# Radon and radium content of some cold and thermal aquifers from Bihor County (northwestern Romania)

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## ABSTRACT

In the present study, two of the major naturally occurring radionuclides ($^{226}$Ra and $^{222}$Rn) were analyzed in water samples from shallow, medium-depth, and deep geothermal aquifers, all of which are located in Bihor County, northwestern Romania. Here, the results of radon and radium measurements, performed from 2008 to 2009 in 50 locations, are reported. Radon proved to have a wide range of activity, with values from 4.5 to 110.8 Bq l$^{-1}$ for shallow aquifers, from 9.3 to 106.0 Bq l$^{-1}$ for medium-depth aquifers, and from 10.1 to 34.8 Bq l$^{-1}$ for deep geothermal aquifers. The shallow aquifers have lower radium concentrations (0.06 to 0.48 Bq l$^{-1}$), compared to medium-depth aquifers (0.1 to 0.52 Bq l$^{-1}$) and deep geothermal aquifers (0.27 to 1.8 Bq l$^{-1}$). The principal aim was a thorough investigation into the possible correlations between the occurrence of radon and radium in different aquifers and the hydrogeological, hydrogeochemical, and geothermal features of the area. Besides the direct link between the occurrence of uranium and thorium and the $^{226}$Ra and $^{222}$Rn contents in groundwater, the measurements we performed have allowed us to identify a secondary control on radionuclide distributions caused by the adsorption of dissolved radium onto clay minerals in exchange for sodium (for the sandy clay aquifer of Săcuieni), the high competition for adsorption sites in aquifers with high concentrations of dissolved calcium and magnesium (for the limestone dolomite aquifer of Oradea), and the role of thermal processes.

Key words: geology, geothermal waters, radioactivity, radionuclide migration

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## INTRODUCTION

The naturally occurring radionuclides, commonly found in surface- and groundwaters, belong to the uranium ($^{238}$U, $^{235}$U) and thorium ($^{232}$Th) decay series. Most attention has been focused on $^{226}$Ra (with a half-life of T$_{1/2}$ = 1600 years) and $^{222}$Rn (T$_{1/2}$ = 3.8 days), two of the daughter isotopes produced during the alpha decay of $^{230}$Th (T$_{1/2}$ = 75200 years) in $^{238}$U (T$_{1/2}$ = 4.468 × 10$^9$ years) decay series. Radon is frequently investigated in hydrogeological studies and used to identify buried uranium deposits (Ramola *et al*. 1989), for searching for hidden faults/thrusts (Etiope & Martinelli 2002; Ramola *et al*. 2008; González-Díez *et al*. 2009), as a tracer for the examination of groundwater inflows (Burnett *et al*. 2003; Kluge *et al*. 2007; Barragan *et al*. 2008), for better understanding of

the subsurface migration and behavior of non-aqueous-phase liquids (Schubert *et al*. 2002), and/or for investigating seismic activity (Yang *et al*. 2005; Einarsson *et al*. 2008). Radon and radium are also analyzed for radiation protection purposes (UNSCEAR 2000). High radon and radium concentrations occur in groundwater in many areas where this resource is used for domestic water supply. Geothermal waters are often used for heating (in dwellings, hospitals, schools, public buildings, churches, etc.), in agriculture (in greenhouse heating, or in cereals drying), for entertainment facilities (swimming pools), or for medical purposes (balneotherapy). The use and release of these waters to the environment may raise concerns regarding aquatic ecology and health risks for local residents (UNSCEAR 2000; Durand & Scott 2005). As a consequence, continuous monitoring of these radionuclides in

groundwater is of great interest, particularly to those who use these waters for domestic purposes.

The activity levels of dissolved radon and radium may vary over a wide range, depending on the specific environments. In surface waters such as lakes and rivers, radon concentrations are generally in the range of a few Bq $l^{-1}$ (Al-Masri & Blackburn 1999), while in groundwaters occurring in sedimentary rock aquifers, levels range from 1 to 50 Bq $l^{-1}$, having higher values (10–300 Bq $l^{-1}$) in deeper aquifers (Akerblom & Lindgren 1996; Hopke *et al.* 2000; Choubey *et al.* 2003; Somlai *et al.* 2007). Some geothermal waters have considerably higher radon levels; e.g., values up to 1868 Bq $l^{-1}$ were reported for some thermal springs used as spas in Spain (Ródenas *et al.* 2008). Generally, radium occurs at significant lower levels (0.0004–0.037 Bq $l^{-1}$) in surface waters, when compared to medium-depth aquifers (0.0185–0.926 Bq $l^{-1}$) or deep aquifers (up to 3.418 Bq $l^{-1}$) (Butler & Helena 1990). High radium levels were found in deep geothermal aquifers; e.g. ,values up to 3.66 Bq $l^{-1}$, or even 29.03 Bq $l^{-1}$, have been reported in some thermal springs from Spain (Ródenas *et al.* 2008), and in some geothermal wells (St. Mary-Louisiana) from the Gulf Coast of the USA (Kraemer 1986).

Radon and radium activities in groundwater are mainly controlled by the primary uranium and thorium contents of the aquifer systems (Butler & Helena 1990; Lauria *et al.* 2004; Added *et al.* 2005). The presence of high geothermal heat flow areas and the hydrogeochemical characteristics of the aquifers may also play a role in the distribution of the above-mentioned elements (Vinson *et al.* 2009). However, the mechanisms of this control are not fully understood. According to some studies, radium mobility may be influenced by chemical parameters, including pH (Szabo *et al.* 2005), salinity (Sturchio *et al.* 2001), redox conditions (Szabo & Zapecza 1987; Vinson *et al.* 2009), and major dissolved ions such as chloride, sulfate, and carbonate that can react with radium by forming weak complexes (Onishchenko *et al.* 2010).

In this study, the results of radon and radium measurements, performed from 2008 to 2009 in 50 locations in Bihor County, Romania, are reported. The analyzed water samples come from domestic wells (shallow aquifers of 2–20 m in depth), tap and spring waters (medium-depth aquifers of 100–200 m in depth), which are the main source of drinking water in the area. Geothermal waters, originating from deep aquifers (1400–3200 m in depth), were also analyzed. Besides the correlation between the radon and radium concentrations and the presence of uranium-reach formations, in this study the correlations between the occurrence of the two radionuclides and the hydrodynamical, geological, hydrogeochemical features of the aquifers and the presence of high geothermal heat flow areas were also investigated. As such, this study aims at contributing to knowledge of secondary control mechanisms on radon and radium activities in groundwater.

## STUDY AREA

### Geological setting

The study area is comprised of two geotectonic units: (i) the eastern margin of the Pannonian Basin, and (ii) the western segment of the North Apuseni Mountains (Fig. 1).

*The Pannonian Basin*
In the investigated area, the 'basement' of the Pannonian Basin consists of pre-Cambrian/Paleozoic metamorphic rocks, covered by the sedimentary sequences of the Bihor Unit, Triassic, Jurassic, and Cretaceous in age. The sedimentary fill of the Pannonian Basin includes some Miocene and Pliocene units of predominantly terrigenous deposits (Săndulescu 1984). The main rock types of the crystalline basement are mica schists with garnet, biotite, and tourmaline, and paragneisses with muscovite and biotite, that belong to the Someş Series (Vasilescu & Nechiti 1968; Ţenu *et al.* 1983).

