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ANALYSIS OF THE RADON CONCENTRATIONS IN NATURAL MINERAL AND TAP WATER USING LUCAS CELLS TECHNIQUE

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Highlights

- This study presents an evaluation of the radioactivity due to ^{222}Rn and ^{3}H in several mineral natural water and tap water samples.
- It shows that the geology and rocks types clearly influence the radon concentration in the water.
- It provides reliable information regarding radon and tritium concentrations, and an estimation of annual effective radiation dose based on the sample results.
- Dose calculations revealed that regular consumption of water does not induce a health risk due to the intake of various radionuclides contained in the water, these being at most of 47.38 μSv/y.

Abstract. The aims of this study were to determine the radon concentration in natural mineral and tap water and to estimate the resulting ingestion doses received by adults. Physical-chemical characteristics of water samples have also been investigated. In the last years have been an increase of water consumption of both, natural mineral and tap, many sources and producers being available on the market. Thus, the physical-chemical and radiologic parameters of water must be in compliance with the Drinking Water Directive (DWD). Thus, the study presents an assessment of the radioactivity due to ^{222}Rn and ^{3}H in several mineral natural water samples from the north region of Romania, but also in several tap water samples. The methods used were based on gamma spectrometry, gross alpha-beta measurements and beta spectroscopy, but also ICP-MS for chemical parameters. The results of this work showed that the geology and rock types clearly influence the water radon concentration. The radon concentration is lower in the water that passes through sedimentary rocks than that passing through granitic rocks. An important aspect of this work is to provide reliable information regarding radon and tritium concentrations. Radon concentration varied between 0.15±0.05 Bq/L and 11.35±2.97 Bq/L in the natural mineral water samples and between 0.17±0.05 Bq/L and 8.51±2.34 Bq/L in the tap water samples. An estimation of annual effective radiation dose based on the sample results was also made. Calculated values for ingestion dose due to regular consumption of water does not induce a health risk because of the intake of various radionuclides contained in the water. The maximum values being of 47.38 μSv/y. The determined values for the collected samples are below recommended reference levels, but more important aspect is that this study emphasise environmental sustainability in the investigated area.

Keywords: radon activity concentration, drinking water, natural mineral waters, Lucas cell, dose estimation.

Introduction

The interest in the radioactivity of natural and drinking mineral waters has grown significantly in the recent years. Natural radionuclides contained in waters give an important exposure to human body, through its ingestion. ^{222}Rn, a natural radioactive gas, has an important part to this exposure from indoor radon exposures (Borio et al., 2005; Nita et al., 2014; Calin et al., 2019; Silva et al., 2019) or through drinking water supplies (2009/54/EC; 2013/51/Euratom; Ro. Law 301/2015; World Health Organization [WHO], 2017). Radon is found in lakes and rivers which

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represent the surface waters, but also groundwater sources may contain elevated concentrations of radon. Higher radon concentrations can be found in groundwater from wells and boreholes compared with surface waters radon concentrations; however, these concentrations can vary considerably. Others well-known radionuclides among ^{238}U, ^{232}Th, and ^{226}Ra are soluble in water, however radon is the most common isotope present in natural mineral waters, being the main contributor of the radioactivity in comparison with ^{226}Ra which is the second contributor (Todorovic et al., 2012).

Because of the intake of radon through water ingestion, the radiation dose to humans will increase. Nevertheless, the screening levels for radon in water must follow the basis of the national and international standards for the reference levels. International Basic Safety Standard (BSS) and the recommendations of the ICRP are the bases for these reference levels recommendations. In Romania, the reference level is set to 100 Bq/L (Ro. Law 301/2015), in compliance with the Directive of the EU Council (2009/54/EC; 2013/51/Euratom).

In such studies, concerning the activity concentrations of radon present in drinking waters rather large variations of measured values have been showed. That is due to various reasons such as the type of water – spring water from volcanic rocks; carbonated water from sedimentary rocks, etc. For instance, in Serbia, measurements performed with RAD7, showed concentration values for bottled water to be between 0.9 Bq/L and 18.3 Bq/L, with one value of 1463 Bq/L that exceeds the international reference value (2013/51/Euratom; Todorovic et al., 2012). The tap water values were between 1.59 Bq/L and 2.30 Bq/L (Todorovic et al., 2012). In other parts of the world such Brazil, the groundwater radon values were found between 0.02 Bq/L and 112.5 Bq/L, for measurements also performed using RAD7 (Oner et al., 2013; Bonotto, 2014). As it is expected, the radon concentration depends firstly of the type of soil and rocks that it crosses (granites, sedimentary, volcanic, etc.) and it may wash out and involve the radionuclides contained in them, and secondly of the type of water (surface, ground, spring, well water). The same scenario is valid for tritium (Baeza et al., 2002; Borio et al., 2005; Palomo et al., 2007; Froehlich, 2010; Patnaik, 2010).

For this reason, potential health risks from natural radionuclides presents in drinking water has an important interest worldwide. In the Euratom Drinking Water Directive it is stated that radon content, from water intended for drinking purposes, has to be analysed (2013/51/Euratom). As regarding the recommended reference level of effective dose received from drinking water consumption, this is 100 mSv/y and was calculated excluding the dose received from ^{3}H, ^{40}K, ^{222}Rn.

In the present research the main goal is to determine the radon concentration in natural mineral and tap water and to estimate the resulting ingestion doses received by adults. In addition to this, another goal is to observe the influence on the activity concentration of radon due to the origin of the water samples. It has been also checked for tritium activity. Tritium reference levels, expressed as volumic activities of treated water (HTO) are the same as those presented above for radon (Ro. Law 301/2015). In this study, the simplified model mentioned can be used, considering that the associated doses of HTO is well below the maximum allowed levels, even if we work with a scenario in which there is a persistent, continuous and daily uptake of the radioactivity, given by water consumption (CNCAN 145/2018). The application of method for determination of radon together with tritium activity in natural water offer important information concerning leaching of the water between surface, subsurface and deeply situated natural mineral water layers. Another relevant aspect in this situation is the lack of data or fewer of them on the ^{222}Rn activity concentration in Romanian waters, and the lack of confident data in determining the health risks from the consumption of this water, together with an incomplete evaluation of the annual effective radiation dose.

