

ASSESSMENT OF CHEMICAL PARAMETERS AND NATURAL RADIONUCLIDES CONCENTRATIONS IN CARBONATED NATURAL MINERAL WATER AND CONTRIBUTION TO RADIATION DOSE

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Abstract. This study has great importance for assuring the quality of natural mineral waters especially regarding the radioactivity concentration: highlighted in the Council Directive 2009/54/EC of June 2009 and Council Directive 2013/51/Euratom of October 2013 on the exploitation and marketing of natural mineral waters, laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption. Seasonal influence over the chemical composition due to long period of water sample collection was studied regarding the major-ion composition and possible rain infiltrations. In this regard, strong correlations were found between Ca^{2+} , Mg^{2+} and HCO_3^- content for the present sample collection. The activity concentrations of gross alpha and gross beta, of ^{40}K and from natural decay chains of ^{238}U , ^{232}Th were determined, as well as the associated effective dose for these radionuclides. The results obtained for the effective doses calculated for an adult member in Romania, derived from the intake of naturally occurring radionuclides in water vary between: 1.24–2.08 ($\mu\text{Sv}/\text{yr}$) for ^{40}K ; 0.90–3.45 for ^{238}U ; 1.00–7.21 ($\mu\text{Sv}/\text{yr}$) for ^{232}Th and 11.24–46.00 ($\mu\text{Sv}/\text{yr}$) for ^{226}Ra . The obtained values are below the *World Health Organization* (WHO) and *United Nations Scientific Committee on the Effects of Atomic Radiation* (UNSCEAR) recommended reference levels.

Key words: Natural mineral water, Ground water, Radioactivity, Gross- α and Gross- β radioactivity, Effective dose, Major ion composition.

1. INTRODUCTION

Mineral water, as microbiologically pure water with a constant chemical composition, represents a source of intake of trace elements for human beings, with about 1000 recognized brands marketed in the European Union (EC, 2013) [1]. The European Community directives emphasize that bottled mineral water must be groundwater and clearly distinguishable from the ordinary drinking water ‘by its nature, which is characterized by its mineral content and by its original purity’ (EU, 1980, 1996; EC 2003, 2009, FAO 1981) [2–5]. According to EU Directive

80/777/EEC [6], natural mineral waters are defined as uncontaminated waters from underground aquifers, bottled without any treatments other than removal of the unstable components (iron, sulfur, manganese, and arsenic) and re-introduction of carbon dioxide. The chemical composition of mineral waters is a result of the chemical processes in natural conditions. During the long contact between the rocks and the water, the chemical composition of the mineral waters is determined by the mineralogical composition of the rocks. The chemical composition of the water will depend on the residence time of the water and the kinetics of the mineral phases. Temperature, CO₂ concentration, redox conditions and the type of adsorption complex further determine the chemistry of the mineral water [7].

The paper presents the activity concentrations of ²³⁸U, ²³²Th, ²²⁶Ra and also for ⁴⁰K in a carbonated Romanian natural mineral water. An assessment of the annual effective doses received from these radionuclides is made. Moreover, the gross α and β activities in waters were measured for screening purposes. According to *World Health Organization* (WHO, 1996, 2011) guidelines [8, 9], the recommended screening levels for drinking water below which no further action is required, are 0.1 Bq/L for gross alpha activity and 1 Bq/L for gross beta activity. Determination of naturally occurring radionuclides in ground water is useful as a direct input to environmental and public health studies. Considering the high radiotoxicity of ²²⁶Ra, its presence in water and the associated health risk requires particular attention. The authors took also into consideration the legislation on radioactive isotopes for drinking water (EU, 2013) [2] when calculating the total effective dose.

The natural mineral water analyzed in this study belongs sources of carbonated ground water from the northern part of Romania, with samples being collected over a two-and-a-half-year period. The water originates in volcanic aquifers containing calcite, dolomite and traces of quartz, muscovite and paragneiss rocks. Analyzed samples were from commercial bottling operations. Correlations between the major ion compositions and seasonal changes were possible using the date of production encrypted on each analyzed sample. These were all slightly acidic (pH ~ 6.1) because of the dissolved carbon dioxide.