Triassic deposits, marked by wide lithological variations, are found directly and transgressively over the crystalline basement. The isobaths, at the top of the Triassic, indicate depths between 1600 and 3200 m. The thickness of the Triassic deposits reaches 500–1000 m in Oradea and is gradually thinning westward and northward to <200 m (Ţenu *et al.* 1981). The Jurassic sequences are displayed in a discordant way because of a long uplift phase, are thinner (50–350 m) than the Triassic, and consist of red clays, packed gritstones, and marls (Vasilescu & Nechiti 1968). In the studied area, the Cretaceous represents the last Mesozoic sedimentation cycle. Cretaceous deposits are found transgressively over the Jurassic sequences, in a wide surface area, and consist of gray-brown and yellow limestone with thin calcite veins and gray-black marlstones (Vasilescu & Nechiti 1968; Ţenu *et al.* 1983).

Neogene deposits are found transgressively over the older sequences and consist of Miocene and Pliocene deposits. The Middle Miocene (Badenian and Sarmatian) deposits are between 50 and 250 m thick. The Upper Miocene (Pannonian and Pontian) are from 350 to 1150 m thick. The Neogene sequences consist of marls, marlstone, gray-green clay with sandstone, and lignite interbeddings (Vasilescu & Nechiti 1968; Săndulescu 1984). Later deposits of the Pannonian Basin belong to the Quaternary and consist of sands and gravel made by the Crişul Repede, the Crişul Negru, the Barcău, and the Ier River alluvium.

*The North Apuseni Mountains*
The other geological unit is represented by the North Apuseni Mountains (Fig. 1) that consist of various basement
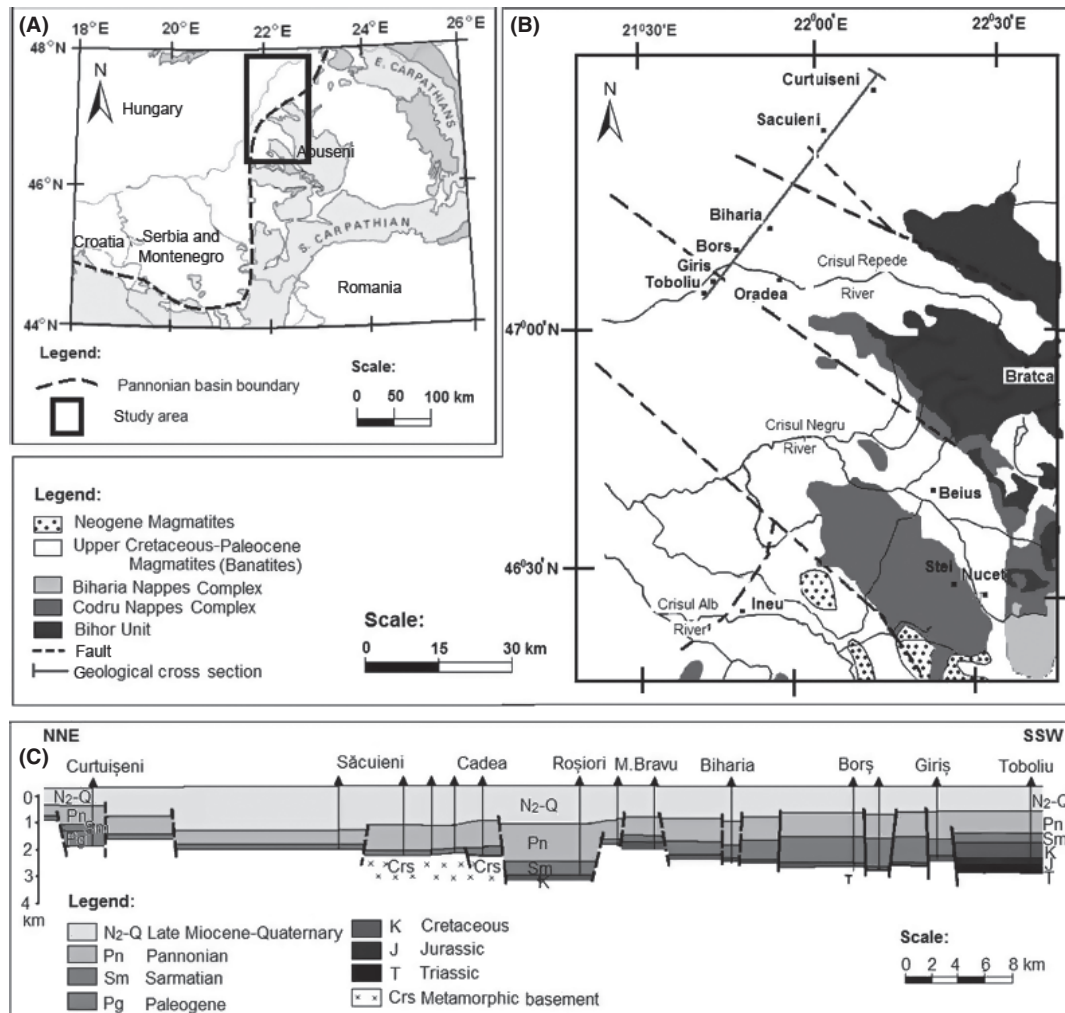
**Fig. 1.** Geology of the area: (A) location in Romania; (B) geology according to Ţenu 1981; modified; (C) geological cross-section, based on Butac & Opran 1985.

tectonic units, made up of early Proterozoic metamorphic rocks (mostly from high-grade metamorphic sequences) and associated granites (late Cambrian, middle to late Devonian, and early Permian), with a Permo-Mesozoic sedimentary and volcanic cover (Stan 1987; Dallmeyer et al. 1999; Pană et al. 2002). They delineate a system of nappes that consists of the Bihor Nappes, the Codru Nappes Complex, and the Biharia Nappes Complex, named the Inner Dacides (Săndulescu 1984), and are well correlated with the Western Carpathians and the Eastern Alps. The nappes were juxtaposed during late Paleozoic (Variscan) orogenic activity. Alpine tectonic activity recorded crustal shortening during the Turonian, followed by the deposition of sediments within Gosau-type basins during the Senonian (Seghedi 2004). The southern basement units of the North Apuseni Mountains recorded younger Alpine events and concomitant low-grade metamorphism that marked the separation of North and South Apuseni (Dallmeyer et al. 1999; Pană et al. 2002).

These tectonic activities have impacted the sedimentation process and the structure of the lithosphere. One important aspect is the Badenian extension episode from the Pannonian Basin, which caused a rise in the partially molten mantle below a thin, continental-type crust. As a consequence, in the Pannonian Basin, the Mohorovicic discontinuity is situated at a 20–25 km depth, when compared to the average depth (30–35 km) of this discontinuity in Europe (Paal 1975, Paraschiv et al. 1975). Crustal thinning caused a heat excess in the area that is reflected in high geothermal gradients ranging from 25 to $70°C\ km^{-1}$, and high geothermic steps (the interval of the crust depth for which the temperature rises by $1°C$) from 13 to 22 m per $°C$ (Paraschiv & Cristian 1973; Paraschiv et al. 1975). In the area, eight significant geothermal localities were identified that are situated close to the Hungarian border. The average heat flow values estimated for these areas are 140 mW m$^{-2}$ (Pişcolt, Galoşpetreu, Ciocaia), 130 mW m$^{-2}$ (Chişlaz, Sântion-Biharia), 125 mW m$^{-2}$

(Abrămuț, Săcuieni), and 120 mW m$^{-2}$ (Mihai Bravu) (Paraschiv & Cristian 1973; Paraschiv *et al.* 1975). These heat flows are higher than the average values (61–94 mW m$^{-2}$) determined for the Pannonian Basin (Paraschiv & Cristian 1973; Paraschiv *et al.* 1975). The presence of high geothermal gradients in the area can contribute to the migration and distribution of radionuclides in groundwaters (Țenu 1981; Ródenas *et al.* 2008).