The research novelty and the significance of this study consist in the radiological characterisation of the Bucovina aquifer, that is applied locally, however this approach can be used for other aquifers, being extensible and scalable method, capable for simultaneously monitoring of ground and surface water, as of the physico-chemical and radiological indicators.

1. Materials and methods

1.1. Study area – Geographical and geological information

In this study, both *in situ* and laboratory experiments were carried out (SALMROM and BETALAB laboratories within IFIN-HH and Department of Analytical Chemistry and Environmental Engineering within UPB Bucharest). The natural mineral groundwater samples were collected from 12 points for analyses, directly from the capture pipes, in 0.5 L bottles, completely filled. The region where these springs of natural mineral water are located is in the north of Romania, in Bucovina region (Figure 1). The water which comes from volcanic aquifers contains dolomite, diorite, basalt, calcite, andasite and traces of quartz, muscovite and paragneiss rocks. It is known that for relatively small area, the variation of rock types is very large and can lead to different concentrations of natural radionuclides

Figure 1. The location of the region in Bucovina in Romania, from where the natural mineral waters were collected

of ^{40}K, ^{238}U, ^{232}Th and ^{226}Ra (Ion et al., 2019; Radulescu et al., 2017; Calin et al., 2016), having as a consequence, a wide variation of radon concentrations. In addition, these waters originate from different depths and go over different geological intermediate layers. While sedimentary rocks contain low level of radioactivity, phosphate rocks and carbonates may have higher concentrations of radionuclides which can be dissolved into the water (Ion et al., 2019), and that can be clearly observed from the radioactivity measurements in currently studied samples.

The drinking water samples (12 tap water samples) were taken from the IFIN–HH institute area and several locations from Magurele city and from Bucharest city.

1.2. Chemical characteristics determination

Twelve natural mineral water samples were collected and analysed, not only for radon and tritium content, but also a number of other chemical characteristics were taken into consideration such as pH, electrical conductivity and the main anions and cations, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, HCO_3^-, NO_3^-, SO_4^{2-}. Metrohm intelligent Partial Loop (MiPT) technique with conductivity detector was used using an 850 Professional IC AnCat-MCS for anions and cations analysis with two separation columns C4-250/4.0, Metrosep ASUP 5. The analyses were done in compliance with EPA Method 300.0 and 300.1 (Yuce et al., 2017).

1.3. Lucas cell scintillation method

To perform the radon measurement, the samples of water were in hermetically closed containers, using polyethylene bottles (PET) of 0.5 L. Three samples were carbonated waters and nine were non-carbonated waters. The bottles were completely filled to avoid air volume insertion between the free surface and the cover. Sampling conditions were also ideal for tritium measurements. Radon levels were determined in less than 12 hours after samples collection (tap and natural mineral water), this to avoid the radioactive decay influence. During the handling of the water, the radon is released into the air with easiness. Thus, measuring the activity concentrations of ^{222}Rn in drinking water difficulties are encountered: when water is transferred from a container to another one and it is stirring, the dissolved radon is released and the remaining water will have lower radon activity; boiling is another process that will completely release radon from the water into the air. At present, there are used various methods for measuring the radon in water: Lucas cell counting, gamma and alpha spectrometry, liquid scintillation counting, (SSNTD) solid-state nuclear track detectors and other (Todorovic et al., 2012; Oner et al., 2013).

Scintillation cell techniques were used to measure these water samples. The radon concentrations were determined using the Pylon-AB 5R system manufactured by Pylon Electronics (Canada) (Pylon Manual, 1991). The Pylon system is a laboratory-grade instrument for fast and accurate measurement of radon levels, it is also radon-in-air monitor, portable, very sensitive, durable, with high efficiency and low background, and can operate in a continuous mode (Nita et al., 2014; Calin et al., 2015). An accessory of the radon monitor was used a Vacuum Water Degassing System, Pylon WG-1001. The radon gas is bubbled through the water for pumping the radon into an evacuated and isolated Lucas ZnS(Ag) coated alpha scintillation cell, model Pylon LC 300 A. The Lucas cell was mounted with the air sample pumping it across the dehumidifier (Figure 2) and the air filter according to the measurement procedure of the double-valve. Following the technical specification of the equipment supplier (Pylon Manual, 1991), prior each sample measurement the system is emptied by purging for 20 minutes to get background values of radon activity concentrations into the detector. Then, the water is inserted into the degassing vessel (190 mL) and the WG 1001 is turned on.

The limit of detection (LD) for radon concentration is influenced by the Lucas cell detector background, and the residual gas contamination in the dehumidifier and in the connecting pipes. Thus, before determining the radon concentration from the water samples, equilibrium measurements were conducted to establish the level of background. A routinely achievable detection limit is 0.005 Bq/L for Pylon.

In order to measure the carbonated natural mineral water samples, a CO_2 degas ultrasound facility was used to remove the high content of CO_2, or a light bubbling with a stream of air was performed for a period of 10 minutes. Thus, 200 mL of each sample was transferred into propylene vials and degassed for 10 minutes before analysis. For each sample of natural mineral water and tap water, measurements of 5 minutes in three consecutive loops

Figure 2. Experimental set-up diagram with the degassing system and Lucas cell coupling, and the laboratory experimental set-up

were done, in total 15 min, thus obtaining 3 values for the number of counts. Subsequently, from the arithmetic mean of each triplicate, the background value previously measured of the Lucas cell was subtracted.

The measurement system has suitable features to analyse the concentration of radon gas in natural mineral waters. The important characteristic of this system is the high sensitivity and very short response time. Figure 2 shows the experimental set-up diagram with the degassing system and Lucas cell coupling to the measuring Pylon system.

The Pylon radon monitor has been check for his calibration factor in the radon chamber at IFIN-HH Department of Radioisotopes and Radiation Metrology (Pierre et al., 2021).

Gamma spectrometry, using an High Purity Germanium detector (GEM 25P4 model, from Ortec Inc., Easley, SC, USA), was the analysis performed on the residue samples after evaporation, in order to be able to calculate the total effective dose considering the other natural radionuclides contained in the samples, such as ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K (Calin et al., 2015).