Studies on the geochemistry of natural mineral waters have been developed in order to study the weathering of the rocks in correlation with the geochemical cycles. The rocks contribution to ground water composition is dependent on in-depth volatile release. In recent studies the dissolution kinetics of carbonates were based on surface complexation. These were built on previous equilibrium and kinetic models, allowing the discrimination of reactive sites on the mineral surfaces. In the dolomite's case, the rock dissolution is high, the dissolution of –Mg-OH reactive surface site being identified as the rate limiting step in mineral dissolution. Mg-bearing carbonates can retain formation stability in the presence of CO₂, while minor amounts of calcite provide a source of HCO₃⁻ to buffer the pH of the water. However, the contribution of the rocks dissolution to the groundwater relative ionic composition is considered limited, even if HCO₃⁻ and CO₃²⁻ are dominant due to the presence of CO₂ both in soil and in the rain water. The purpose

of this study is also to evaluate possible seasonal variability of the chemical and radiochemical compositions of the aquifer geochemistry, even though the low permeability of the aquifer leads to reduced local rain water infiltration. The results showed good chemical stability, the variation was within a range of 10%, between the maximum and the minimum values.

2. MATERIALS AND METHODS

2.1. SAMPLE COLLECTION AND PREPARATION FOR PHYSICAL-CHEMICAL CHARACTERIZATION

The data set on the major ion composition of carbonated natural mineral waters consisted of 30 samples (finished products of the same source). These samples were commercial ones, bought from the supermarket, every month during two-and-a-half-year. Results were obtained over two-and-a-half-year, from spring to winter, meaning that seasonal correlations can be done, based on the measurements.

From bottles opened in the laboratory, 50 mL beakers were filled with mineral water and the pH and the electrical conductivity were measured. The HCO_3^- concentration was measured immediately after opening the bottles. Samples were filtered on 0.45 μm cellulose membrane filters and were analyzed by standardized methods of ion chromatography. Fluoride was measured using ion-selective electrodes method previously developed in our group. Specific electric conductivity (EN 27888:1993-11) and pH (DIN 38404-5:1984-01, C5) were immediately analyzed after opening the bottles. The analytical methods use were IC standardized SR EN ISO 10304-1: 2009 and SR EN ISO 14911:1999. The instrument was calibrated weekly using external standards.

All bottles were soaked in Milli-Q water, placed in an ultrasonic bath and rinsed three times with Milli-Q water before use. An aliquot (20 mL) of the samples was transferred into propylene vials and degassed for 30 minutes before analysis. A regression fit value of over 0.995 was obtained for each element. Preparation and analysis of samples, standards and blanks were carried out in triplicate. The method detection limit (MDL) for the anions was calculated three times the standard deviation of the signal of the blank sample analyzed 10 times. Depending on their characteristics the mineral water samples were differently treated before analysis [10].

2.2. INSTRUMENTATION AND CHEMICAL REAGENTS

In order to perform chemical measurements the following instruments and methods were used: Ion chromatograph – 850 Professional IC AnCat-MCS using *Metrohm intelligent Partial Loop* (MiPT) technique with conductivity detector; anion and cation separation columns Metrosep ASUP 5 and C4-250/4.0; anion suppressor device SMARTPACK anion self – regenerating suppressor with external

ultrapure water source; 850 Professional conductivity detector (0–15000 $\mu\text{S}/\text{cm}$); professional sample processor; Metrohm patented Dosino technology. The materials used were: reagent water – *ultrapure water* (UPW) from Millipore Direct Q3 with UV lamp: resistivity $>18.2 \text{ M}\Omega \times \text{cm}$ (25°C); flow = 0.5 L/min; total organic carbon TOC < 5 ppb; particles not larger than 0.22 μm ; eluent solution: 3.2 mM Na_2CO_3 solution and 1.0 mM NaHCO_3 and cation eluent 2.5 mM HNO_3 ; Suppressor regeneration and rinsing solution: *Metrohm suppressor module* (MSM) for chemical suppression during anion analysis using 100 mM H_2SO_4 in *ultrapure water* (UPW) with resistivity $> 18.2 \text{ M}\Omega \times \text{cm}$ (25°C) and *Metrohm CO₂ suppressor* (MCS). Stock standard ion solutions: 1000 mg/L are purchased as certified solutions, or prepared from ACS 70 reagent grade, potassium or sodium, or other carbonate salts.

2.3. SAMPLE COLLECTION AND PREPARATION FOR RADIOMETRIC MEASUREMENTS

The radiometric measurements were focused and 30 frequently visited and regularly consumed natural mineral waters sample have been measured from the northern part region from one source of carbonated water (Figure 1). The activity concentrations of various radionuclides were analyzed monthly in samples of water for the mentioned time interval. More than 5 L were collected and used for analyses for each water sample. For the alpha, beta and gamma spectrometry analyses a fixed quantity of 5 L of water was used, that was subject to an evaporation process at the temperature of 80°C . The total solid residue obtained after evaporation has values between 0.92–1.50 g/L. For gross alpha and gross beta analysis a smaller portion of the resulting residue was used with mass between 0.5–1.2 g for *up alpha – beta* working geometry and for gamma spectrometry was used the entire mass of the resulting residue [11]. Both systems for gross alpha-beta measurements and gamma spectrometry were calibrated for various working geometries.

