Radiological investigation of natural carbonated spring waters from Eastern Carpathians, Romania

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Abstract
The current study presents a radiological water-quality assessment on 64 spring water samples from four Romanian counties. The study area is abundant in CO2-rich spring waters consumed by locals and tourists. Gross alpha activities ranged between 21 ± 2 and 7530 ± 658 mBq L⁻¹, with 27% of the samples exceeding the WHO threshold. Gross beta values ranged from 40 ± 2 to 5520 ± 430 mBq L⁻¹, with 29% exceeding the recommended values. Radionuclide activities fluctuated between 0.6 ± 0.08 and 81 ± 6 Bq L⁻¹ for 222Rn, 15 ± 2 to 1154 ± 112 mBq L⁻¹ for 226Ra, and from 18 ± 2 to 64 ± 5 mBq L⁻¹ for 210Po. The annual effective doses attributed to radium varied between 0.002 and 0.23 mSv yr⁻¹.

Keywords Gross alpha · Gross beta · Potable spring waters · Eastern Carpathians

Introduction

Water is an essential resource and a basic human right. In order to be suitable for human consumption, it has to meet quality standards for microbial, chemical and radiological properties. Radionuclides are naturally present in water, resulting mainly from processes of dissolution, leaching and desorption of the surrounding geological environment (rocks and sediments) [23]. The primary alpha-emitting natural radionuclides present in water are 224Ra, 226Ra and 210Po. Gross beta activities are mainly attributed to 228Ra, 210Pb and 40K [7]. Water is a factor that can potentially increase the internal exposure to natural radiation [37], and for this reason, national and international guidelines were issued to ensure the safety of drinking water [9, 13, 21, 38]. World Health Organization (WHO) [38] recommends a threshold value of 0.5 Bq L⁻¹ for gross alpha activity and 1.0 Bq L⁻¹ for gross beta activity, for water to be considered radiologically safe for consumption. These values were established in regard to the Individual Dose Criterion (IDC) adopted, of 0.1 mSv yr⁻¹ for a 2 L daily water consumption. Romanian law 301/2015 was issued considering the same IDC, and establishes a guidance level of 0.1 Bq L⁻¹ for gross alpha, and 1.0 Bq L⁻¹ for gross beta activity.

In Romania, more than 2000 natural spring waters are documented [3, 30], many of which are located in the Eastern Carpathians. This region is characterized by the proximity of the Neogene Călimani-Gurghiu-Harghita and Oaș-Gutâi volcanic ranges. Therefore, manifestations of post-volcanism in the area are leading to the occurrence of sparkling, CO2-rich mineral waters [18, 34]. Thousands of local inhabitants are consuming raw water directly from the local springs on a daily basis, as their main source of drinking water or for medicinal purposes [6, 10]. The water resources in this region are also accounting for 45% of the bottled mineral waters from Romania [10]. Beside drinking, the mineral waters are often associated with balneological practices [17] and is an important factor for tourism in the Eastern Carpathians [8]. Therefore, determining the radioactivity levels of these water resources is important for public health safety, and allows for the assessment of radiation exposure resulted from water ingestion. Few studies on the radiological quality of drinking water were conducted in the Eastern Carpathians, Romania [4, 24, 25]. Most studies are

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focusing mainly on $^{222}\text{Rn}$ and $^{226}\text{Ra}$ radionuclides, but the present-day state of knowledge in the area remains scarce.

The aim of the present study is to perform a radiological survey on 64 natural carbonated water samples collected from four counties in Romania, namely Covasna, Harghita, Bistrița-Năsăud and Maramureș, located in close proximity to the Eastern Carpathians and the Neogene volcanic ranges that it hosts. Water physico-chemical parameters (temperature, pH, redox potential, electrical conductivity, total dissolved solids (TDS) and salinity) were measured for each sample. Gross alpha and beta activity measurements, along with specific radionuclide determinations ($^{210}\text{Po}$, $^{222}\text{Rn}$, $^{226}\text{Ra}$, $^{40}\text{K}$) were conducted and the results compared with the guidance levels for radioactivity in drinking water, established by WHO [38] and the national law [21]. The annual effective doses attributed to $^{226}\text{Ra}$ were calculated to assess the exposure to internal radiation.