1.4. Ultra Low-Level Liquid Scintillation Counting method

In addition, for the natural mineral water samples, Liquid Scintillation Counting (LSC) analyses were done for determining tritium levels, as this can be considered an indicator of any surface infiltration or interference, as well as for the aquifer stability. Tritium measurements were performed using the Quantulus 1220™ equipment from Canberra – Packard/Perkin-Elmer, USA. In the last years, the preparation, measurement and performance protocols of Quantulus 1220™ have been continuously improved at BETALAB by adapting the literature recommendations (Broda et al., 2007; Varlam et al., 2009; Schäfer, 2010). Also, the detection limit of LSC for tritium was improved to be lower than 0.5 Bq/L. Standard deviation values were less than 5% measured with Quantulus 1220™ ultra-low level analyser. The total measuring time resulted too be a multiple of 500 min/sample, using as scintillation cocktails, UltimaGold uLLT® or UltimaGold® commercial products and standard 20 cm^3 polyethylene measuring vials. Methods for obtaining HTO-based analytes provide for the removal by distillation of chemical and radiochemical contaminants. Some of them remain in the blazer (products with a boiling point higher than that of water), others are separated from the distillate by releasing into the air (International Organization for Standardization, 2015).

2. Results and discussions

2.1. Chemical and radiometric data

The study conducted for physical-chemical analysis on the 12 natural mineral water samples showed slightly variations of the major components of anions, cations and physical parameters (Table 1).

The geo-chemical properties of the area represent one of the reasons of these variations. Dolomite and calcite containing traces of quartz, muscovite, biotite, goethite and limonite represent the mineral water source geological description. For the water samples, the nine main ions concentration (SO_4^{2-}, HCO_3^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, F^-), pH, electrical conductivity and dry residue, were determined as a characteristic composition for the local geology and for the aquifer position, showing the dominant Ca-Mg-HCO3 nature of the studied water (Table 1).

In the tap water samples, only three ions (Na^+, NO_3^- and SO_4^{2-}), pH and electrical conductivity were determined (Table 2).

Table 1. Main natural mineral water samples physico-chemical characteristics

Natural mineral waters chemical data												
	pH	C.e. (µS/cm)	Anions (mg/L)					Cations (mg/L)				Res. Sec 180° (mg/L)
			K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	HCO_3^-	NO_3^-	SO_4^{2-}	F^-	
Min	5.85	1588	1.4	3.0	216	69	0.05	1150	0.1	7	0.10	63
Max	6.23	1881	3.9	6.4	315	88	0.20	1364	3.9	24	0.76	3026
Mean	6.05	1735	2.4	4.7	283	78	0.11	1278	2.7	13	0.25	545

Table 2. Physico-chemical characteristics of the tap water samples

Tap water samples chemical data					
	pH	C.e. (µS/cm)	Anions (mg/L)	Cations (mg/L)	
			Na^+	NO_3^-	SO_4^{2-}
Min	7.10	80.5	2.1	1.42	7
Max	7.34	124.6	12.7	7.30	54
Mean	7.24	98.8	5.4	3.21	24
Directive 98/83/CE values	≥6.5; ≤9.5	2500	200	50	250

Over the years, anthropogenic activities have affected the quality of surface and groundwater. The values presented in Table 2 showed in all cases acceptable values according to the 83 Directive/98 for the parameters measured in this study. However, public information regarding the water quality (Tudor, 2018) showed the problems occurred sometimes are related to iron concentration, turbidity and free residual chlorine at the end of the pipeline systems, resulting in non-compliant results with the 83 Directive/98.

To evaluate the activity concentration of ^{222}Rn in the natural mineral water samples and tap water samples was used the following formula (Pylon, 1991; Nasir et al., 2015):

$$C_{Rn} = \frac{(C-B)}{F\times 6.66\times D\times S\times V}\times 37\times 10^{-3}\ [\text{Bq/L}], \qquad (1)$$

where: C_{Rn} represents ^{222}Rn activity concentration in [Bq/L], C represents the sample gross count rate (in CPM), B represents the background rate (in CPM), F represents the cell counting efficiency (0.745), D represents the degassing efficiency of 300 A Lucas cell (0.9), S being the time correction for the decay of radon from the sampling time T_s, between 0.6701 and 0.8217, V represents the sample volume in litres (190 mL), and 37×10^{-3} represents the conversion factor between pCi and Bq. The calculated values of radon activity concentration for all samples are shown in Table 3.

Measurements showed very low values of radon activity concentrations in these water samples, both natural mineral and drinking. One can be noticed that for natural mineral water values ranges from 0.15±0.05 Bq/L to 11.35±2.97 Bq/L with an average of 3.69±0.95 Bq/L, since for the tap water the values are in general slightly lower values, between 0.17±0.05 Bq/L to 8.51±2.34 Bq/L with an average of 1.40±0.40 Bq/L. This was expected because of the fact that tap water is in most cases from surface water, which generally records lower values of radon concentration than groundwater. NMW3 and NMW4 have high concentrations of radon, but both are carbonated water. NMW5 originates from the same aquifer, but is non-carbonated. It can be seen from the Table 3 that natural carbonated mineral waters have higher radon concentrations.

Other studies for Romanian carbonated and noncarbonated water, in field measurements, showed higher values than in this study that ranges between 1.6–69 Bq/L and 13–166 Bq/L of radon activity concentrations (Nita et al., 2014). Certainly, the study area of these waters was different, and consequently the values are quite different, but factors that can contribute to this significant variation are containers for transportation; the operations of bottling and packing that could influences the radon concentration in water, reducing it. Same situation can be encountered in tritium volumic activities determination.

In other study for Romania, where the water samples collected from springs, the radon concentration showed very low values that ranged between Minimum Detectable Activity (MDA = 0.5 Bq/L) to 20 Bq/L for the majority of the samples, 4 samples having measured values of 20–40 Bq/L (Nita et al., 2014). In Cucos et al. (2021) values measured were between 2.1–19.7 Bq/L.