2.4. INSTRUMENTS FOR RADIOMETRIC MEASUREMENTS

Gross alpha–beta measurements were performed using the low background system PROTEAN ORTEC MPC-2000-DP, with a scintillation radiation detector ZnS dual detector phosphor. The calibration of the acquisition system was done using sets of standard radioactive sources manufactured by Radionuclide Metrology Laboratory (LMR IFIN-HH), such as ^{241}Am -alpha source ($T_{1/2} = 432.6 \pm 0.60$ years) and ^{90}Sr -Y – beta source ($T_{1/2} = 28.80 \pm 0.07$ years).

The working geometry was fixed in metallic trays, inside the lead castle system, directly facing the probe-detector. For the measurement geometry *UP ALPHA + BETA* manual count the metallic tray is at 3 mm below the probe-detector [11–14]. To ensure accurate measurements, it is necessary to determine both detector efficiency and crosstalk as a function of sample mass-geometry used. Efficiency determination

as a function of sample mass-geometry is equivalent to determining a zero-mass efficiency with an associated self-absorption factor. The samples were measured in 10 intervals of 100 minutes, the total acquisition time being 16.7 hours.

In addition, a measurement with empty metallic tray for used geometries was performed to establish the background count rate. A low background coaxial HPGe detector (model GEM 25P4, Ortec Inc., Easley, SC, USA) with a relative efficiency of 35% and energy resolution of 1.73 keV at 1332.5 keV for ^{60}Co was used to determine the activity concentrations of the ^{40}K , ^{238}U , ^{232}Th and their progenies. The detector was linked to a DigiDART Ortec data acquisition system and to a Gamma Vision spectrum analysing software tool. The calibration of the detector for energy, peak shape and efficiency was carried out using certified volume source for: ^{60}Co , ^{134}Cs , ^{137}Cs , ^{152}Eu and ^{241}Am , supplied by the institute's radiation metrology laboratory. These radioisotopes cover a relatively wide energy range from 59.54 keV for ^{241}Am to 1408.00 keV for ^{152}Eu [11–15]. A 10-cm thickness lead shielding and 2 mm of copper lining was built around the detector to diminish the contribution of environmental radioactivity to its background.

For the total annual effective dose calculation (D_{EFF}) relation 1 was used:

$$D_{EFF} = \sum_i [C_i(\text{Bq} / \text{L}) \times K(\text{L} / \text{yr}) \times F_i(\mu\text{Sv} / \text{Bq})] \quad (1)$$

where: D_{EFF} is the annual effective ingestion dose due to relevant radionuclide in $\mu\text{Sv}/\text{yr}$, C_i is radionuclide activity concentration in the water sample in Bq/L , K is the annual consumption rate (of 150 L/yr for infants, 350 L/yr for children and 500 L/yr for adults, respectively), according to the IAEA, WHO and UNSCEAR (WHO 1996, 2011; UNSCEAR 2000; IAEA 1996, 2011) [8, 9, 16–18] F_i is the dose coefficient (conversion factors: 2.8×10^{-7} , 2.3×10^{-7} , 4.5×10^{-8} and 6.2×10^{-9} Sv/Bq for ^{226}Ra , ^{232}Th , ^{238}U and ^{40}K of the relevant radionuclide).

However, the present study took into consideration an average consumption of 365 L/year of mineral water considering that the rest of 135L/year of water was tap water, for an adult (UNSCEAR 20000) [16].

3. RESULTS AND DISCUSSION

3.1. CHEMICAL ANALYSIS RESULTS

The study was conducted based on the chemical and radio-chemical analysis of bottled samples of natural mineral waters in an area with certain geo-chemical properties.

The original geological description of the source of the mineral water consisted of dolomite and calcite containing traces of quartz, muscovite, biotite, goethite and limonite. For the water samples, the concentration of eight main ions (Cl^- , SO_4^{2-} , HCO_3^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , NO_3^- , O_2 Diss., CO_2 free, and Dry rez.), pH, and electrical conductivity, were determined as a compositional fingerprint characteristic to the local geology and to the position of the aquifer (Table 1).