**Materials and methods**

**Study site**

Sixty-four water samples were collected from sparkling mineral springs in four counties in Romania (Fig. 1). The first area includes Covasna and Harghita counties (32 samples labeled as CVHR), which are in the proximity of the Călimani-Gurghiu-Harghita volcanic range, and subjected to the post-volcanic manifestations associated with it. The second area, represented by Bistrița-Năsăud and Maramureș counties (32 samples labeled as BNMM), is located nearby the Oaș-Gutăi volcanic range. The samples were collected in 2 L plastic containers and acidified with 65% nitric acid ($\text{HNO}_3$), to avoid the adsorption losses of radionuclides on the container walls. At the time of sampling, water physico-chemical parameters (temperature, pH, redox potential, electrical conductivity, TDS and salinity) were measured in 50 ml beakers using an XS-PC5 multiparameter.

**Gross alpha/beta specific activity measurements**

For gross alpha and beta activity measurements, 1 l of each sample was evaporated to dryness on a hot plate ($< 85 \, ^\circ\text{C}$) without boiling. Subsequently, 0.2 g of the resulted residual material was dissolved with 3 ml 3 M HCl, and mixed with 15 ml GoldStar Quanta scintillator cocktail in a plastic 20 ml vial. The samples were then measured using a TRICARB 2300 TR Liquid Scintillation Counter with a 65% efficiency for alpha and 85% for beta activity ($\text{tSIE} = 479$), a minimum detectable activity (MDA) of 25 mBq L$^{-1}$ and a measurement time of 21,600 s. The calibration was performed using a $^{210}\text{Pb}$ standard in equilibrium with its successors, $^{210}\text{Bi}$ and $^{210}\text{Po}$, purchased from the Czech Methodology Institute. The resulting values are representing the total activity of the sample (alpha and beta), as TriCarb 2300 does not allow separation of impulses according to their origin. Gross alpha activities were determined by alpha counting, 0.1 g of the residual was milled and transferred to 45 mm diameter aluminum discs, ensuring the distribution of the mass. The discs were then covered with silver activated zinc sulphide.

![Fig. 1 Location of the water samples collected from carbonated springs in four counties in Romania, along with the local geology of the Eastern Carpathians](image-url)
(ZnS(Ag)) sheets for alpha particle detection and were measured using an MEV NP-420 alpha counting system, for 10,000 s. The calibration was performed using a $^{209}$Po for a sample density of 25 mg/cm$^2$. The minimum detectable activity for gross alpha activity was 20 mBq L$^{-1}$. Gross beta activities were achieved by subtracting gross alpha from the total activity of the sample, previously measured by LSC.

**Radionuclide-specific measurements**

**Radon ($^{222}$Rn) specific activity measurements**

The $^{222}$Rn activity measurements were carried out by Liquid Scintillation Counting (LSC) technique [16]. The method involves adding 10 ml of water, at the time of sampling, to 10 ml mineral oil scintillator cocktail (ProScint Rn A/B) in a 20 ml glass vial using a plastic syringe, after which the vial was sealed and shaken vigorously. The samples were then set aside for a minimum of 3 h to allow for the ingrowth of the short-lived progenies of $^{222}$Rn [22, 33]. The measurements were carried out using a TRICARB 2300 TR Liquid Scintillation Counter calibrated with a standard NIST RaCl solution with an activity of 6 Bq L$^{-1}$, dissolved in water. The MDA was 0.3 Bq L$^{-1}$ and the measurement time 10,800 s.

**Radium ($^{226}$Ra) specific activity measurements**

The $^{226}$Ra activity analysis procedure is based on the liquid scintillation technique, $^{226}$Ra is determined through $^{222}$Rn and its progenies, which are extracted by the scintillation cocktail from the water phase. In this regard, one liter of each sample was acidified with 65% nitric acid (HNO$_3$), and concentrated at least ten folds, in order to reach a lower detection limit, by gentle evaporation on a hot plate, at a temperature of $\leq 85$ °C. To avoid the occurrence of precipitation during the pre-concentration phase, all salts were converted in nitrates, which have a high solubility in water. Furthermore, 10 ml of the pre-concentrated sample were transferred in a polyethylene vial, and 10 ml scintillation cocktail (ProScint Rn A/B) were added. The vials were then stored in the dark at a constant temperature (16 °C), for 30 days, to allow for the $^{222}$Rn ingrowth period. After the secular equilibrium between $^{226}$Ra and $^{222}$Rn was established, the samples were measured using a TRICARB 2300 TR Liquid Scintillation Counter, calibrated with a standard NIST RaCl solution, with an MDA of 20 mBq L$^{-1}$, and a measurement time of 10,800 s.