Other international studies provided similar data for both types of water, and are represented in Figure 3 (Biancotto et al., 1991; Somlai et al., 2007; Wallner & Steininger, 2007; Seiler, 2011; Todorovic et al., 2012; Nita et al., 2014; Bonotto, 2014; Alonso et al., 2015; Nasir et al., 2015; Nandakumaran et al., 2016). For instance, in Sukanya et al. (2020) radon activities concentration were between 0.17–68.3 Bq/L and other authors found rather large variation of the radon concentrations ranged from 0.07±0.12 Bq/L to 187±12 Bq/L (Ismail et al., 2021).

Table 3. Radon concentrations in natural mineral water and tap water samples and its associated total effective dose

No.	Samples ID	Type of water/source	Radon concentration (Bq/L)	Total effective dose (μSv/y)
Natural mineral waters				
1.	NMW 1	mineral spring	0.73±0.12	1.28±0.21
2.	NMW 2	mineral spring	1.08±0.34	1.89±0.60
3.	NMW 3	natural carbonated spring	7.78±1.59	13.62±2.78
4.	NMW4	natural carbonated spring	11.35±2.97	19.86±5.20
5.	NMW5	mineral spring	9.35±2.28	16.36±3.98
6.	NMW6	mineral spring	1.67±0.56	2.92±0.97
7.	NMW7	mineral spring	2.08±0.41	3.64±0.72
8.	NMW8	mineral spring	4.01±1.27	7.02±2.22
9.	NMW9	mineral spring	2.09±0.58	3.66±1.02
10.	NMW10	mineral spring	0.60±0.11	1.05±0.20
11.	NMW11	mineral spring	0.15±0.05	0.26±0.08
12.	NMW12	natural carbonated spring	3.37±1.12	5.90±1.96
	Arithmetic mean		3.69±0.95	6.45±1.70
Drinking water				
13.	DW1	tap water	0.17±0.05	0.30±0.08
14.	DW2	tap water	0.23±0.08	0.40±0.13
15.	DW 3	tap water	0.39±0.09	0.68±0.16
16.	DW 4	tap water	0.45±0.11	0.90±0.20
17.	DW 5	tap water	0.21±0.07	0.37±0.12
18.	DW 6	tap water	2.79±0.85	4.88±1.48
19.	DW 7	tap water	1.26±0.41	2.20±0.70
20.	DW 8	tap water	0.56±0.13	0.98±0.23
21.	DW 9	tap water	1.21±0.39	2.12±0.68
22.	DW 10	tap water	0.72±0.25	1.26±0.44
23.	DW 11	tap water	8.51±2.34	14.90±4.10
24.	DW 12	tap water	0.19±0.04	0.33±0.12
	Arithmetic mean		1.39±0.40	2.43±0.70

One can observe from Figure 3 that the variations are considerable large, up to few orders of magnitude, not only for natural mineral water where the geology has an high influence on the content of the radionuclides dissolved in water, but also for the tap water, where in many cases the water supply is surface water. Another interesting observation is the fact that the radon concentrations measured do not show significantly lower values in the tap water compared to values in natural mineral water (Figure 3). Furthermore, it was noticed that for both cases, one or two values were extremely high, >600 Bq/L for tap water (Nasir et al., 2015) and >1,000 Bq/L for natural mineral water (Todorovic et al., 2012).

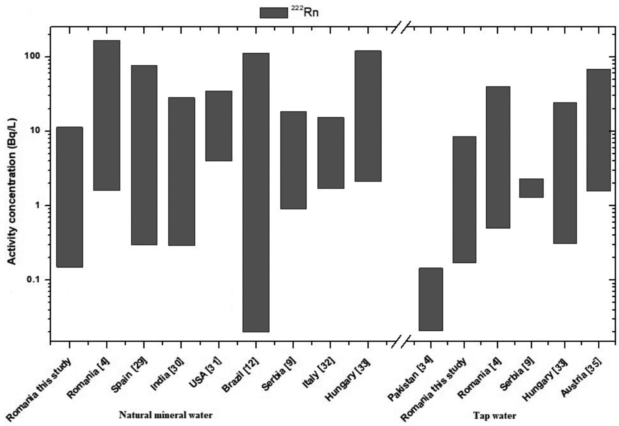

Figure 3. Radon activity concentrations in natural mineral water and in tap water from different countries

Hoehn et al., Kendall and McDonnell, showed in their studies that radon can be used as a hydrogeochemical tracer (Hoehn et al., 1992; Kendall & McDonnell, 1998). ^{226}Ra can be found in the reservoir of the rock. Its content and its emanation coefficient represent the factors that influence the presence of ^{222}Rn in groundwater (Alonso et al., 2015). ^{226}Ra is a natural radioactive isotope from the ^{238}U series which can be found in different concentrations in rocks and soils depending of the constituting mineral types (de Meijer, 1998) and which can have a higher concentration in volcanic acid rocks (Alonso et al., 2015). Thus, important concentrations of ^{222}Rn should be present in groundwaters leaching through volcanic acid rocks layers. The properties of the rock regarding its porosity and fractures, where the interchange with groundwater and with the distribution of ^{226}Ra occurs, has an important influence on the amount of dissolved ^{222}Rn in groundwater. Consequently, ^{222}Rn dissolved in water can "travel" large distances (hundreds of meters), also taking into account the 3.8 days half-life, reaching the surface and thereby, its concentration in a sample is representative to the location from which the sample was taken. Based on other factors, not part of this study, the radon concentrations in water can be influenced. For example, mixing processes with water with low radon concentrations. Also the groundwaters temperatures can influence the radon concentrations, since the radon gas solubility go up with temperature. Finally, that the geology and the types of the rocks clearly influence the radon concentration in the water, also in the region studied.

As the studied area consists mainly of carbonate sedimentary rocks (calcite, dolomite, etc.) and volcanic rocks (basalt, andesite, dacite, etc.) with some interference of feldspars, the concentrations of natural radionuclides are lower than for instance in granite rocks which might contain 10 to 20 ppm of uranium, as well as for thorium. Mafic rocks like basalt or diorite contain up to 1–5 ppm uranium and equally low amount as for limestones and sedimentary rocks, up to 10-fold or 100-fold lower than in granitic rocks (Figure 4). This explains why the concentrations of radon measured in natural mineral water samples have such low values as presented in Table 3 and Figure 4.