In the aquifer, the thermodynamic equilibrium between the underground water and the rocks consisted in the dilution of the water from the upper part of the aquifer and the salvation of the boreholes walls:

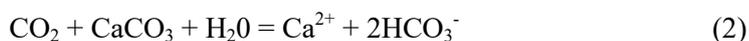
Table 1

Mineral waters chemical data: mean values of pH, electrical conductivity and major ion composition

Sample/Code	Mineral waters chemical data	Min	Max	Mean
Samples SW1 – SW30	pH	5.87	6.17	6.04
	C.e. (μS/cm)	1567	1883	1743.6
	Cl ⁻ (mg/L)	1	7.4	4.98
	SO ₄ ²⁻ (mg/L)	7	24.3	12.37
	HCO ₃ ⁻ (mg/L)	1311.7	1355	1326.96
	Na ⁺ (mg/L)	2.9	6.4	4.72
	K ⁺ (mg/L)	1.4	3.4	2.30
	Ca ²⁺ (mg/L)	253	311	287.82
	Mg ²⁺ (mg/L)	73	85	77.23
	F ⁻ (mg/L)	0.08	0.22	0.16
	O ₂ Diss.	2.43	10.53	9.29
	CO ₂ free	3.3	4.4	3.67
	NO ₃ ⁻ (mg/L)	0.1	3.95	2.71
Dry rez. (mg/L)	158	191	173.33	

In this natural mineral water the main ions are: Ca²⁺, Mg²⁺ and HCO₃⁻. The mineral water presented in this study (Figure 1) had relatively high mineralization as shown by the electrical conductivity measurements ranging from 1567 to 1883 μS/cm with an average of 1743.6 μS/cm. High values were registered at the end of summer, being probably a result of the dry summer period in the mountain area where the studied springs were located. Water is slightly acidic, with a pH range between 5.85 and 6.17 with an average of 6.04, lower values being registered during autumn, but the range of variation was very narrow. The pH varies in the range 5.87–6.17, the waters having slightly acidic character. The main control of the pH of natural waters is given by the carbonate system and generally is considered that CO₂-rich waters are slightly acidic.

The dissolution of primary minerals is limited and the carbonation of water may lower the pH by 1–2 units transforming the CO₂ in HCO₃⁻. The CO₂ dissolved in water exists primarily as three different ions, carbonic acid, bicarbonate ions and carbonate ions. In the studied water, both dissolved CO₂ and H₂S have mophetic provenience. In contact with calcite, this will be dissolved and if CO₂ is considered in equilibrium, this will be described by the following equation:



The groundwater composition is dominated by HCO₃⁻, as well as by Ca²⁺ and Mg²⁺, reflected by the values of the electrical conductivity. The studied natural carbonated mineral waters are Ca-Mg-HCO₃⁻ ones, the correlation between the HCO₃⁻ (mg/L) vs. conductivity plot for the dataset depicting the contribution of HCO₃⁻ to groundwater chemistry.

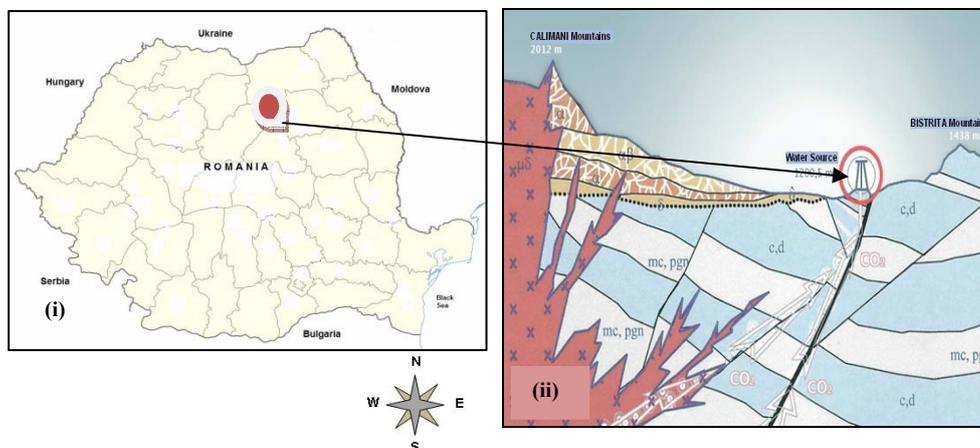


Fig. 1 – (i) Investigated test area on Romania's map; (ii) Geological map for the water source with flows of andesitic pyroclastics (α), basalt (β), dacite (δ), microdiorite intrusions ($\mu\delta$), dolomite limestone (magnesium) (c, d), micaschists and paragneisses (mc, pgn). (Modified figure from the manufacturer web-site (<http://www...ro/#/ro/tara-izvoarelor/hidrogeologie>, 2016).