As a result of late Cretaceous/Paleogene tectogenesis and Neogene subsidence (Săndulescu 1984) that took place in the area, a system of faults and thrusts was developed (Fig. 1). These faults can facilitate the circulation of significant amounts of water in the aquifers located within the area (Țenu 1981). High radon and radium level can be associated with the presence of faults that allow radionuclides to move more quickly from deeper aquifers reach in radioactive elements. The main water flow is orientated from northeast to west, along some preferential pathways (Țenu 1981).

## Hydrogeological setting

The main aquifers of the area are contained in Holocene, Pleistocene-Upper Pliocene, Lower Pontian, Lower Cretaceous, and Triassic formations. The first two aquifers contain cold water, while the other three aquifers contain thermal waters.

The Holocene reservoir contains recent alluvia and is a phreatic system that consists of one or more interconnected layers usually reaching 15–30 m in depth (Table 1)

(Țenu *et al.* 1981). The waters in these areas are cold, with temperatures ranging between 17 and 19°C. The chemical composition of the major dissolved cations identified in waters originating from the Holocene aquifer is dominated by calcium (20–99.7 mg l$^{-1}$) and magnesium (12.8–48 mg l$^{-1}$). For this aquifer, the major dissolved anions are bicarbonate (198.7–506.8 mg l$^{-1}$) and sulfate (2.3–55.6 mg l$^{-1}$) (Țenu 1981). As the Piper diagram (Fig. 2) shows, these waters can be classified as a bicarbonate-sulfate-calcium-magnesium type, with a relatively low scattering of the points on the graph.

The Pleistocene aquifer lies just below the phreatic one, and it is a medium-depth reservoir reaching from 50 to 130 m in depth and has temperatures from 16 to 18°C at the surface. The aquifer has a complex of permeable layers of different thickness and grain size, with good hydraulic connections (Țenu 1981). When compared to the Holocene aquifer, the Pleistocene aquifer shows a decrease in magnesium (3.6–26.1 mg l$^{-1}$), sulfate (2.2–25.9 mg l$^{-1}$), and chloride (1.8–13.8 mg l$^{-1}$) concentration, while the sodium concentration increases (1.8–158 mg l$^{-1}$). The high concentrations of sodium can be correlated with the presence of clay-bearing sands in the area (Țenu 1981). The cation concentrations have a larger variance compared to anion values (Fig. 2). Based on their chemical composition, these waters can be classified as a bicarbonate-sulfate-sodium-calcium type.

The Upper Pliocene reservoir reaches 150 and 400 m in depth and contains thin, irregular layers of very fine grain size separated by thick impermeable clayey-marly horizons.

**Table 1** Hydrogeochemical features of the sampled aquifers.

| Aquifers | | | Shallow aquifers | Medium-depth aquifers | Deep aquifers | |
|---|---|---|---|---|---|---|
| Depth | | | 15–30 m* | 50–150 m* | 1250–1680 m* | 2200–3400 m* |
| Water type | | | Cold | Cold | Geothermal | Geothermal |
| Collector age | | | Holocene* | Pleistocene* | Lower Pontian* (Upper Miocene) | Triassic* |
| Lithology | | | Sands and gravels* | Sands* | Sands with clay and marls* | Limestone and dolomite* |
| Hydrochemistry | Dissolved gases (mg l$^{-1}$) | $CO_2$ | <10[†] | <10[†] | 100–560[†] | 8–42[†] |
| | | $H_2S$ | | | ~112[†] | 0.2[†] |
| | Dissolved ions (mg l$^{-1}$) | $Ca^{2+}$ | 20.04–99.79[†] | 12.02–87.37[†] | 4.83–7.08[‡] | 142.41–268.67[‡] |
| | | $Mg^{2+}$ | 12.88–48.03[†] | 3.64–26.14[†] | 2.07–4.02[‡] | 41.01–63.02[‡] |
| | | $Na^+$ | 1.37–70[†] | 1.83–158[†] | 1239.24–1396.21[‡] | 25.48–61.84[‡] |
| | | $K^+$ | 0.50–4.46[†] | 0.30–4.70[†] | 39.82–58.15[‡] | 2.78–11.67[‡] |
| | | $SO_4^{2-}$ | 2.38–55.68[†] | 2.20–25.99[†] | 6.04–8.69[‡] | 352.30–730.80[‡] |
| | | $Cl^-$ | 1.81–43.14[†] | 1.81–13.88[†] | 542.87–625.21[‡] | 17.47–49.25[‡] |
| | | $HCO_3^-$ | 198.73–506.82[†] | 198.70–523.34[†] | 2195.37–2403.65[‡] | 182.69–259.19[‡] |
| Hydrochemical facies | | | $HCO_3$–$SO_4$–Ca–Mg[†] | $HCO_3$–$SO_4$–Na–Ca[†] | $HCO_3$–Na–Cl[‡] | $SO_4$–$HCO_3$–Ca–Mg[‡] |
| Wellhead temperature (°C) | | | 17–19[‡] | 16–18[‡] | 50–85[‡] | 70–105[‡] |
| pH | | | 5.8–8.0[‡] | 5.8–8.3[‡] | 7.55–8.15[‡] | 6.3–7.61[‡] |
| $^{222}$Rn (Bq l$^{-1}$) | | | 4.5–110.8[‡] | 9.3–106.0[‡] | 20.15–26.94[‡] | 10.12–34.82[‡] |
| $^{226}$Ra (Bq l$^{-1}$) | | | 0.06–0.48[‡] | 0.1–0.52[‡] | 0.92–1.1[‡] | 0.27–1.8[‡] |

*From Țenu (1981).
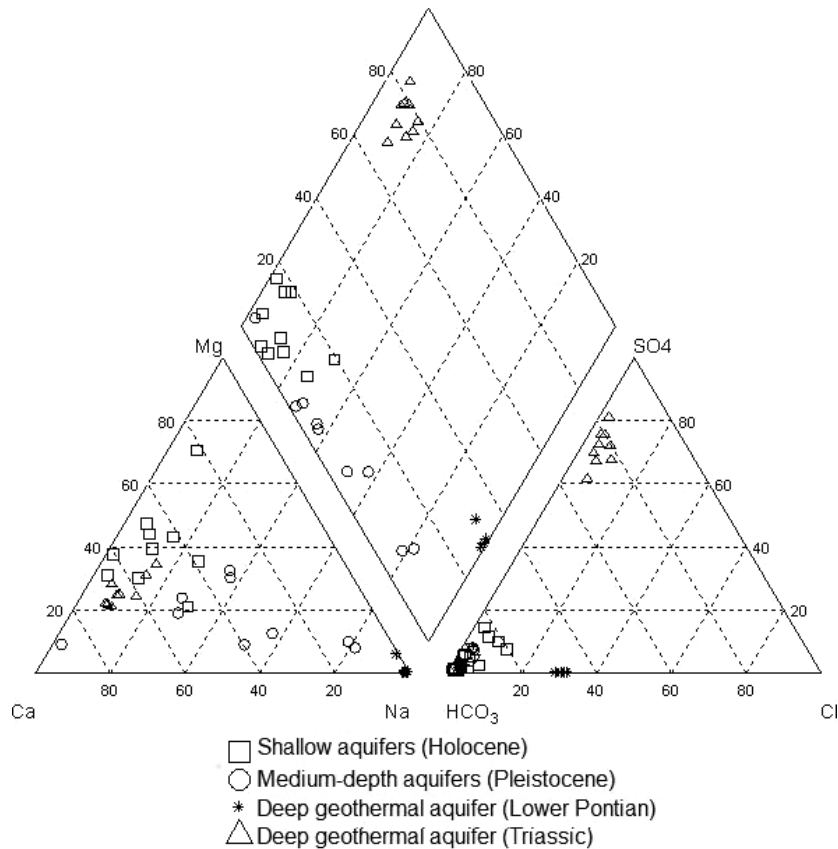[†]From Gilău (1997).
[‡]Original data.