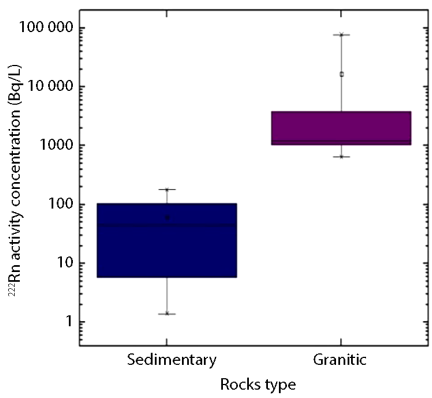

Figure 4. Radon concentrations in different water sources depending on the rock type

The average concentrations of radon in water as a function of the rock type lie between 36.6–120 Bq/L for sedimentary rocks (Gibbons & Kalin, 1997; Ladygiene et al., 1999; Somlai et al., 2007) and between 644–1220 Bq/L for granitic rocks (Trautmannsheimer et al., 2002; Wallner & Steininger, 2007; Lerena et al., 2013). Exceptionally, extremely high values can be recorded, such as those in Finland (Salonen, 1988), where radon activity concentration in granitic bedrock water samples was 77 000 Bq/L.

The application of method for determination of radon in Bucovina aquifer lead to an important observation: the radiological characterisation of the an aquifer, regarding radon activity concentration is in close connection with its properties as hydrogeochemical tracer, and even if there are many other factors that can bias this concentration in water, the geology and the types of rocks clearly are the main influence to it.

2.2. The annual effective dose

The annual effective dose [μSv/y], for the adults, caused by intake of radon from water, has been determined using the following expression (Somlai et al., 2007):

$$ED_{Ing} = C_{Rn} \times DCF \times V, \quad (2)$$

where: C_{Rn} [Bq/L] represents the activity concentration of ^{222}Rn, DCF [nSv/Bq] represents the dose conversion factor (3.5 nSv/Bq for an adult) (Table 20 Committed effective doses per unit intake by ingestion of natural radionuclides, United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR], 2000) and V[L] represents the annual intake of water by an adult.

In Table 3 are highlighted the results. The annual effective dose values are low, varying from 0.26 μSv/y to 20 μSv/y. The average value of ED_{Ing} due to radon in tap water is more than 2-fold lower than that in natural mineral water, as was expected. It should be mentioned that for the calculation of the dose in tap water it was considered that the consumption of water the annual intake is 500 L for an adult (as in Table 4), considered the reference annual intake of air, food and water, (UNSCEAR, 2000) and not 60 L, as weighted the estimate of consumption. There are some controversies concerning the numerical values the volume of annual ingested water and dose conversion coefficient. For the annual consumption volume of water, some authors are using the weighted estimate, 60 L/year (Alonso et al., 2015; UNSCEAR, 2000), someone others, 500 L/year as in Annex A: Methodologies for dose evaluation (UNSCEAR, 2000) for water and beverages estimate, and starting from the fact that the volume of water ingested per year (2 L per day) is 730 L, others use established guidance levels for radionuclides in drinking water (WHO, 2017). In this study, was found that less than 2 L is the average consumption per day per individual with considerable variations from person to person. The drinking water may vary with climate, physical activity, habits of life and economic status (Somlai et al., 2007). The dose conversion coefficient factor varies from 3.5×10^{-9} Sv/Bq to 10^{-8} Sv/Bq (UNSCEAR, 2000; Somlai et al., 2007; Nandakumaran et al., 2016).

There are two facts when radon from tap water can lead to exposures, one when the drinking water is ingested and second the inhalation of radon released into air when water is used. The parameters for the inhalation pathway are: the concentration of the radon [Bq/m^3], air-water concentration ratio of 10^{-4}, indoor occupancy of 7,000 hours per year, equilibrium indoor factor of 0.4, and dose conversion factor established value of 9 nSv (Bq h m^{-3})$^{-1}$. The inhalation dose (ED_{inh}) due to radon released from water is calculated accordingly to Eq. (3) (Khan et al., 2019).

$$ED_{Inh} = C_{Rn}\ [\mathrm{Bq/m^3}] \times 1/10^4 \times (7 \times 10^3)\ \mathrm{h/y} \times 0.4 \times 9\ \mathrm{nSv/(Bq \times h \times m^{-3})}. \quad (3)$$

10 kBq/m^3 value is the average concentration of radon in water given by UNSCEAR report. This implies a contribution of 1 Bq/m^3 to radon in air in indoor. Taking these into account and following Eq. (3), results an estimated total effective dose for inhalation because of the exposures from radon in water of 25 μSv/y. In the present case, for the average of 3.70 kBq/m^3 of radon concentration in natural mineral water will result an effective dose of 9.3 μSv/y. As the average concentration in tap water is 1.40 kBq/m^3, the effective dose is 3.5 μSv/y. Both values are well below the reference values given in UNSCEAR. The total committed effective dose, for the general population caused by the occurrence of radon in drinking water and its domestic use is the sum of the effective doses caused by radon ingestion with water, $ED_{Rn,\ Ing}$, and inhalation from waterborne radon, $ED_{Rn,\ Inh}$.

$$ED_{Rn} = ED_{Rn,\ Ing} + ED_{Rn,\ Inh}. \quad (4)$$

Comparing the average values of doses due to ingestion, from Table 3, of 6.45 μSv/y for natural mineral water and of 2.45 μSv/y for tap water, and the dose due to inhalation of 9.3 μSv/y and 3.5 μSv/y for the same samples, one can clearly state that the risk of inhalation of radon released from water is higher than the risk from the ingestion pathway (Poe et al., 1998; UNSCEAR, 2000; Kitto et al., 2005). The outcomes of Eq. (4), the total committed effective dose, are 15.75 μSv/y and 5.95 μSv/y, for natural mineral water and for tap water, respectively, which are considered low values in respect to the reference values given by UNSCEAR.