The values of the electrical conductivities of this mineral water are high (Figure 2). The total ionic strength is high because of the hydro-geochemical dissolution in the presence of HCO_3^- ions. The widespread of the conductivity values were due to the small seasonal variability of this mineral water and had a slight increase during time. The small contribution of Cl^- and Na^+ to the ionic content of the groundwater is reflected by the no correlation between their concentrations and the electrical conductivity (Figure 3). These results suggest the insignificant contribution of NaCl salts and of the rainwater chemistry control over the spring, because of the efficient caption of the source. The chloride and sodium concentration ranges are smaller in comparison with other mineral water from the same geological area, suggesting their possible use in low sodium diets for adults. It is well known that a high intake of Na is detrimental for human health, increasing the incidents of heart diseases. The studied bottled mineral carbonated water was the Ca- HCO_3^- type, the dolomite dissolution being the main geochemical process in influencing the concentration of the Cl^- ions in the water.

The dependence between Cl^- and SO_4^{2-} shows that the composition of the samples was not much influenced by the presence of Cl^- ions (Figure 4). The regional hydrogeology data [10] indicated that the carbonate rock components contribution can be explained by the SO_4^{2-} enrichment by oxidation of reduced S species from volatile releases. Even if there were very small variations of the temperature at the depth where from the spring belongs, these variations can affect the $\text{Cl}^-/\text{SO}_4^{2-}$ distribution ratio. The main source of the sulfate ions present in the chemical composition of the studied water comes from the mophetic H_2S , the aquifer itself containing no sulfates in its geochemical composition. The important

spread of SO_4^{2-} concentrations indicates also possible connection to the seasonal temperatures. The alkali metals are randomly correlated with HCO_3^- (Fig. 5), the data depicting a large excess of HCO_3^- in relation with $\text{Na}^+ + \text{K}^+$, which does not depend on the season. The trend of the data suggests mineralization processes specific to carbonate rocks, but also it indicates that a part of the HCO_3^- is derived from the CO_2 in the soil.

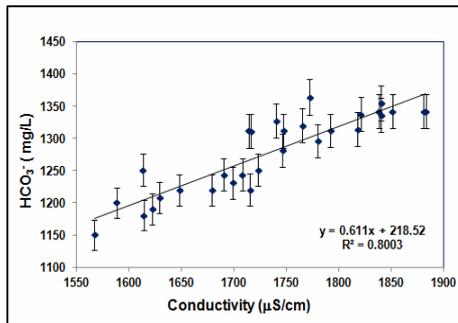


Fig. 2 – HCO_3^- (mg/L) vs. electrical conductivity ($\mu\text{S}/\text{cm}$) plot for the dataset.

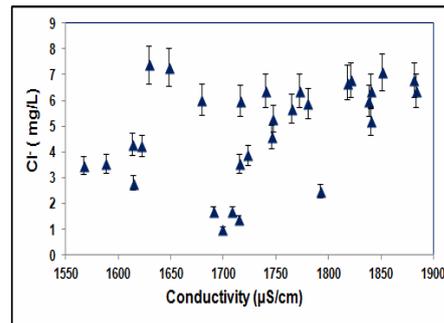


Fig. 3 – Cl^- (mg/L) vs. electrical conductivity ($\mu\text{S}/\text{cm}$) plot from the dataset.

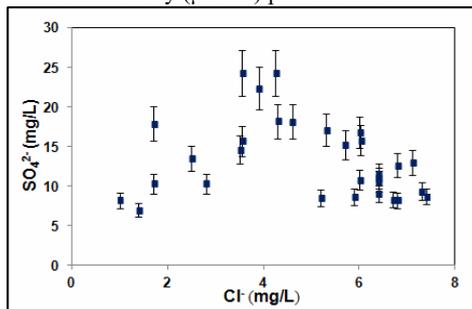


Fig. 4 – SO_4^{2-} (mg/L) vs. Cl^- (mg/L) plot from the data set.

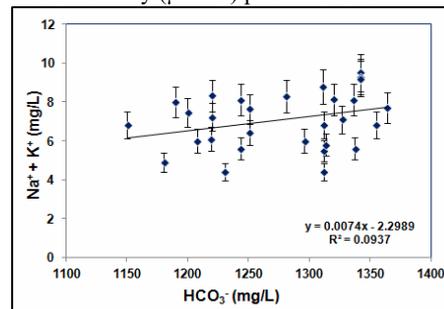


Fig. 5 – $\text{Na}^+ + \text{K}^+$ (mg/L) vs. HCO_3^- (mg/L) plot from the data set.

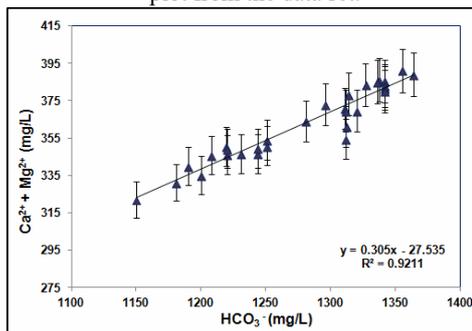


Fig. 6 – $\text{Ca}^{2+} + \text{Mg}^{2+}$ (mg/L) vs. HCO_3^- (mg/L) plot from the dataset.