Fig. 2. Piper diagram reflecting the abundance of major dissolved ions in the aquifers located in the studied area.

The hydraulic connectivity between the layers is not as good as the Pleistocene aquifer (Ţenu et al. 1981). These waters are relatively similar to those from the Pleistocene aquifer, except for higher concentrations of sodium (35.1–214 mg l$^{-1}$) and bicarbonate (193.2–585.3 mg l$^{-1}$), which can be correlated with the presence of clayey sands and marls identified in the area, and with the low dynamics of this aquifer (Ţenu 1981).

The deep aquifers identified in the area contain geothermal waters, located in Cenozoic and Mesozoic rocks at depths >1200 m (Paraschiv & Cristian 1973; Ţenu 1981). In this study, two geothermal aquifers were investigated: (i) the Lower Pontian (Upper Miocene) aquifer of Săcuieni and (ii) the Triassic aquifer of Oradea. In Săcuieni, geothermal waters originating from the Lower Pontian aquifer, located at depths of 1250–1680 m, are exploited. The wellhead temperature of the waters ranges from 50 to 85°C. The complex is multilayered and consists of a series of sandy permeable interbeddings (30–40 layers), and sandy clay and clay impermeable layers (Ţenu 1981), having a total thickness of 1320–1550 m (Ţenu 1981). These waters bear relatively high concentrations of dissolved gases, mainly $CO_2$ (100–560 mg l$^{-1}$) and $H_2S$ (around 112 mg l$^{-1}$), and are classified as a bicarbonate-

sodium-chloride type (Gilău 1997). The high concentrations of bicarbonate (2195.3–2403.6 mg l$^{-1}$) can be correlated with the low dynamics of these waters (Ţenu 1981). In a practical sense, this thermal aquifer is a closed system, with a low recharge (Ţenu ş1981). High concentrations of sodium (1239.2–1396.2 mg l$^{-1}$) and chloride (542.8–625.2 mg l$^{-1}$) can be associated with the presence of sodium-bearing clay layers in the area or may result from mixing with connate waters from deep reservoirs (Ţenu 1981).

In Oradea, which is located approximately 45 km southwest of Săcuieni, the Triassic geothermal aquifer is exploited. Terrestrial heat flow in the area is approximately 90 mW m$^{-2}$, and the geothermal gradient ranges from 2.6 to 7°C per 100 m (Ţenu 1981). The Triassic reservoir contains limestones and dolomites at depths of 2200–3400 m (see Fig. 1 and Table 1) and belongs to the Inner Dacides (Săndulescu 1984), and to be more precise to the Bihor Unit, as an underground extension of the rocks exposed in the Pădurea Craiului Mountains and covered by the Cenozoic formations of the Pannonian Basin. The aquifer probably has an active recharge, and its waters likely originate from the Apuseni Mountains, located approximately 80 km east of Oradea. The main flow of

these waters is orientated from the northeast toward the west (Ţenu 1981). A secondary flow direction, likely connected to the main flow, trends north-northwest toward the south-southeast (Ţenu 1981). These waters have low contents of dissolved gases, mainly $CO_2$ (8–42 mg $l^{-1}$) and $H_2S$ (0.2 mg $l^{-1}$), and are classified as a sulfate-bicarbonate-calcium-magnesium type (Gilău 1997). The high levels of sulfate (352.3–730.8 mg $l^{-1}$), bicarbonate (182.6–259.1 mg $l^{-1}$), calcium (142.4–268.6 mg $l^{-1}$), and magnesium (41–63 mg $l^{-1}$) could reflect the presence of anhydrite ($CaSO_4$), limestone ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) in the area (Gilău 1997).

## MATERIALS AND METHODS

### Sampling procedure

Water samples, originating from different aquifers located in Bihor County, were collected in 2008 and 2009 during spring and summer, when the air temperature was over 12°C (spring) and 16°C (summer). Waters were sampled using 500-ml polyethylene bottles that had been previously washed three times with high-purity water (Millipore Milli-Q). Prior to sampling, the bottles were rinsed two times on-site, with the water sampled. Domestic well waters were collected at a level of 0.5 m below the surface, the tap waters were sampled after 10 min of running, and geothermal waters were collected at the wellhead. Bottles containing water samples were fully filled and sealed to prevent possible radon loss. The water samples collected for major dissolved ions analyses were filtered in the field using 0.45-μm cellulose acetate filters. Samples for cation determinations were acidified using concentrated analytical grade nitric acid.

Sampling flasks were transported to the laboratory, stored at room temperature, and analyzed within the specific time required for each type of analysis.

### Methodology

#### Radionuclide analysis

Water samples were initially collected in polyethylene bottles. Studies performed in our laboratory indicated that radon loss because of diffusion through the polyethylene bottles is small, approximately ≤5% during a period of 2 days. Similar results have been reported in other studies (Wojcik 1991). For the radium analysis, after arrival in the laboratory, water samples were transferred into glass bottles and completely filled and hermetically sealed. The radium analysis was made by measuring the generated radon, after 1 month from the time of sampling when radium–radon equilibrium was established at a rate of over 98% (Cosma *et al.* 2002). Keeping the samples in glass bottles prevented radon loss by diffusion through the container walls (De

Corte *et al.* 2006). Radon and radium analyses were conducted using a LUK-VR system equipped with Lucas cells and a special device for dissolved gas extraction (Plch 1977).

For measurements, a known volume (300 ml) of a water sample was introduced into a 500-ml glass container (V = 500 ml) that was used for the extraction of the dissolved gas. After 1 min of vigorous shaking, the equilibrium between the activities of radon from the water ($A_w$) and radon from the air ($A_a$) above the liquid ($V_a$ = air volume above the liquid) was established. The solubility constant was determined as follows:

$$\alpha = \frac{A_w}{A_a} \cdot \frac{V_a}{V} \tag{1}$$

(Plch 1977).

The scrubber was coupled to a Lucas cell (previously held under vacuum) by a stopcock and to a Janet syringe containing 150 ml of distilled water. By opening the stopcock, the air-containing radon was transferred from the scrubber into the Lucas cell (145 ml). Between the scrubber and the Lucas cell, a filter was inserted to prevent the radon progeny from entering the cell. Measurement of the activity in the Lucas cell was made by using the photomultiplier inserted in the LUK-3A instrument. For a normal temperature of 20°C, the solubility coefficient ($\alpha$) of radon in water is 0.254. A correction is necessary for other working temperatures using the following equation:

$$\alpha = 0.1057 + 0.405 \cdot \exp(-0.0502 \cdot t) \tag{2}$$

(Hunyadi *et al.* 1999).

where $t$ is the water temperature in the scrubber.