The activity concentrations of the natural mineral water samples are displayed in Table 4, for the minimum, maximum and average concentration of tritium, ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K.

It is worth mentioning that for tritium most of the samples were less than the Minimum Detectable Activity MDA (0.7 Bq/L) and only in three samples very low activity was measured. Also in some samples, ^{232}Th was not detected as it has a low solubility.

The total effective dose resulted from the ingestion of radionuclides contained in water is calculated according to (Ion et al., 2019), ranging from 15.45±4.90 μSv/y to 47.38±16.71 μSv/y. These values are below the reference value of 100 μSv/y.

Concerning tritium analyses for tap water samples, the results are well below the limits allowed in Romania for drinking water (100 Bq/L), ranging from 2.90±0.15 Bq/L

Table 4. Tritium and natural radionuclides concentrations in natural mineral water samples and the resulting total effective dose

Natural mineral water samples						
	Tritium	^{238}U	^{226}Ra	^{232}Th	^{40}K	Total effective dose
	Activity concentration [Bq/L]					[μSv/y]
Min	1.33±0.05	0.06±0.01	0.11±0.02	0.012±0.002	0.55±0.06	15.45±4.90
Max	1.45±0.05	0.21±0.06	0.45±0.05	0.086±0.010	0.92±0.11	47.38±16.71
Mean	1.39±0.07	0.12±0.02	0.28±0.03	0.100±0.005	0.80±0.08	34.50±7.85

to 5.20±0.28 Bq/L, and suggesting water supplies from a large area of surface water resource. The corresponding set of samples for natural mineral water represents the lowest values (≤MDA; MDA = 0.7 Bq/L). Among them, excepting of NW7 and NW10, no surface water infiltration or interferences were assigned. The values above MDA obtained for these two samples (see Table 4) could be caused by a different dynamic of resilience time of water source near the surface.

One the one side, analysing the above results clearly outlines the hypothesis that there are no anthropogenic inputs to the water sources of the ground, more likely suggesting major contribution from the carbonate rocks weathering. The main geochemical process that influences the chemical composition is represented by dolomite dissolution.

On the other side, the present study supports the consumers of natural mineral water and tap water, taking into account the effect of low doses on human health, considered that the consumption of natural mineral water is a market segment that shows an upward trend.

Conclusions

The radon concentration values found in this study were quite low, with an average of 1.39 Bq/L. An interesting conclusion is the fact that the radon concentrations measured in tap water samples do not show significantly lower values compared to values in natural mineral water. In compliance with radiological protection point of view, in the present work the radon levels measured in groundwater and in drinking water samples are below than 100 Bq/L which is the level established by the European Commission.

From the results presented in this study, it can be noted a correlation between aquifer characteristics. A clear distinction was made between contributions of different types of rocks to radon activity concentration in water, the sedimentary rocks type leading to a lower radon activity concentration in water than granitic type. The tritium concentrations were used as an indicator if there were surface water infiltration or interferences. Low values were obtained for the majority of the samples, below minimum detectable activity.

The annual effective dose was estimated according with measured radionuclides activity concentrations. From this point of view, the radon associated dose due to inhalation of radon released from water (9.3 μSv/y) is higher compared to radon associated dose due to ingestion (6.45 μSv/y). Both values were considered low with respect to the reference values given by UNSCEAR. As a major interest in this study is that the annual ingestion dose for the analysed water samples is lower than the accepted reference level.

The total effective dose resulted from the intake of ^{40}K ^{238}U, ^{232}Th and ^{226}Ra was at maximum 47.38 μSv/y and the total amount of all being well below 100 μSv/yr which is the reference level of the committed effective dose. Some physico-chemical characteristics such as pH, electrical conductivity and nine main ions were determined to identify directions in the chemical evaluation relating to rock type compositions and variations. It was observed that in the aquifers with carbonate rocks, the waters expose higher concentrations of alkali-earth metals (Ca^{2+} and Mg^{2+}) in correlation with HCO_3^-, which is less correlated with the reduced amounts of Na^+ and K^+ from these rocks. The research made in this study showed that mineral waters expose good chemical stability with values below 10%, and from this point of view admitting a low infiltration of the rain water or other external influence.

Another relevant aspect is to increase the amount of data on the ^{222}Rn activity concentrations in Romanian waters. The research significance of this study consists in the radiological characterisation, activity concentrations and associated dose, but also physical-chemical parameters indicators, that constitute an extensible and scalable method for other aquifers or water sources. This study is of great importance for ensuring the quality of natural mineral waters, but tap waters, investigated here, with regard to the radioactivity in accordance with the Council Directives 2009/54/EC and 2013/51/Euratom.

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Disclosure statement

The authors declare none conflict of interest.

References

Alonso, H., Cruz-Fuentes, T., Rubiano, J. G., González-Guerra, J., del Carmen Cabrera, M., Arnedo, M. A., Tejera, A., Rodríguez-Gonzalez, A., Pérez-Torrado, F. J., & Martel, P. (2015). Radon in groundwater of the Northeastern Gran Canaria aquifer. *Water*, *7*, 2575–2590. https://doi.org/10.3390/w7062575

Baeza, A., Díaz, M., García, E., & Miró, C. (2002). Influence of interbasin transfers between the Alcántara and Guadiloba reservoirs on the radiological quality of the drinking water of the city of Cáceres (Spain). *Journal of Radioanalytical and Nuclear Chemistry*, *252*, 441–449. https://doi.org/10.1023/A:1015853614972

Biancotto, R., Lafisca, S., Lucchese, R., Martinelli, C., Predicatori, F., Rosa, M., Tacconi, A., & Trotti, F. (1991). Radon concentration in mineral and thermal waters of Veneto: An estimate of ingestion and inhalation doses. *Radiation Protection Dosimetry*, *36*, 129–135. https://doi.org/10.1093/oxfordjournals.rpd.a080983

Bonotto, D. M. (2014). ^{222}Rn, ^{220}Rn and other dissolved gases in mineral waters of southeast Brazil. *Journal of Environmental Radioactivity*, *132*, 21–30. https://doi.org/10.1016/j.jenvrad.2014.01.005