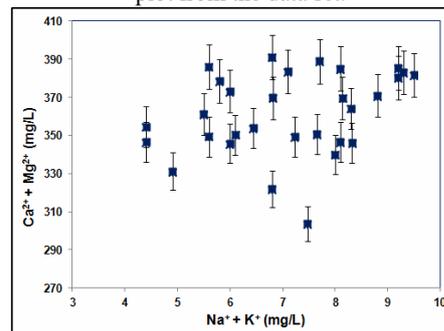
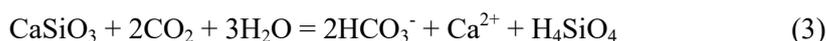


Fig. 7 – $\text{Ca}^{2+} + \text{Mg}^{2+}$ (mg/L) vs. $\text{Na}^+ + \text{K}^+$ (mg/L) plot from the dataset.

This assumption is based on the fact that carbonate-rich sedimentary rocks are by far the most common geogenic source of alkalinity of water [19]. The alkalis enrichment of the mineral water may be attributed to silicate weathering, which also contributes to HCO_3^- increased content. Rock weathering involves both silicate and carbonate minerals as represented by Eq. 2 and can be described by the following simplified reaction:



Thus HCO_3^- is derived from soil CO_2 [20]. The water will partially dissolve the carbonate rocks, consequently, high concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- are transferred to water chemical compositions. The relation between alkali-earth and HCO_3^- shows a linear dependence suggesting a basic rock aquifer reach in Ca^{2+} , Mg^{2+} and HCO_3^- species (Fig. 6). All the samples display Mg^{2+} contents above 10% of the cations, but the dominant one remains Ca^{2+} . The greater release rate of Ca^{2+} compared to Mg^{2+} is a function of the calcite component of the carbonates which would preferentially dissolve over dolomite [21].

A greater length of the Ca-O bond in comparison with the Mg-O one makes the release of Ca^{2+} energetically more favorable, this being more common in natural systems. The relation between alkali and alkali-earth metals depicts a scattered pattern, consistent with the high water mineralization (Fig. 7). The water of the spring has short residence time, involving a high water-rock ratio, with almost no effect of silicate hydrolysis. The concentrations of Na^+ and K^+ are lower than the Ca^{2+} and Mg^{2+} concentrations. The K^+ content was less than 2 % in all samples due to the weathering of silicate and to the high content of CO_2 of the water infiltrating into the aquifer [22]. The presence of Zn^{2+} ions in solution causing an elevated release rate of Ca^{2+} and a near identical release rate of Mg^{2+} . This specie is ranging between 0.02 mg L^{-1} and 0.05 mg L^{-1} in the studied mineral water and is altering the dissolution rate as well as the ratio of release of Ca^{2+} to Mg^{2+} . This seems to affect the application of rate constants of natural systems in comparison with the synthetic ones for a simplified aqueous chemistry [23, 24]. Based on the concentrations of the major anions and cations from the samples an attempt was made to show the Piper diagram, to provide the overall characterization of the water. In general, by using the Piper diagram the water can be classified into 6 fields: Ca- HCO_3 type, Na-Cl type, Ca-Mg-Cl type, Ca-Na- HCO_3 type, Ca-Cl type and Na- HCO_3 type. However, all points plot on top of each other, clearly showing the dominant Ca-Mg- HCO_3 nature of the studied water, but rendering the exercise of specifying individual point's more-or-less useless. The evaluation of the water types suggests a clear contribution from the weathering of carbonate rocks, the dolomite dissolution being the main geochemical process that influences the chemical composition. It can be seen that the studied natural mineral water show a small seasonal influences (less than 10%), which confirms a good caption and no infiltrations.

3.2. RADIOMETRIC ANALYSIS RESULTS

All mineral natural water produced in Bucovina region have been examined from the radiometric point of view. The activity concentrations for gross-alpha, gross-beta and annual effective doses are presented in Table 2. Radiochemical characterization of 30 spring waters was performed. It can be established these range between 1.03 mBq/L to 5.50 mBq/L for gross-alpha, and 15.9 mBq/L to 31.40 mBq/L for gross-beta activities. Although the measured data belong to samples from one source, one can observe variation of the alpha-beta activities; however these activities are within the same order of magnitude. These variations could be due to contribution of different features of geological formations of Eastern Carpathian Mountains. Geological formations that make up the region are constituted of ancient rocks (proterozoic) and newer rocks (neogene). Crystalline old rocks were formed through multiple transformations (poly-metamorphism) of some sedimentary rocks (sandstone, limestone, marl, clay) or igneous rocks (basalt, granite, volcanic tuffs) and are now represented by quartz, micaschiste, limestone crystal, green schist, gneisses. The new rocks are the product of volcanic activity of Calimani Mountains: flows of andesitic pyroclastic breccias, dacitic intrusions, dioritic and microdioritic lava [25]. These characteristics of various rocks seem to affect the radionuclide content in samples, reflected in gross alpha-beta measurements but also ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra results presented in Tables 2–3. The data obtained from gross alpha-beta measurements can provide basic information for consumers and competent authorities regarding the internal exposure risk due to water intake.