For a temperature of 20°C between the radon content in water A [Bq $l^{-1}$] and the number of counts/second N [c $s^{-1}$] recorded by the device, the following relationship is obtained:

$$A(Bq/l) = 9.85 \cdot N(c/s) \tag{3}$$

(Cosma *et al.* 2008).

Radon was analyzed within a maximum of 12 h from the sampling time. Correction for the sampling time was made using the formula:

$$A_{(0)} = A \cdot \exp(\lambda \cdot \Delta t) \tag{4}$$

where $A_{(0)}$ represents the initial activity (at the time of sampling), A is the measured activity (at a maximum of 12 h), $\Delta t$ is the time period between the sampling moment and the time of the measurement, and $\lambda = \ln2/T$ is the radioactive constant of radon (T = 3.82 days, the half-life of radon).

For the radon analysis, the detection limit (LD) of the method was 0.2 Bq $l^{-1}$, for a measurement time of 300 sec, while for radium, the detection limit was 0.05 Bq $l^{-1}$, for a measuring time of 3000 sec (Cosma *et al.* 2008). Statistical errors associated with the radon analysis were 5–6%,

and in the range of 5–15% for the radium (Cosma *et al.* 2008). The error domains were deduced by using the following formula:

$$LD = 2.71 + 3.29\sqrt{2F} \tag{5}$$

(Currie 1968) where LD is the limit of detection and F is the background (cpm).

The efficiency detection of the Lucas cell was determined using a control source manufactured and certified by the State Metrological Institute of the Czech Republic.

*Chemical analysis*

The unstable parameters like pH and temperature (T) were measured in the field with a portable multiparameter device. The concentrations for the major anions ($Cl^-$, $HCO_3^-$, $SO_4^{2-}$) and cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) were measured by ion chromatography using a Shimadzu 10 fitted with a conductivity detector and the two columns: Universal Cation HR 100 mm × 4.6 mm, 7 μm (for cations) and Allsep A-2 150 mm × 4.6 mm, 7 μm (for anions). The mobile phase was 0.85 mM l$^{-1}$ NaHCO$_3$ and 0.90 mM l$^{-1}$ Na$_2$CO$_3$.

All chemicals used were of high purity, and all the solutions were prepared by using high-purity water (Millipore Milli-Q). All glasswares were soaked in 5 M HNO$_3$ for a minimum of 12 h and were washed with ultra pure water.

## RESULTS

### Radon and radium in shallow aquifers

Domestic wells and spring waters originating from shallow aquifers (2–20 m in depth) were sampled. Radon proved to have a wide range of activity, with values from 4.5 to 110.8 Bq l$^{-1}$ (Table 1). In the domestic wells, radon activity ranged from 4.5 to 110.8 Bq l$^{-1}$, having a mean value of 29.4 Bq l$^{-1}$, and a median value of 20.3 Bq l$^{-1}$, when compared to the spring waters that had radon activities ranging from 14.6 to 50.0 Bq l$^{-1}$ and a mean of 33.1 Bq l$^{-1}$ and median of 35.4 Bq l$^{-1}$. According to the frequency distribution diagram (Fig. 3), most of the water samples (82%) had a radon concentration under 40 Bq l$^{-1}$. The samples that exceed this value are domestic well waters from southeast of the area (North Apuseni Mountains)
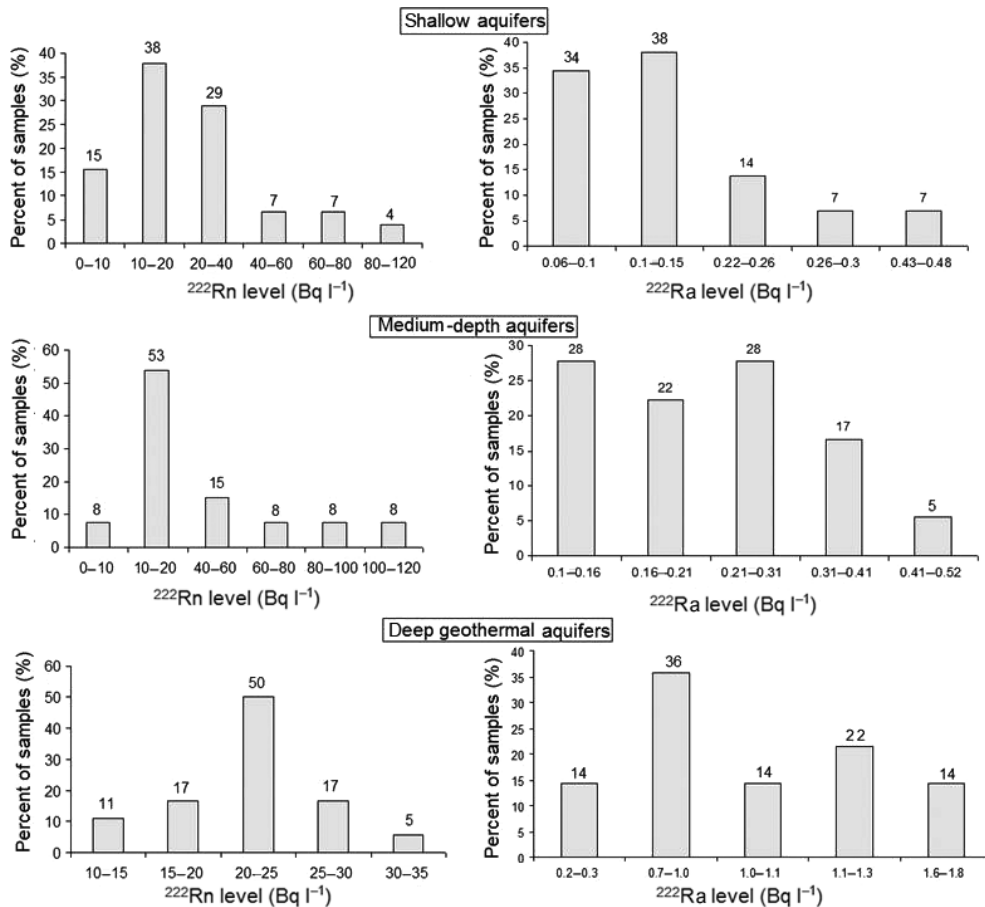