**Polonium ($^{210}$Po) specific activity measurements**

For $^{210}$Po activity measurements, residue of samples that exceeded a gross alpha activity of 0.5 Bq L$^{-1}$ was subjected to acidic digestion. To each sample, 0.3 mL (100 Bq·mL$^{-1}$) $^{209}$Po tracer was added. The samples were treated with HNO$_3$ and HCl. Subsequently, they were brought to 100 ml using distilled water, the pH was adjusted in the 0.1–0.3 range and the samples were left on a hot plate ($<85$ °C) for three hours to allow for the spontaneous deposition of $^{210}$Po on high nickel content stainless steel discs [5]. The discs were then analyzed using an ORTEC SOLOIST Alpha Spectrometer System with Ultra ENS-U900 detectors and an active surface of 900 mm$^2$ with a resolution greater than 29 keV, calibrated using a $^{209}$Po standard solution. The minimum detectable activity for $^{210}$Po was 15 mBq L$^{-1}$.

**Potassium ($^{40}$K) activity measurements**

The activity of $^{40}$K was measured for 1 g of dry residue from each sample using a Well-type High-Purity Germanium (HPGe) Gamma Spectrometric System (ORTEC GWL-120-15 detector with a resolution of 2.08 keV for 1.33 MeV $^{60}$Co and 1.1 keV for 122 keV $^{57}$Co gamma lines). The detector was calibrated with a Merck KCl solution, and has an MDA of 250 mBq L$^{-1}$. The specific activity of $^{40}$K was determined from its 1460.7 keV gamma-ray lines after a measurement time greater than 120,000 s. Spectrum acquisition was performed using the MAESTRO multi-channel analyzer software.

**Annual effective dose calculation**

The annual effective dose (AED) was calculated for $^{226}$Ra activities from each sample, using the following equation [29]:

$$\text{AED}_{Ra-226} = \Lambda_{Ra-226} \cdot \text{IRw} \cdot \text{CF}$$

where: $\text{AED}_{Ra-226}$ stands for $^{226}$Ra Annual Effective Dose (mSv yr$^{-1}$).

$\Lambda_{Ra-226}$ stands for $^{226}$Ra activity in the sample (mBq L$^{-1}$).

$\text{IRw}$ stands for the annual ingested volume of drinking-water (L yr$^{-1}$).

$\text{CF}$ stands for the dose coefficient (Sv Bq$^{-1}$).

The dose coefficient value of 2.8×10$^{-7}$ Sv Bq$^{-1}$ as well as the IRw value of 730 L yr$^{-1}$ were extracted from Romanian law 301/2015 [21].

**Results and discussions**

**Water physico-chemical parameters measured values**

The measured values for water physico-chemical parameters at the time of sampling (temperature, pH, conductivity, oxidation–reduction potential (ORP), TDS and salinity) in the
studied area are presented in Table 1. Temperature ranged between 11.7 and 25 °C; pH values ranged between 1.71 and 8.18; ORP values were in the −56.7 to 296 mV interval; conductivity values were between 252 and 10,560 µS; TDS ranged from 178.5 to 7500 ppm, and salinity between 56.7 and 5850 mg L⁻¹.

**Specific activity measured values**

The specific activity values of gross alpha and beta along with ²²²Rn, ²²⁶Ra and ²¹⁰Po radionuclides are presented in Table 2. WHO, 2017 and the national law 301/2015 are both stating that initial determinations of gross alpha and beta activities are required as the first step in assessing radiological safety of drinking water. Furthermore, if any guidance level for these activities is exceeded, specific determinations of radionuclides have to be followed. In the present study, gross alpha and beta, as well as ²²²Rn and ²²⁶Ra determinations were carried out for the whole set of samples. Subsequently, for the samples exceeding the guidance level of 0.5 Bq L⁻¹ for alpha and respectively 1 Bq L⁻¹ for gross beta activities, stipulated in WHO Guidelines for Drinking-water Quality [38], further investigations were carried out, by measuring ²¹⁰Po and ⁴⁰K specific activities. In some cases, when the residue mass of the sample permitted further investigations to be performed, ²¹⁰Po was also measured for samples with activities below WHO guidance level for gross alpha.

Gross alpha activities (excluding ²²²Rn), which are presented in Fig. 2, ranged between 21 ± 2 and 2440 ± 210 mBq L⁻¹ for the samples collected in Covasna and Harghita (CVHR), and between 40 ± 6 and 7530 ± 658 mBq L⁻¹ for those from Bistrița-Năsăud and Maramureș (BNMM). 26.7% of samples exceeded the guidance level of 500 mBq L⁻¹ stated in WHO, 2017 for alpha activity, and 53.5% exceeded the Romanian legislation threshold of 100 mBq L⁻¹. 12 samples had activities under the detection limit (< 20 mBq L⁻¹), and an additional 8 samples could not be measured for gross alpha activity, due to insufficient residue. Therefore, these samples were only measured for gross alpha and beta (total) activity.