It can possibly serve as a comparison when evaluating the dose contribution from artificial radionuclide's released to the environment as a result of any human practices and accidents in the studied area.

Table 2

The activity concentration for gross alpha, gross beta and annual effective dose of the natural mineral water samples

Sample/code	Mean Residue	Mean Gross α	Mean Gross β	Mean Annual Effective Dose/ D_{EFF}
	[g/L]	[mBq/L]		[$\mu\text{Sv}/\text{year}$]
SW1 ÷ SW9	0.9167	5.50 ± 0.70	21.40 ± 4.80	33.95
SW10 ÷ SW17	1.5022	2.40 ± 1.30	15.90 ± 5.40	47.38
SW18 ÷ SW25	1.1229	1.03 ± 0.16	31.40 ± 3.11	15.45
SW26 ÷ SW30	1.1296	4.56 ± 1.30	28.34 ± 7.70	41.23

Regarding the measured radionuclides in the analysed water samples, the total effective doses are in the range of: 15.45 – 47.38 $\mu\text{Sv}/\text{yr}$ with mean value of 33.95 $\mu\text{Sv}/\text{yr}$ (samples SW1–SW9); mean value of 47.38 $\mu\text{Sv}/\text{yr}$ (SW10–SW17);

mean value of 15.45 $\mu\text{Sv/yr}$ (SW18–SW25), and 41.23 $\mu\text{Sv/yr}$ (SW26–SW30) (see Table 2). All values are well below the reference level of the committed effective dose (100 $\mu\text{Sv/yr}$) recommended by the WHO (WHO 1996, 2011) [8, 9]. For more accurate dose evaluation, the doses from some other important alpha and beta emitters, such as radon should also be included.

Table 3 presents the activity concentrations of ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra in the residue of the water samples for the mentioned time interval. It can be observed, the activity concentration for ^{40}K is in the range of MDA – 0.92 Bq/L, for ^{238}U of 0.055–0.21 Bq/L, for ^{232}Th of MDA – 0.086 Bq/L and for ^{226}Ra of 0.11–0.45 Bq/L. Other reported values of ^{226}Ra activity concentrations in drinking water samples were up to 1.37 Bq/L in [26, 27], since for ^{238}U values up to 0.103 Bq/L were measured by.

Table 3

The activity concentrations of ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra in the residue of the water samples

Sample/code	Mean ^{40}K	Mean ^{238}U	Mean ^{232}Th	Mean ^{226}Ra
	[Bq/L]			
SW1 ÷ SW9	0.92 ± 0.11	0.055 ± 0.006	0.028 ± 0.003	0.28 ± 0.03
SW10 ÷ SW17	<0.83 (MDA)	0.084 ± 0.008	<0.28 (MDA)	0.45 ± 0.05
SW18 ÷ SW25	0.55 ± 0.06	0.12 ± 0.02	0.012 ± 0.002	0.11 ± 0.02
SW26 ÷ SW30	0.87 ± 0.08	0.21 ± 0.06	0.086 ± 0.010	0.280 ± 0.006
Mean ± 1 σ	0.79 ± 0.08	0.12 ± 0.02	0.100 ± 0.005	0.28 ± 0.03
Range [Bq/L]	MDA – 0.92 ± 0.11	0.055 ± 0.006 – 0.21 ± 0.06	MDA – 0.086 ± 0.010	0.11 ± 0.02 – 0.45 ± 0.05

MDA-Minimum Detectable Activity

From the scientific literature, the activity concentrations for the above radionuclides varies from few mBq/L or detection limit up to almost 1 Bq/L in case of ^{40}K , while for ^{238}U varies from low values of a few mBq/L or detection limit up to few hundreds of mBq/L [28–32].

Considering the amount of residue remaining after evaporation can be observed that ^{226}Ra activity slightly increases with increasing of the amount of residue, as expected (Tables 2–3).