**Fig. 3.** Frequency distribution diagrams of radon and radium activities for the investigated aquifers.
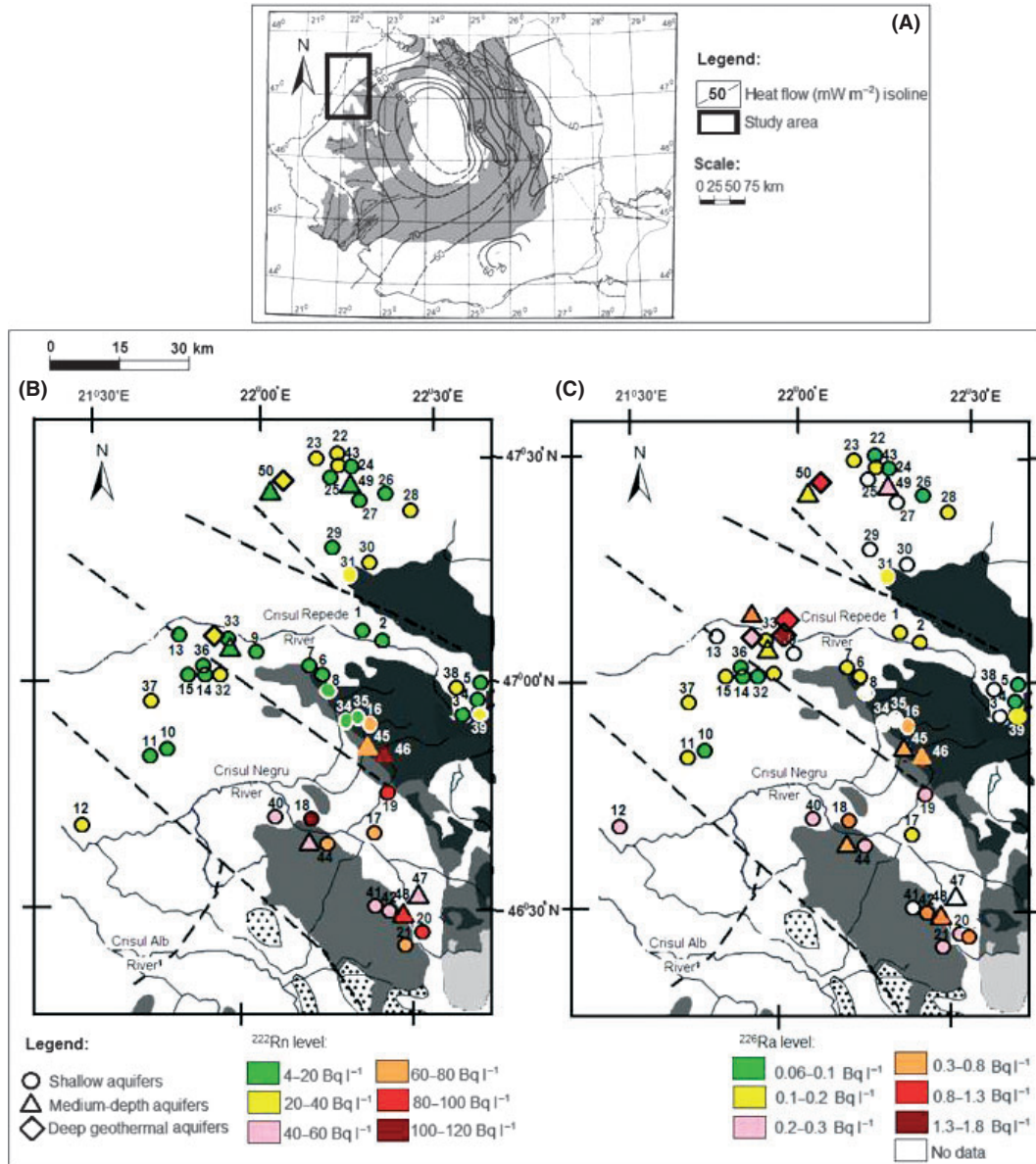
**Fig. 4.** Spatial distribution map for radionuclide activities; (A) heat flow map of the studied area (modified after Milcoveanu 1984); (B) spatial distribution of radon concentrations; (C) spatial distribution of radium concentrations. (1)Aleșd; (2) Aușeu-Groși; (3) Bratca; (4) Vadul Crișului; (5) Borod; (6) Tileagd; (7) Ineu; (8) Săcădat; (9) Oșorhei; (10) Salonta; (11) Ciumegiu; (12) Avram Iancu; (13) Sântandrei; (14) Apateu; (15) Gepiu; (16) Roșia; (17) Beiuș; (18) Pocola; (19) Remetea; (20) Nucet; (21) Vașcău; (22) Valea lui Mihai; (23) Şimian; (24) Sălacea; (25) Cherechiu; (26) Viișoara; (27) Abram; (28) Bâlc; (29) Tăuteu; (30) Derna; (31) Brusturi; (32) Sânmărtin; (33) Oradea; (34) Ceica; (35) Dobrești-Topa de Jos; (36) Nojorid; (37) Cefa-Inand; (38) Şuncuiuș; (39) Bulz; (40) Căpâlna; (41) Drăgănești; (42) Rieni; (43) Suplacul de Barcău; (44) Beiuș; (45) Căbești; (46) Curătele; (47) Pietroasa; (48) Ştei; (49) Marghita; (50) Săcuieni.

(samples 17, 18, 19, 20, 21, 40, 41, 42, and 44) (Fig. 4B).

The shallow aquifers proved to have the lowest radium concentrations, with values ranging from 0.06 to 0.48 Bq l$^{-1}$. As the frequency distribution diagram indicates, most of the samples (72%) had radium levels between 0.06 and 0.15 Bq l$^{-1}$. The spatial distribution map for radium activities (Fig. 4C) showed that the samples originating from the southeast part of the study area (samples 12, 18–21, 40, 42 and 44) exceeded these values, having higher radium content, up to 0.48 Bq l$^{-1}$.

The analyzed domestic wells and spring water samples proved to have radon and radium contents broadly similar to values reported in the literature (Burkhart *et al.* 1999; Karahan *et al.* 2000; Zouridakis *et al.* 2002; Somlai *et al.* 2007).

## Radon and radium in medium-depth aquifers

Drinking water samples originating from medium-depth (80–130 m) aquifers proved to have relatively low radon contents, between 9.3 and 106.0 Bq $l^{-1}$, with a mean value of 36.4 Bq $l^{-1}$ and a median value of 15.7 Bq $l^{-1}$. As the frequency distribution diagram shows, most of the samples (61%) had a radon level from 9.3 to 20 Bq $l^{-1}$. In five locations (samples 44–48) from the southern part of the area, higher values (from 40 to 110.8 Bq $l^{-1}$) were registered.

The medium-depth aquifers had higher radium content than the shallow ones. Radium activities ranged from 0.1 to 0.52 Bq $l^{-1}$, with a mean value of 0.28 Bq $l^{-1}$. As is shown in Fig. 3, most of the samples (78%) had radium levels from 0.1 to 0.31 Bq $l^{-1}$. In the northwest of the study area, only some of the water samples from Oradea (sampling point 33) exceeded these values, having a radium content up to 0.37 Bq $l^{-1}$, while in the sampling points (44–46 and 48) located in the southeastern part of the area, the radium concentration was higher, having values up to 0.52 Bq $l^{-1}$ (Fig. 4C).

Similar radon and radium levels have been reported in other studies (Villalba *et al.* 2006) for drinking water originating from wells located at similar depths.

The waters originating from the shallow and medium-depth aquifers represent the main drinking water source in the area. The European Commission (Euratom/928/2001) recommended a reference level for the $^{222}$Rn in drinking water of 100 Bq $l^{-1}$, while the US-EPA proposed a MCL (maximum contaminant level) of 11 Bq $l^{-1}$ and an AMCL (alternative maximum contaminant level) of 148 Bq $l^{-1}$ (US-EPA 1991) for radon. Regarding the presence of radium in drinking water, the US-EPA has established the MCL at 0.185 Bq $l^{-1}$ (5 pCi/l) for combined $^{226}$Ra and $^{228}$Ra (US-EPA 1976). As is shown in Figs 3 and 4B,C, for some of the analyzed water samples, these international recommendations were exceeded. As a consequence, the use of the drinking waters from these particular areas may raise concern about the health risk for local residents.