Gross beta activities ranged between 50 ± 3 and 4160 ± 398 mBq L⁻¹ for CVHR samples, and between 40 ± 3 and 5520 ± 430 mBq L⁻¹ for BNMM. A total 26% of the samples exceeded the guidance level of 1000 mBq L⁻¹ (stated in both law 301/2015 and WHO, 2017), and 13 samples were below the MDA of 25 mBq L⁻¹. Subsequently, as guidelines are indicating, ⁴⁰K measurements were performed for the samples exceeding the recommended level for gross beta. The potassium activities are radiologically negligible, due to the age-dependent effective dose conversion factor for adults (CF₇₋₅₆ = 6.2 × 10⁻⁶ mSv Bq⁻¹), which is the least of the other radionuclides [12]. Thus, the ⁴⁰K contribution should be extracted from the gross beta activity in order to accurately assess safety of drinking water [38]. ⁴⁰K activities could be detected in 8 samples from BNMM. The activities ranged from 260 ± 30 to 4368 ± 390 mBq L⁻¹, with another 7 values under the detection limit. The gross beta activities and ⁴⁰K contribution are presented in Fig. 3. It can be observed that after ⁴⁰K subtraction, gross beta activities of three samples decreased under the guideline level.

Radon (²²²Rn) is not regulated by WHO Guidelines for Drinking-water Quality, 2017, as 90% of the dose attributable to radon in drinking-water comes from inhalation rather than ingestion [37]. Thus, controlling the inhalation pathway is the most effective way to control radon internal exposure [38]. Romanian law 301/2015 imposes a recommended value of 100 Bq L⁻¹ for ²²²Rn in drinking water. However, radon in not to be included in the gross alpha activity of the samples. The ²²²Rn activity values ranged between 0.6 ± 0.08 and 81 ± 6 Bq L⁻¹ for the whole set of samples, and did not exceed the national legislation recommendations.

Radium (²²⁶Ra) is one of the most dangerous and widely distributed long-lived α-emitters found in environmental samples [31] due to a combination of its long half-life (T¹/₂ = 1602 years) and radiological effects [1]. In the present study, the ²²⁶Ra specific activities ranged between 21 ± 1 and 429 ± 40 mBq L⁻¹ for CVHR and between 24 ± 2 and 1154 ± 112 mBq L⁻¹ for BNMM area. Only one sample has exceeded the WHO guidance level of 1000 mBq L⁻¹ and 5 that of national legislation, which is 500 mBq L⁻¹. 35 samples had activities under the detection limit (< 20 mBq L⁻¹). ²²⁶Ra activity values and their compliance with the guidance level can be observed in Fig. 4.

Furthermore, the annual effective doses (AED) were calculated in order to assess ²²⁶Ra contribution to the received dose, resulting from water ingestion. The recommended maximum value for AED attributed to drinking water, considering a daily consumption of 2L, is 0.1 mSv yr⁻¹ [21, 38]. For the calculation, the national legislation dose coefficient (CF) of 2.8·10⁻⁷ Sv·Bq⁻¹ was considered. The values are presented in Fig. 5, and ranged from 0.002 to 0.23 mSv yr⁻¹, with 5 samples exceeding the guidance value.

Polonium (²¹⁰Po) activities were generally low, ranging between 18 ± 2 and 64 ± 5 mBq L⁻¹, with only 4 samples exceeding the minimum detectable activity, and 32 being below it (< 15 mBq L⁻¹). The activities did not exceed, in any case, the guidance level for ²¹⁰Po, which is 100 mBq L⁻¹, adopted by both WHO and Romania.

**Data analysis**

The relationships between gross alpha, gross beta and ²²⁶Ra specific activities with water physico-chemical parameters (T, pH, ORP, conductivity, TDS and salinity) were investigated by performing Pearson's correlations, and the results
Table 1 Measured values of water parameters for the samples collected