In the case of ^{232}Th , there aren't many reference values reported in the scientific literature. Some reported values for ^{232}Th in natural mineral water are lower than our measured values. Table 4 shows the total effective doses per each years for an adult member from the Romanian public from in taking of naturally occurring radionuclides (^{40}K , ^{238}U , ^{232}Th and ^{226}Ra) in drinking water. The mean effective doses are: 1.24–2.08 ($\mu\text{Sv/yr}$) for ^{40}K ; 0.90–3.45 ($\mu\text{Sv/yr}$) for ^{238}U ; 1.00–7.21 ($\mu\text{Sv/yr}$) for ^{232}Th and 11.24–46.00 ($\mu\text{Sv/yr}$) for ^{226}Ra . The variation of activity concentrations of water samples analysed (Tables 2–3) seems to be influenced by multiple geological formations of the mountains area.

Table 4

Total effective doses for an adult member of the public in Bucovina-Romania resulting from intaking of naturally occurring alpha or beta radionuclide's in natural mineral water

Sample/code	Mean ⁴⁰ K	Mean ²³⁸ U	Mean ²³² Th	Mean ²²⁶ Ra
	[μSv/yr]			
SW1 ÷ SW9	2.08	0.90	2.35	28.62
SW10 ÷ SW17	nd	1.38	nd	46.00
SW18 ÷ SW25	1.24	1.97	1.00	11.24
SW26 ÷ SW30	1.96	3.45	7.21	28.61
Mean ± 1σ	1.76	1.93	3.52	28.62
Range [μSv/yr]	1.24–2.08	0.90–3.45	1.00–7.21	11.24–46.00

For the calculation of the total effective doses, per member of the public from Romania, an average consumption of 1 litre per day × 365 days, and the F_i coefficients (UNSCEAR 2000) [16] has been considered.

4. CONCLUSIONS

The manuscript reports a novel dataset on the radiochemical composition of mineral waters from Romania. The results of the major ion chemistry helped us to identify the trends of the chemical evolution in connection with seasonal variations. The evaluation of the studied mineral water shows good chemical stability oscillating around less than 10%. It was also observed that the low permeability of the aquifer allows a reduced infiltration of the rain water. In the aquifers containing carbonate rocks, the waters present higher concentrations of alkali-earth metals in correlation with HCO_3^- , which is less correlated with the reduced amounts of Na^+ and K^+ from these rocks. Variations of the concentrations of ⁴⁰K, ²³⁸U, ²³²Th and ²²⁶Ra from one site in the Bucovina area indicate that although the origins of these water samples are the same, they come from different depths and pass through different geological layers. The application of radiometric spectrometry methods for determination of radionuclide activity give valuable information concerning water transportation between surface, subsurface and deeply situated natural mineral water layers. At this stage of study a direct correlation cannot be made between contribution of different geological layers to the activity concentration of ⁴⁰K, ²³⁸U, ²³²Th and ²²⁶Ra in water. Longer time observations and correlations within a more complex study regarding the ⁴⁰K, ²³⁸U, ²³²Th and ²²⁶Ra content of the existing geological layers will emphasize this water transportation pathway. The natural radioactivity levels in the investigated natural mineral waters vary in a relatively broad range but within the same order of magnitude. The ²²⁶Ra radionuclide content varies from 0.11 Bq/L to about 0.45 Bq/L. The ²²⁶Ra radionuclide, with a half-life of 1630 years, can supply important scientific information concerning mechanisms and rates of water–rock interaction and transport of this element in aquifers. The ²³²Th isotopes content varies from 0.028 Bq/L to about 0.086 Bq/L, ⁴⁰K between 0.55–0.92 Bq/L and ²³⁸U between 0.055–0.21 Bq/L.

The results obtained are very well in agreement with those reported in many European countries. The natural mineral water was investigated with regard to the natural radionuclides activity concentration and their contribution to the annual effective dose. The total effective doses for an adult member of the public in Romania, resulting from the intake of naturally occurring alpha or beta radionuclides in natural water, are: 1.24–2.08 ($\mu\text{Sv}/\text{yr}$) for ^{40}K ; 0.90–3.45 ($\mu\text{Sv}/\text{yr}$) for ^{238}U ; 1.00–7.21 ($\mu\text{Sv}/\text{yr}$) for ^{232}Th and 11.24–46.00 ($\mu\text{Sv}/\text{yr}$) for ^{226}Ra . The mean annual effective doses for all the analysed drinking water samples are in the range of 15.45–47.38 $\mu\text{Sv}/\text{yr}$, all being well below the reference level of the committed effective dose (100 $\mu\text{Sv}/\text{yr}$) recommended by the WHO.

The surveillance of the natural mineral water and their springs is not a new subject, however, this has to be done continuously. Analyses performed on samples of mineral natural waters are consistent with the Directive 2009/54/EC of the European Parliament. The obtained data provide basic information for consumers and competent authorities, making them aware of the actual problem of the variation of the chemical composition and of the radiation.

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