Borio, R., Rongoni, A., Saetta, D. M. S., Desideri, D., & Roselli, C. (2005). Radon and tritium measurements in drinking water in a region of central Italy (Umbria). *Journal of Radioanalytical and Nuclear Chemistry*, *266*, 397–403. https://doi.org/10.1007/s10967-005-0923-2

Broda, R., Cassette, Ph., & Kossert, K. (2007). Radionuclide metrology using liquid scintillation counting. *Metrologia*, *44*, S36–S52. https://doi.org/10.1088/0026-1394/44/4/S06

Calin, M. R., Ion, A. C., & Radulescu, I. (2015). Evaluation of quality parameters and of natural radionuclides concentrations in natural mineral water in Romania. *Journal of Radioanalytical and Nuclear Chemistry*, *303*, 305–313. https://doi.org/10.1007/s10967-014-3401-x

Calin, M. R., Ivan, C., Dragusin, M., & Radulescu, I. (2019). Measurement and assessment of radon gas concentration in IFIN-HH and ELI-NP using the active method. *Romanian Journal of Physics*, *64*, 813.

Calin, M. R., Radulescu, I., Ion, A. C., & Sirbu, F. (2016). Radiochemical investigations on natural mineral waters from Bucovina region, Romania. *Romanian Journal of Physics*, *61*, 1051–1066.

Council of the European Union. (2013, October 22). *Laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption* (Council Directive 2013/51/Euratom). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32013L0051

Cucos, A. L., Moldovan, M. C., & Burghele, B. D. (2021). Radiological risk assessment for karstic springs used as drinking water in rural Romania. *Atmosphere*, *12*, 1207. https://doi.org/10.3390/atmos12091207

de Meijer, R. J. (1998). Heavy minerals: From 'Edelstein' to Einstein. *Journal of Geochemical Exploration*, *62*, 81–103. https://doi.org/10.1016/S0375-6742(97)00073-3

European Parliament and the Council of the European Union. (2009, June 18). *Exploitation and marketing of natural mineral waters* (Directive 2009/54/EC). https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009L0054

Froehlich, K. (Ed.). (2010). Radioactivity in the environment. In *Environmental radionuclides: Tracers and timers of terrestrial processes* (Vol. 16). Elsevier.

Gibbons, D., & Kalin, R. (1997). A survey of radon-222 in ground water from the Sherwood Sandstone Aquifer: Belfast and Newtownards, Northern Ireland. *Groundwater Monitoring & Remediation*, *17*, 88–92. https://doi.org/10.1111/j.1745-6592.1997.tb01281.x

Hoehn, E., von Gunten, H. R., Stauffer, F., & Dracos, T. (1992). Radon-222 as a groundwater tracer. A laboratory study. *Environmental Science & Technology*, *26*, 734–738. https://doi.org/10.1021/es00028a010

International Organization for Standardization. (2015). *Water quality. Determination of the volumic activity of Tritium. Method by counting scintillations in liquid medium* (SR ISO 9698). https://www.iso.org/obp/ui/fr/#iso:std:iso:9698:ed-3:v1:en

Ion, I. I., Ion, A. C., Calin, M. R., Radulescu, I., & Bogdan, D. (2019). Assessment of chemical parameters and natural radionuclides concentrations in carbonated natural mineral water and contribution to radiation dose. *Romanian Journal of Physics*, *64*, 804.

Ismail, N. F., Hashim, S., Sanusi, M. S. M., Rahman, A. T. A., & Bradley, D. A. (2021). Radon levels of water sources in the southwest coastal region of Peninsular Malaysia. *Applied Sciences*, *11*, 6842. https://doi.org/10.3390/app11156842

Kendall, C., & McDonnell, J. J. (1998). *Isotope tracers in catchment hydrology*. Elsevier.

Khan, A. R., Rafique, M., Rahman, S. U., Basharat, M., Shahzadi, C., & Ahmed, I. (2019). Geo-spatial analysis of radon in spring and well water using kriging interpolation method. *Water Supply*, *19*(1), 222–235. https://doi.org/10.2166/ws.2018.070

Kitto, M. E., Parakh, P. P., Torres, M. A., & Shneider, D. (2005). Radionuclide and chemical concentrations in mineral waters at Saratoga Springs, New York. *Journal of Environmental Radioactivity*, *80*, 327–339. https://doi.org/10.1016/j.jenvrad.2004.10.006

Ladygiene, R., Mastauskas, A., Morkunas, G., & Gasiunas, K. (1999). Determination of ^{222}Rn concentrations in Lithuanian spa waters by liquid scintillation counting. *Czechoslovak Journal of Physics*, *49*, 473–478. https://doi.org/10.1007/s10582-999-0063-y

Lerena, J. J., Cortina, D., Durán, I., & Sorribas, R. (2013). Impact of the geological substrate on the radiological content of Galician waters. *Journal of Environmental Radioactivity*, *116*, 48–53. https://doi.org/10.1016/j.jenvrad.2012.08.014

Nandakumaran, P., Vinayachandran, N., Anitha Shyam, T. S., Jose, B., Sreehari Sarangan, M. S., & Santhana Subramani, M. (2016). Radon in groundwater in parts of coastal tracts of southern Kerala, India. *Journal of Radioanalytical and Nuclear Chemistry*, *308*, 99–104. https://doi.org/10.1007/s10967-015-4272-5

Nasir, T., Matiullah, M., Rafique, K. M., & Rubeena, T. (2015). Measurement of waterborne radon in the drinking water of the Dera Ismail Khan city using active and passive techniques. *Nuclear Technology and Radiation Protection*, *30*, 139–144. https://doi.org/10.2298/NTRP1502139N

National Commission for Controlling Nuclear Activities. (2018). Norms regarding the estimation of the effective doses and of the equivalent doses due to the internal and external exposure (CNCAN Order no. 145/2018). *Official Gazette of Romania*, Part I, no. 555.