| Sample | T (°C) | pH  | ORP* (mV) | Cond (µS) | TDS (ppm) | Sal.* (mg L⁻¹) |
|--------|--------|-----|-----------|-----------|-----------|---------------|
| CVHR-1 | 20     | 7.53| −23.5     | 1102      | 702       | 482           |
| CVHR-2 | 21.2   | 7.14| −37.17    | 957       | 686       | 472           |
| CVHR-3 | 17.2   | 7.93| −37.6     | 326       | 233       | 158.3         |
| CVHR-4 | 13.4   | 6.73| 21.5      | 3640      | 2610      | 2100          |
| CVHR-5 | 12.5   | 7.14| −2.4      | 1337      | 945       | 686           |
| CVHR-6 | 17     | 6.45| 35.5      | 4140      | 2900      | 2200          |
| CVHR-7 | 14.8   | 6.75| 29.9      | 5410      | 3880      | 3000          |
| CVHR-8 | 16.2   | 6.16| 53        | 1212      | 848       | 600           |
| CVHR-9 | 12.2   | 7.93| −37.6     | 326       | 233       | 158.3         |
| CVHR-10| 14.4   | 6.44| 38.3      | 2410      | 1723      | 1342          |
| CVHR-11| 17.8   | 6.1  | 57.1      | 2540      | 1798      | 1425          |
| CVHR-12| 21.2   | 2.93| 226       | 1082      | 769       | 539           |
| CVHR-13| 18     | 6.65| 27        | 4750      | 3350      | 2570          |
| CVHR-14| 15     | 6.48| 35.8      | 4110      | 2930      | 2280          |
| CVHR-15| 16.8   | 6.16| 53.3      | 2210      | 1572      | 1162          |
| CVHR-16| 16.7   | 7.53| −18.6     | 4660      | 304       | 189           |
| CVHR-17| 19.4   | 6.2  | 52.3      | 1222      | 849       | 585           |
| CVHR-18| 21.2   | 2.93| 226       | 1082      | 769       | 539           |
| CVHR-19| 17.8   | 6.1  | 57.1      | 2540      | 1798      | 1425          |
| CVHR-20| 20.2   | 2.12| 272       | 4850      | 3440      | 2620          |
| CVHR-21| 21.9   | 1.71| 296       | 10,560    | 7500      | 5850          |
| CVHR-22| 19.1   | 5.67| 79.1      | 2000      | 1425      | 1009          |
| CVHR-23| 18.4   | 5.77| 74.7      | 2030      | 1400      | 992           |
| CVHR-24| 17     | 6.31| 48.1      | 923       | 659       | 455           |
| CVHR-25| 19.1   | 6.13| 5.47      | 1494      | 1054      | 764           |
| CVHR-26| 22.3   | 6.49| 36.1      | 1822      | 1294      | 942           |
| CVHR-27| 20     | 6.05| 61.4      | 1092      | 775       | 543           |
| CVHR-28| 21.7   | 6.2  | 52.1      | 1682      | 1177      | 870           |
| CVHR-29| 13.7   | 5.33| 98.3      | 303       | 207       | 1348          |
| CVHR-30| 14.9   | 6.08| 57.2      | 1106      | 783       | 549           |
| CVHR-31| 15.6   | 6.14| 53.9      | 1954      | 1390      | 985           |
| CVHR-32| 17.1   | 6.18| 51.9      | 2730      | 1956      | 1605          |
| CVHR-33| 17.4   | 5.77| 74.4      | 650       | 455       | 305           |

Min 11.7 1.71 −56.7 252 120 130.7
Max 25 8.18 296 10,560 7500 5850

*ORP refers to Oxidation–Reduction Potential
Cond. refers to conductivity
Sal. refers to salinity
Table 2

Specific activity values of the samples for gross alpha/beta, along with 222Rn, 226Ra and 210Po

