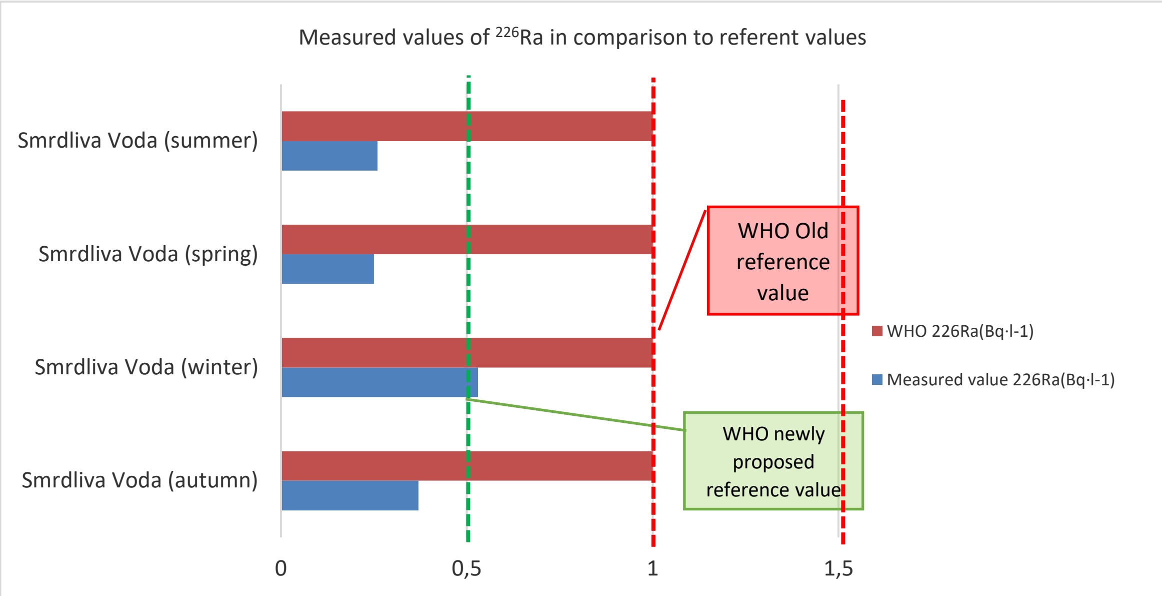


Fig. 7. Radium concentration in drinking water from the Smrdliva Voda public fountain area during four seasons

Opposite to as we initially supposed, no correlation has been found between the concentrations of ^{222}Rn and ^{226}Ra. The disequilibrium observed between these two radionuclides, already seen in underground waters (Hess et al., 1985; Asikainen, 1986) leads one to assume that the radon does not come exclusively from the decay of the radium dissolved in the water, but rather that the ^{222}Rn, because it is a noble gas, has a behavior pattern that is basically determined by physical processes and not by the possibilities of chemical interaction that characterize ^{226}Ra.

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 Smrdliva Voda public drinking water fountain area (during 4 seasons) was estimated using the concentration of ^{222}Rn and ^{226}Ra in water samples and directions given in UNSCEAR (2000), WHO (2011), and Shivakumara et al. (2014). Inhalation dose parameters 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 ingestion dose mainly was defined as dependant 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).

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

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

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

Calculated values for the exposure during inhalation of radon and ingestion of radon and radium within water samples from the Smrdliva Voda public water fountain, during four seasons, are given in Table 3.

As already mentioned elsewhere (Moldovan et al., 2014; Tasev et al., 2021; Tasev et al., 2022; Tasev et al., 2023), the dose due to ^{222}Rn is divided into two parts, dose from ingestion and 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 (for all four seasons), proved the total dose due to ingestion and inhalation varies from 40.51 to 75.81 μSv y^{-1}, which is below the recommended dose limit of 100 μSv y^{-1} by WHO (2011), 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).