## Radon and radium in deep geothermal aquifers

The radon content of deep geothermal waters originating from both investigated aquifers did not show great variance, with values ranging from 10.1 to 34.8 Bq $l^{-1}$ (mean value of 21.8 Bq $l^{-1}$ and median of 21.9 Bq $l^{-1}$). According to the frequency distribution diagram, 78% of the samples had radon activity under 25 Bq $l^{-1}$, while 22% had radon values from 25 to 34.8 Bq $l^{-1}$.

The radon level measured in the deep geothermal reservoirs (up to 34.8 Bq $l^{-1}$) was lower than in the medium-depth (up to 106.0 Bq $l^{-1}$) and shallow-depth (up to 110.8 Bq $l^{-1}$) aquifers. In contrast, radium levels increased considerably with aquifer depth, reaching 1.4 Bq $l^{-1}$

(Săcuieni) and 1.8 Bq $l^{-1}$ (Oradea) in the deep thermal aquifers, when compared to the medium-depth (0.52 Bq $l^{-1}$) and shallow (0.48 Bq $l^{-1}$) aquifers. The analyzed thermal waters have radium activities from 0.27 to 1.8 Bq $l^{-1}$, with a mean value of 1.01 Bq $l^{-1}$ and a median of 1.02 Bq $l^{-1}$. Most of the samples (86%) have radium activities from 0.27 to 1.3 Bq $l^{-1}$. Extreme values up to 1.6 Bq $l^{-1}$ and 1.8 Bq $l^{-1}$ were registered in some thermal waters from Oradea (wells 4795 and 4795).

## DISCUSSION

### Correlations between the radionuclide occurrence and hydrogeological characteristics of the aquifers

As shown in the spatial distribution map of radon activities (Fig. 4B), the water samples originating from aquifers located in the north and northwest of the area had a radon content under 40 Bq $l^{-1}$, while the samples from the southern part of the area had higher radon levels, from 40 to 110.8 Bq $l^{-1}$. As mentioned previously, the North Apuseni Mountains consist of various basement tectonic units, made up of metamorphic rocks and associated granite with sedimentary and volcanic cover (Stan 1987; Dallmeyer *et al.* 1999; Pană *et al.* 2002). The high radon levels determined in the southeastern section of the county may be the consequence of the presence of igneous and metamorphic rocks in the basement of the area and/or of the detrital sediments resulted from the erosion of the mountain ridge. Some of these rock categories are generally associated with high amounts (up to 5 ppm) of uranium (Tzortzis & Tsertos 2004; Skeppström & Olofsson 2007).

In the southeastern section of the area, there is a relatively high abundance of radioactive minerals. From this point of view, a representative area is the large open pit mine of Băita-Plai, situated near Nucet village (sampling point number 20), where uranium deposits have been mined for almost 60 years. Băita represents the largest uranium deposit in Romania, having estimated reserves of 450 000 tones, from which 300 000 tones have already been mined (Dumitrescu 2010). The uranium deposit exploited at Băita had high uranium content: from 1% to 5% U in radiometric sorted material (Dumitrescu 2010). In the southeast of the study area, two 'hot spots' were identified: Pocola (sample 18) and Curătele (sample 46), where the radon content exceeded 100 Bq $l^{-1}$. In the basement of the two locations, two major tectonic units occur (Săndulescu 1984): the Codru Nappes Complex (in Pocola) and the Biharia Unit (in Curătele), which consist of granite and volcanic rocks. The presence of these rocks can be associated with high levels of radon in underground waters.

In the northern section of the study area, black shales are present, rocks which can have a high concentration of

uranium (Chyi 2008), but in many cases is lower than those found in granite and some volcanic rocks. The presence of radon in the shallow and medium-depth aquifers located especially between the Crişul Repede and Crişul Negru rivers can be correlated with the presence of limestone and dolomite in the area (see the Geological setting section). These rocks are highly permeable, fractured, and faulted and provide channel ways that allow the passage of radon, giving high radon levels at surface, although these areas had fairly low concentrations of uranium (Ball *et al.* 1991).

At the northern site of the Crişul Repede River, most of the shallow water samples contained relatively low radon levels (up to 20 Bq l⁻¹). The radon content can be correlated with the presence of the clay deposits identified in the area (see section on Hydrogeochemical setting). Impermeable rocks, like mudstones, can contain more uranium than limestone and dolomite (Ball *et al.* 1991), but may not show high radon values as the gas cannot easily pass to the surface.

Because of the lack of detailed geostructural studies, fault mapping of the eastern part of Pannonian Basin is incomplete and, therefore, it was not possible to examine the potential correlations between radionuclide levels and faults. For the identified faults (Fig. 4B), the correlations are not obvious. Some areas located close to fracture zones (samples 13–15, 32–36) proved to have a lower concentration than expected. In other cases (samples 16, 19, 45, and 46), high levels of radon could be associated with the presence of faults, which allow radon to move quickly from deeper sources.

The spatial distribution of radium activities (Fig. 4C) is relatively similar to that of radon (Fig. 4B). The shallow and medium-depth aquifers located in the northwestern part of the area had lower radium level, when compared to the aquifers located in the southeastern part of the investigated area. The highest radium concentrations (0.3–0.52 Bq l⁻¹) were registered in the sampling points 20, 42, 44–46, and 48. In the basement of these locations, two major tectonic units are present (Codru Nappes Complex and Biharia Unit), which consists of granite and volcanic rocks (Săndulescu 1984). As for radon, the presence of high radium activities in the southeastern part of the area is mainly controlled by the geological features of the area, such as the presence of granite and volcanic rocks that are enriched in uranium minerals. The presence of these rocks is associated with high levels of radium in underground waters.

The hydrodynamic features of the aquifers may also influence the distribution of the two radionuclides. This remark supports the previously mentioned Ţenu's hypothesis (1981) related to the active recharge of Oradea aquifer from the Apuseni Mountains. In transit to the deep geothermal aquifer, these recharging waters may bring new amounts of dissolved radioactive minerals. As a consequence, the radon and radium levels are higher in the thermal aquifer of Oradea than in the Săcuieni aquifer that has a closed circuit with a low recharge (Ţenu 1981).

## Correlations between the radionuclide occurrence and the hydrogeochemical characteristics of the aquifers

As an inert gas, radon is relatively unaffected by the chemical buffering reactions that often control the generation and the migration of other radionuclides (Fig. 5). The behavior of radon is basically determined by physical processes and not by the chemical interactions (Table 1). However, radon levels can indirectly reflect radium concentration because of their parent–daughter relationship (Stoker & Kruger 1975). This phenomenon is evidenced in Fig. 6, where the radon concentration is plotted versus major dissolved ions identified in the two investigated geothermal aquifers, which proved to have the most different hydrogeochemical features. On the other hand, once dissolved in groundwater, radium is available for different chemical reactions that lead to its wide incorporation into carbonates, sulfates, hydroxides, oxides, and salts (Onishchenko *et al.* 2010).