| Sample | Λ α (mBq L⁻¹) | Σ α (mBq L⁻¹) | 222Rn (Bq L⁻¹) | 226Ra (mBq L⁻¹) | 210Po (mBq L⁻¹) |
|--------|---------------|----------------|----------------|-----------------|----------------|
| CVHR-1 | 190 ± 10      | < 25           | 3.7 ± 0.29     | 88 ± 8          | 1.1 ± 0.15     |
| BNMM-1 | 110 ± 10      | 260 ± 18       | 4.7 ± 0.5      |  < 20           | 2.1 ± 0.25     |
| CVHR-2 | 130 ± 10      | 620 ± 50       | 10 ± 1.28      | 193 ± 18        | 1.5 ± 0.18     |
| BNMM-2 | 170 ± 20      | < 25           | 13 ± 1.08      |  < 20           | 1.8 ± 0.26     |
| CVHR-3 | < 25          | 2.5 ± 0.23     | < 20           | 6.2 ± 0.42      |  < 20          |
| BNMM-3 | 60 ± 8        | < 25           | 10.2 ± 0.94    |  < 20           | 3.1 ± 0.35     |
| CVHR-4 | 2440 ± 210    | 4160 ± 398     | 3.6 ± 0.32     | 429 ± 40        | 2.3 ± 0.27     |
| BNMM-4 | < 20          | 300 ± 34       | 9.7 ± 0.77     |  < 20           | 1.5 ± 0.16     |
| CVHR-5 | < 20          | 290 ± 30       | 6.8 ± 0.7      | 71 ± 10         |  < 15          |
| BNMM-5 | 21 ± 2        | 40 ± 3         | 5.5 ± 0.48     | < 20            | < 20           |
| CVHR-6 | 410 ± 60      | 1080 ± 120     | 10.4 ± 1.23    | 169 ± 15        |  < 15          |
| BNMM-6 | 490 ± 50      | 120 ± 10       | 2.6 ± 0.19     | 43 ± 4          | < 15           |
| CVHR-7 | 40 ± 4        | 740 ± 50       | 7.6 ± 0.9      | 105 ± 8         |  < 15          |
| BNMM-7 | 70 ± 8        |  < 0.3         |  < 20          | 7.3 ± 0.49      | < 20           |
| CVHR-8 | < 20          | 2920 ± 240     | 81 ± 6         | 23 ± 2          | 18 ± 2         |
| BNMM-8 | 120 ± 14      | 8.4 ± 0.63     |  < 20          |  < 20           |  < 20          |
| CVHR-9 | 280 ± 10      | 650 ± 60       | 9.1 ± 1.2      | 137 ± 14        |  < 15          |
| BNMM-9 | < 25          | 1.4 ± 0.13     | < 20           | 7.3 ± 0.49      | < 20           |
| CVHR-11| 190 ± 20      | 50 ± 3         | 16.3 ± 1.52    | < 20            | 2.3 ± 0.27     |
| BNMM-10| 110 ± 10      | 10.3 ± 0.98    | < 20           | < 20            | 2.1 ± 0.25     |
| CVHR-12| 570 ± 53      | 480 ± 50       | 5.6 ± 0.53     | 47 ± 4          | < 15           |
| BNMM-11| 2430 ± 220    | 3080 ± 270     | 15 ± 1.3       | 189 ± 17        | < 15           |
| CVHR-13| 300 ± 40      | 530 ± 40       | 13.4 ± 1.42    | 135 ± 12        | < 15           |
| BNMM-12| < 20          | 130 ± 10       | 20.6 ± 2.12    |  < 20           | < 20           |
| CVHR-14| 1410 ± 120    | 220 ± 20       | 7 ± 0.86       | 45 ± 5          | < 15           |
| BNMM-13| 100 ± 13      | < 25           | 39.6 ± 4.1     | < 20            | < 20           |
| CVHR-15| 80 ± 9        | 610 ± 50       | 23.3 ± 2.9     | < 20            | < 15           |
| BNMM-14| < 20          | < 25           | 10.5 ± 1.18    | < 20            | < 20           |
| CVHR-16| 22 ± 1        | 60 ± 4         | 22.4 ± 2.4     | < 20            | < 20           |
| BNMM-15| 4100 ± 386    | 1830 ± 200     | 9 ± 1.03       | 614 ± 78        | < 15           |
| CVHR-18| 70 ± 6        | 0.9 ± 0.08     | < 20           | 1.4 ± 0.11      | 769 ± 68       |
| BNMM-17| 4100 ± 340    | 1880 ± 160     | 1.7 ± 0.21     | 669 ± 64        | < 15           |
| CVHR-19| 70 ± 9        | 80 ± 7         | 1.6 ± 0.2      | 22 ± 2          | < 20           |
| BNMM-18| 3830 ± 300    | 3870 ± 400     | 50.1 ± 5.77    | 255 ± 30        | < 15           |
| CVHR-20| 40 ± 5        | 560 ± 60       | 1.2 ± 0.11     | 85 ± 9          | < 20           |
| BNMM-19| 120 ± 10      | 160 ± 14       | 7.3 ± 0.6      |  < 20           | 2.9 ± 0.35     |
| CVHR-21| 22 ± 1        | 60 ± 4         | 22.4 ± 2.4     | < 20            | < 20           |
| BNMM-20| 2560 ± 290    | 4780 ± 440     | 1.4 ± 0.1      | 541 ± 49        | < 15           |
| CVHR-23| 240 ± 18      | 180 ± 20       | 1.1 ± 0.12     | 61 ± 5          | < 15           |
| BNMM-22| 7530 ± 658    | 2050 ± 170     | 3.7 ± 0.49     | 1154 ± 112      | < 15           |
| CVHR-24| 120 ± 10      | 220 ± 17       | 6.7 ± 0.57     | 36 ± 4          | < 15           |
| BNMM-23| 1110 ± 136    | < 25           | 4.1 ± 0.33     | < 20            | < 20           |
| CVHR-25| < 20          | 290 ± 20       | 8.5 ± 0.7      | < 20            | < 15           |
| BNMM-24| 540 ± 50      | 1010 ± 80      | < 0.3          | < 20            | < 15           |
| CVHR-26| < 20          | 290 ± 20       | 8.5 ± 0.7      | < 20            | < 15           |
| BNMM-25| 40 ± 6        | < 25           | 5 ± 0.46       | < 20            | < 20           |
are presented in Table 3. Significant positive correlations can be observed between specific activities and salinity, with a correlation coefficient of $R = 0.62$ for $\alpha$ and $R = 0.59$ for $\beta$ and $^{226}\text{Ra}$, considering a confidence interval of $\alpha = 0.01$. Other authors have previously observed such relationships between salinity and dissolved radium [19, 20], which could imply ion-exchange dynamics. As salinity and conductivity are related (both measures being increased by dissolved ions), the positive correlations between gross alpha, beta as well as radium activities and conductivity are expected ($R = 0.60$ for $\alpha$; 0.57 for $\beta$; 0.59 for $^{226}\text{Ra}$, $\alpha = 0.01$). Another positive correlation can be established between specific activities and TDS ($R = 0.63$ for $\alpha$ and $R = 0.59$ for $\beta$ and $^{226}\text{Ra}$, $\alpha = 0.01$). In literature, [32] also noticed positive correlations between TDS and uranium, as well as [27], who found similar relationships for $^{226}\text{Ra}$ and $^{228}\text{Ra}$. TDS, salinity and conductivity have similar $R$ values when correlated to gross alpha, beta and radium activities, which is the result of the strong correlations between these parameters alone. Additionally, no correlations could be settled between the activity of the samples and temperature, pH or oxidation–reduction potential, implying that these parameters do not affect radionuclide concentrations in water.