Table 3

Exposure dose due to inhalation of radon and ingestion of radon and radium within water samples in this study (4 seasons)

Sampling location	Smrdliva Voda			
	Autumn, 2022	Winter, 2023	Spring, 2023	Summer,2023
Number of measurements	34+35	37+34	35+35	37+35
pH	5	5.3	5.2	4.6
EC (μS cm^{-1}), (Rn_{meas}/$Ra_{meas.}$)	750	780	700	500
^{222}Rn (Bg l^{-1})	7.15	5.7	3.94	5.28
^{226}Ra (mBg l^{-1})	370.00	530.00	250.00	260.00
Inhalation dose ^{222}Rn (μSv y^{-1})	18.02	14.36	9.93	13.31
Ingestion dose ^{222}Rn (μSv y^{-1})	9.13	7.28	5.03	6.75
Ingestion dose ^{226}Ra (μSv y^{-1})	37.81	54.17	25.55	26.57
TOTAL dose (μSv y^{-1})	64.97	75.81	40.51	46.62
TOTAL dose (mSv y^{-1})	0.064966125	0.07581175	0.04051215	0.0466228
TOTAL ingestion dose (mSv y^{-1})	0.046948125	0.06144775	0.03058335	0.0333172
TOTAL inhalation and ingestion ^{222}Rn (μSv y^{-1})	27.15	21.65	14.96	20.05

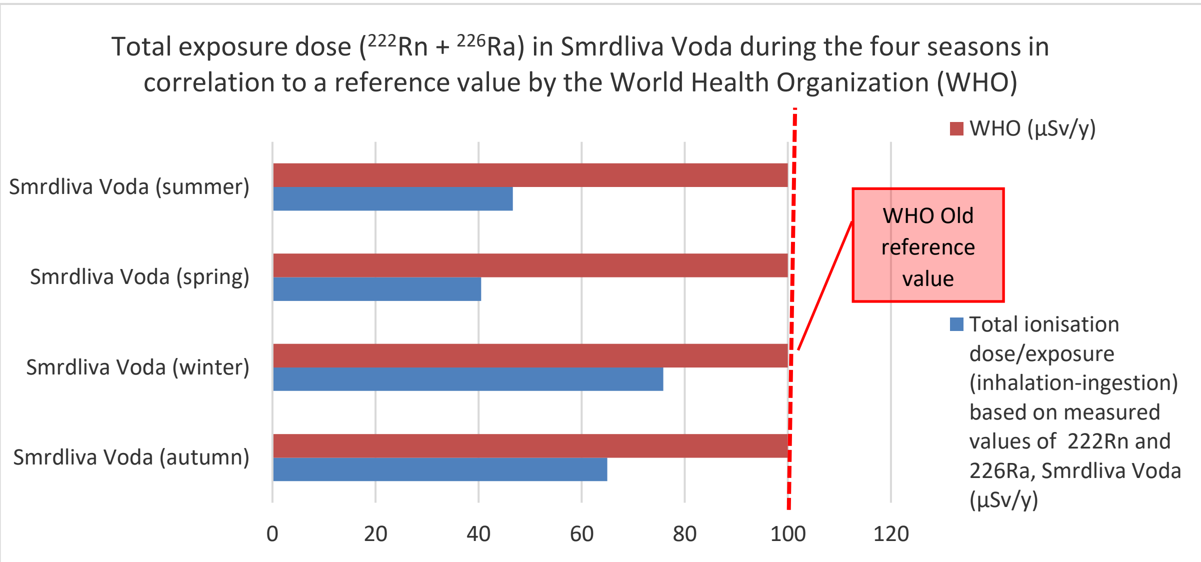


Fig. 8. Total exposure dose for both ^{222}Rn and ^{226}Ra in water from the public water fountain at the Smrdliva Voda area (autumn, winter, spring, and summer)

Discharging waters of the Smrdliva Voda locality, during the four seasons sampling, are characterized by medium total dissolved solid content (TDS), as well as medium to low temperature and by reducing conditions, and therefore with certain uranium content and therefore their radium content is probably lower (Soto et al., 1995a; Tasev et al., 2021).