Nita, D. C., Moldovan, M., & Cosma, C. (2014). Radon measurement in carbonated water with the Lucas cell and charcoal adsorption methods. *Journal of Radioanalytical and Nuclear Chemistry*, *299*, 25–30. https://doi.org/10.1007/s10967-013-2829-8

Oner, F., Yigitoglu, I., & Yalim, H. A. (2013). Measurements of radon concentrations in spa waters in Amasya, Turkey. *Radiation Protection Dosimetry*, *157*, 221–224. https://doi.org/10.1093/rpd/nct130

Palomo, M., Penãlver, A., Borrull, F., & Aguilar, C. (2007). Measurement of radioactivity in bottled drinking water in Spain. *Applied Radiation and Isotopes*, *65*, 1165–1172. https://doi.org/10.1016/j.apradiso.2007.04.022

Patnaik, P. (Ed.). (2010). *Handbook of environmental analysis: Chemical pollutants in air, water, soil, and solid wastes*. Taylor & Francis Group, LLC. https://doi.org/10.1201/b10505

Pierre, S., Cassette, P., Sabot, B., Fréchou, C., Antohe, A., Barna, C., Blahušiak, P., Cardellini, F., Dersch, R., Honig, A., Juget, F., Krivošík, M., Luca, A., Maringer, F. J., Mertes, F., Röttger, S., Sahagia, M., Slučiak, J., Stietka, M., Szűcs, L., & Teodorescu, C. (2021). International comparison of activity measurements of radon 222 – EURAMET Project no 1475 – EURAMET.RI(II)-S8.Rn-222. *Metrologia*, *58*, 06015. https://doi.org/10.1088/0026-1394/58/1A/06015

Poe, G. L., van Es, H. M., VandenBerg, T. P., & Bishop, R. C. (1998). Do participants in well water testing programs update their exposure and health risk perceptions? *Journal of Soil and Water Conservation*, *53*, 320–325.

Pylon Electronic Development Company Ltd. (1991). *Vacuum water-degassing system manual* (A900037, Rev. 2. 147). Colonnade Road, Ottawa, Canada.

Radulescu, I., Calin, M. R., Ion, I. I., Ion, A. C., Capra, L., & Simion, C. A. (2017). Gross alpha, gross beta and gamma activities in bottled natural mineral water from Romania. *Romanian Reports of Physics*, *69*, 710.

Romanian Parliament. (2015, November 27). *Establishing the requirements for the protection of the health of the population regarding radioactive substances in drinking water* (Romanian Law no. 301). https://www.dspbihor.gov.ro/legislatie/Lege%20301%202015.pdf

Salonen, L. (1988). Natural radionuclides in groundwaters in Finland. *Radiation Protection Dosimetry*, *24*, 163–166. https://doi.org/10.1093/oxfordjournals.rpd.a080263

Schäfer, I. (2010). *Determination of Tritium activities in ground and surface water after electrolytic enrichment* (Application Note 46, R. Edler, Rev. and Trans.). PerkinElmer® Inc.

Seiler, R. L. (2011). ^{210}Po in Nevada groundwater and its relation to gross alpha radioactivity. *Groundwater*, *49*, 160–171. https://doi.org/10.1111/j.1745-6584.2010.00688.x

Silva, C. R., Machado, D. V., & da Silva-Filho, E. V. (2019). Determination of the natural radioactivity in the mineral water distributed in the Salutaris Park, Paraíba do Sul, Brazil. *Environmental Earth Sciences*, *78*, 639. https://doi.org/10.1007/s12665-019-8661-x

Somlai, K., Tokonami, S., Ishikawa, T., Vancsura, P., Gáspár, M., Jobbágy, V., Somlai, J., & Kovács, T. (2007). ^{222}Rn concentrations of water in the Balaton Highland and in the southern part of Hungary, and the assessment of the resulting dose. *Radiation Measurements*, *42*, 491–495. https://doi.org/10.1016/j.radmeas.2006.11.005

Sukanya, S., Sabu, J., & Noble, J. (2020). Evaluation of radiation dose from radon ingestion and inhalation in groundwater of a small tropical river basin, Kerala, India. *Isotopes in Environmental and Health Studies*, *57*, 204–215. https://doi.org/10.1080/10256016.2020.1835889

Todorovic, N., Nikolov, J., Forkapic, S., Bikit, I., Mrdja, D., Krmar, M., & Veskovic, M. (2012). Public exposure to radon in drinking water in SERBIA. *Applied Radiation and Isotopes*, *70*, 543–549. https://doi.org/10.1016/j.apradiso.2011.11.045

Trautmannsheimer, M., Schindlmeier, W., & Hübel, K. (2002). Radon exposure levels of the staff in the drinking water supply facilities in Bavaria, Germany. *International Congress Series*, *1225*, 81–86. https://doi.org/10.1016/S0531-5131(01)00517-9

Tudor, A. (2018). *The quality of drinking water distributed in a centralized system in the supply areas with over 5,000 inhabitants or with a distributed water volume of over 1000 m^3/day* (National synthetic report year).

United Nations Scientific Committee on the Effects of Atomic Radiation. (2000). Annex B: Exposures from natural radiation sources. In *Sources and effects of ionizing radiation*. https://www.unscear.org/docs/publications/2000/UNSCEAR_2000_Report_Vol.I.pdf

Varlam, C., Stefanescu, I., Duliu, O. G., Faurescu, I., & Popescu, I. (2009). Applying direct liquid scintillation counting to low-level tritium measurement. *Applied Radiation and Isotopes*, *67*, 812–816. https://doi.org/10.1016/j.apradiso.2009.01.023

Wallner, G., & Steininger, G. (2007). Radium isotopes and ^{222}Rn in Austrian drinking waters. *Journal of Radioanalytical and Nuclear Chemistry*, *274*(3), 511–516. https://doi.org/10.1007/s10967-006-6939-4

World Health Organization. (2017). *Guidelines for drinking-water quality* (4^{th} ed.). Geneva.

Yuce, G., Fu, C. C., D'Alessandro, W., Gulbay, A. H., Lai, C. W., Bollomo, S., Yang, F., Italiano, F., & Walla, V. (2017). Geochemical characteristics of soil radon and carbon dioxide within the Dead Sea, Turkey. *Chemical Geology*, *469*, 129–146. https://doi.org/10.1016/j.chemgeo.2017.01.003