For a better representation and understanding of the activity values, the frequency distributions of gross alpha and beta specific activities were analyzed (Fig. 6). First, an initial distribution revealed that the highest number of cases are contained in the first class interval (between 0 and 1000 mBq L$^{-1}$) for both alpha and beta activities, representing 77% of gross alpha, respectively 71% of gross beta.
Fig. 4 $^{226}$Ra specific activity values of the examined water samples in distinction to national and international guidance level.

Fig. 5 Annual effective doses (AED) attributed to $^{226}$Ra activities, in distinction to the reference dose established by Romanian law 301/2015.
values from the total set of samples (Fig. 6, panels A and C). The higher class intervals showed a reduced frequency. Considering this observation, further statistical analyses were performed for an in-depth look at this specific class interval. As such, a second frequency distribution performed on the values in the 0–1000 mBq L⁻¹ interval highlighted that the highest number of cases are present in the 0–100 mBq L⁻¹ range, with 46% of the total samples for gross alpha activities, respectively 29% of the gross beta activities (Fig. 6, panels C and D) being contained in it. From the frequency distributions presented, it can be concluded that both gross alpha and beta activities are falling mostly in the low activity class intervals, and the cases are exponentially decreasing with activity.

For an enhanced visual representation of the specific activity data, a spatial distribution map was constructed, displaying the location of the samples and their corresponding gross alpha, beta and ²²⁶Ra activity values (Fig. 7). It can be observed that Bistrița-Năsăud (BN) county hosts the highest activity samples for all three parameters, clustered in a “hotspot” area, near Sângëorz-Băi town. The highlighted area includes the samples labeled BNMM 15–20, and 22, which are among the highest activity samples in the dataset, and are also exceeding the guidance levels set by national legislation. An explanation for the cluster formation is that the springs are closely located and similar in water physicochemical parameters values, and thus could be sourced from the same underground aquifer. In contrast, the other studied areas generally showed low specific activities, with sporadically occurrences of higher concentration values and no distinguishable patterns or hotspots.