Dissolution of ^{222}Rn in water has been controlled by different physical mechanisms and variables such as temperature, pressure, pH, water and rock interaction time, etc. (González-Díez, 2009). When the waters arrive on the earth surface it releases ^{222}Rn that is taken up during its contact with rock pores at depth (Davis and Watson, 1990; Lawrence et al., 1991; Ball et al., 1991). It is certain that radon concentration in spring waters could change due to meteorological and seasonal factors (Virk, 1993, Wattananikorn et al., 1998) and we had that in mind when we initiated our measurements in this study. Our results studying the seasonal variations of ^{222}Rn concentration in the waters from Smrdliva Voda has not revealed any significant concentration differences in the majority of the samples, which is representative for waters with constant volume and deep recharge zone. This is very similar to findings of Soto et al. (1995a, b) and Maraver et al. (2003).

CONCLUSIONS

A systematic survey of natural mineral spring water Smrdliva Voda, supposedly with healing properties, originating from Kožuf Mountain, Republic of North Macedonia, was carried out during four seasons (autumn, winter, spring, and summer). The survey was performed to evaluate if contained radon and radium levels may be of public health concern due to human consumption as self-bottled water directly from the public fountain. Namely, the radon concentrations were 7.15 Bq·l^{-1}, 5.70 Bq·l^{-1}, 3.94 Bq·l^{-1} and 5.28 Bq·l^{-1}, respectively for autumn, winter, spring, and summer measurements. Radium concentrations were 0.37 Bq·l^{-1}, 0.53 Bq·l^{-1}, 0.25 Bq·l^{-1} and 0.26 Bq·l^{-1}, respectively for autumn, winters, spring, and summer measurements. Except winter radium measurement value (slightly above), all other radon and radium values were bellow the strictest USEPA and WHO reference values for drinking waters. Calculated committed effective doses for the population consuming the self-bottled water from the Smrdliva Voda public drinking water fountain area (during 4 seasons) were based on dose due to radon ingestion (ranging 5.03–9.13 μSv y^{-1}) while dose from radon inhalation ranged from 9.93 to 18.02 μSv y^{-1}. Combined ingestion and inhalation dose due to radon ranged 14.96–27.15 μSv y^{-1}. Radium ingestion dose only (due to solid nature of radium) ranged 25.55–54.17 μSv y^{-1}. Combined inhalation and ingestion due to radon and ingestion due to radium were 64.97, 75.81, 40.51, and 46.62 μSv y^{-1}, respectively. None of those values were above the recommended dose limit of 100 μSv y^{-1} as suggested by World Health Organization. This study proved that human consumption of water, from radiological point, is on the safe side although additional chemical and bacteriological analyses are necessary for its complete quantifycation.

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Р е з и м е

СЕЗОНСКО СЛЕДЕЊЕ НА РАДОН И РАДИУМ ВО „ЛЕКОВИТАТА ВОДА“ ОД МЕСНОСТА СМРДЛИВА ВОДА, РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: радон, радиум; вода; јавна чешма; ефективна доза; Смрдлива Вода

Нашето тековно проучување се фокусираше на сезонските мерења на радонот и радиумот во водата за пиење од јавната чешма позната како Смрдлива Вода, за која се верува дека помага при одредени здравствени проблеми кај луѓето. Резултатите за радонот во мерењата на водата, за сите 4 сезони, се движеа од 3,94 до 7,15 $Bq\cdot l^{-1}$. Добиените резултати за радиумот во водата за сите 4 сезони се движеа од 0,25 до 0,53 $Bq\cdot l^{-1}$. Мерењата на радонот и радиумот во примероците на вода од оваа конкретна јавна чешма покажаа вредности пониски од најстрогите стандарди дадени од Агенцијата за заштита на животната средина на САД (USEPA) и Светската здравствена организација (WHO), соодветно.

Примената ефективна доза за населението што ја консумира водата директно од чешмата или како флаширана вода од областа Смрдлива Вода, проценета со употреба на концентрациите на ^{222}Rn и ^{226}Ra во примероците на вода, се движи од 40,51 $mSv\cdot y^{-1}$ до 75,81 $mSv\cdot y^{-1}$, што повторно за сите 4 сезони е под препорачаните вредности на WHO од максимум 100 $mSv\cdot y^{-1}$.