Furthermore, a comparison between the results obtained in the present study for gross alpha and beta activities and the results of other similar studies in literature has been performed (Table 4). It can be observed that, except for [2], in Jordan, the present study has higher mean values for the gross alpha/beta activities, as well as maximum values, in comparison to the other studies cited. The difference in values between the results of [28] in Galați county, Romania, and the results of the present work could be explained by the

| Table 3 Pearson’s correlations between water parameters and gross alpha, beta, and ²²⁶Ra specific activities of the samples |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Λ Σ α            | Λ Σ β          | Λ ²²⁶Ra | T      | pH     | ORP   | Conductivity | TDS  | Salinity |
| Λ Σ α          | 1.00             | 0.68           | 0.91    | −0.004 | 0.07   | −0.06 | 0.60          | 0.63  | 0.62     |
| Λ Σ β          | 1.00             | 0.52           | −0.03   | 0.14   | −0.13  | 0.57  | 0.59          | 0.59  | 0.59     |
| Λ ²²⁶Ra        | 1.00             | −0.02          | 0.14    | −0.12  | 0.59   | 0.59  | 0.59          | 0.59  | 0.59     |
| T              | 1.00             | 0.60           | 0.57    | 0.59   | 0.59   | 0.59  | 0.59          | 0.59  | 0.59     |
| pH             | 0.60             | 0.14           | −0.03   | 0.14   | −0.12  | 0.59  | 0.59          | 0.59  | 0.59     |
| ORP            | 1.00             | 0.22           | 0.24    | 0.24   | 0.26   | 0.26  | 0.26          | 0.26  | 0.26     |
| Conductivity   | 0.57             | 0.22           | 0.24    | 0.24   | 0.26   | 0.26  | 0.26          | 0.26  | 0.26     |
| TDS            | 0.59             | 0.59           | 0.59    | 0.59   | 0.59   | 0.59  | 0.59          | 0.59  | 0.59     |
| Salinity       | 0.59             | 0.59           | 0.59    | 0.59   | 0.59   | 0.59  | 0.59          | 0.59  | 0.59     |

Highlighted in italics—relevant correlations for α = 0.01 confidence interval

![Fig. 6 Frequency distribution of gross alpha and beta specific activities Panel (a) represents the gross alpha frequency distribution for the whole set of samples; panel (b) represents a focused gross alpha frequency distribution on the 0–1000 mBq L⁻¹ interval; panel (c) represents the gross beta frequency distribution for the whole set of samples; panel (d) represents a focused gross beta frequency distribution on the 0–1000 mBq L⁻¹ interval](image-url)
The Neogene volcanic mountain ranges that are located close to the study site could influence the values and lead to higher activities, as radioactivity concentration in soil is relatively higher in areas with volcanic rocks [35]. Beside geology, the high specific activity cluster located in Bistrița-Năsăud county has considerably raised the mean values for both gross alpha and beta, as well as the maximum values.

**Conclusions**

Sixty-four carbonated water samples collected from natural springs were analysed from a radiological perspective, in order to evaluate their compliance with national [21] and international [38] guidance levels for radioactivity in drinking water. Initial gross alpha and beta specific activity measurements revealed that for alpha activities,
26.7% of the samples exceeded the WHO, 2017 guidance level of 500 mBq L\(^{-1}\), and 53.5% exceeded the Romanian law threshold of 100 mBq L\(^{-1}\). Gross beta common which one was above 1000 mBq L\(^{-1}\) (WHO recommended 0–1000 mBq L\(^{-1}\)), and the frequency decreases exponentially with activity. \(^{226}\)Ra activity values exceeded the national guideline level by five samples (500 mBq L\(^{-1}\)), of which one was above 1000 mBq L\(^{-1}\) (WHO recommended value). The highest values from the dataset for gross alpha, beta and radium-226 are concentrated in a hotspot area composed of 7 samples, in Bistrița-Năsăud county. Polonium-210 specific activities were low and did not exceed the guidance levels. After calculating the Annual Effective Dose (AED) attributable to radium-226, five samples had a value above the reference dose of 0.1 mSv yr\(^{-1}\). The mean and maximum values for specific activities for gross alpha/beta were generally higher than those found in other studies, which could be attributed to the presence of volcanic rocks in the study area, and the post-volcanic emanations associated with the adjacent Neogene volcanic range. The guidance levels, the dose coefficients and the AED calculations performed considered a water consumption rate of 2L/day for the investigated spring waters. Daily consumption from springs exceeding guidance levels should be avoided, and not used as a primary source of drinking water. Being the first investigation performed on the post-volcanic region of Romania, and one of the few conducted in the country, the present work reveals an insight regarding the quality and radiological properties of the natural mineral water sources in this region. By assessing the compliance of the specific activity values of the samples with the recommendations contained in international and national guidelines, the present study provides useful information regarding public health safety. The high percentage of samples exceeding the recommended values for the investigated parameters highlights the importance of studying potable natural water from a radiological perspective.

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