As previously mentioned, the radium concentration increased with aquifer depth, and the highest values were registered in the deep geothermal aquifers. Still, there was a significant difference between the radium level in the two thermal aquifers (up to 1.1 Bq l⁻¹ in the sandy clay aquifer and up to 1.8 Bq l⁻¹ in the limestones and dolomites aquifer) (Table 1). The lower radium concentration from the sandy clay aquifer is the consequence of adsorption of dissolved radium (as Ra⁺²) onto mineral surfaces through ion exchange (Smith & Amonette 2006). Compared to other alkaline earth elements, radium is the most strongly adsorbed by ion exchange on clay minerals, especially near neutral and alkaline pH conditions (US-EPA 2004). The availability of surface adsorption sites, because of the clay content of Săcuieni
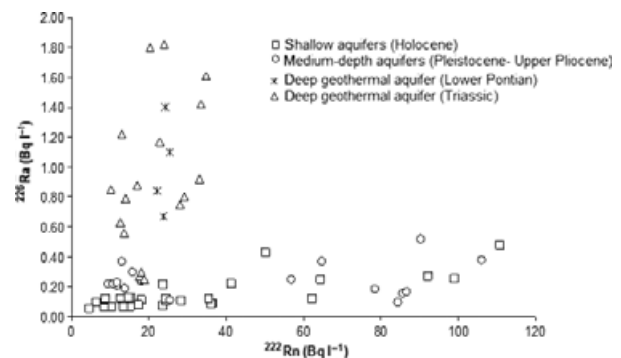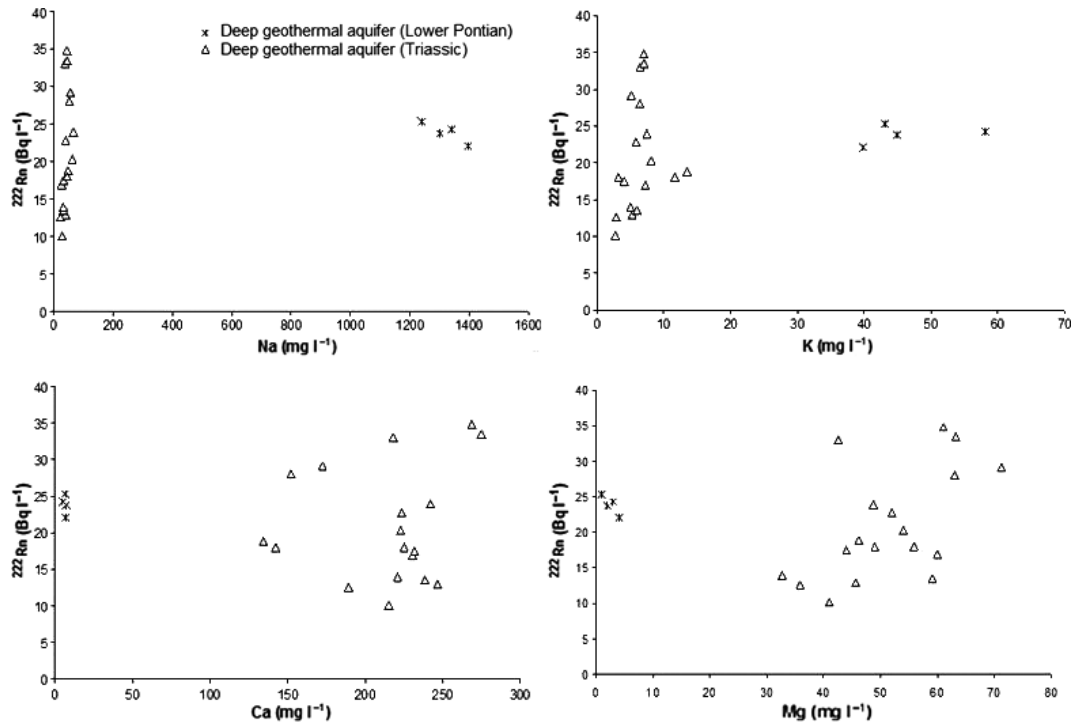


**Fig. 5.** Radium versus radon concentration.

Fig. 6. Radon versus sodium, potassium, calcium, and magnesium concentration.
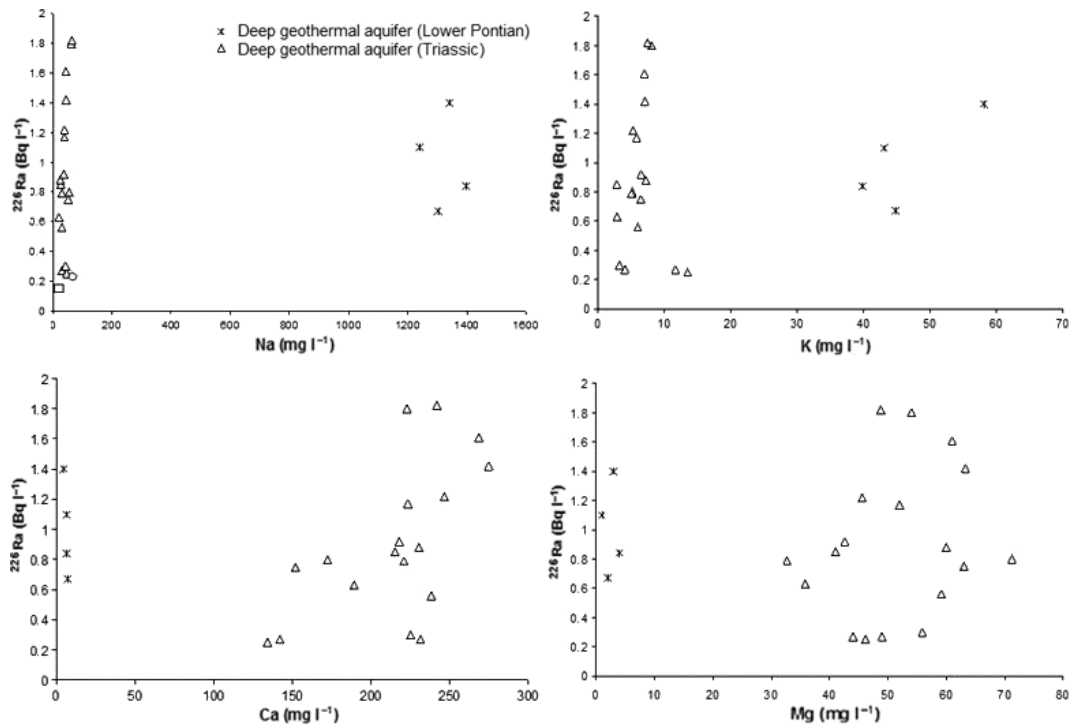


Fig. 7. Radium versus sodium, potassium, calcium, and magnesium concentration.

aquifer rocks, and the presence of neutral and alkaline conditions (water with pH = 7.55–8.15) represent important constraints for radium activity in sandy clay aquifers.

Clay minerals enhance the sorption of radium onto clay minerals in exchange for sodium (Fig. 7; and see Hammond *et al.* 1988; Appello & Postma 1994; and Vengosh

*et al.* 2009). On the other hand, the data presented in Table 1 and Figs 7 and 8 show a negative correlation between the monovalent and divalent cations identified in the sandy and sandy clay aquifers (the shallow, medium-depth, and deep geothermal aquifer of Săcuieni). As sodium and potassium concentrations increase, there is a decrease in the calcium, magnesium, and radium concentrations. As a consequence, these correlations emphasize the influence of the monovalent/divalent cation-exchange mechanism on all hydrogeochemical processes registered in these aquifers.

In addition to the presence of the above-mentioned conditions, there are a number of other factors that influence the adsorption of radium onto mineral surfaces. For example, radium adsorption is strongly dependent on the concentration of other competing ions (US-EPA 2004). The adsorption of radium decreases with the increasing of the concentration of other dissolved divalent cations (US-EPA 2004). Nathwani & Phillips 1979 measured the adsorption of $^{226}$Ra on soils as a function of calcium concentrations. All experiments were conducted with a constant total concentration of $^{226}$Ra of 10 pCi ml$^{-1}$. The dissolved concentrations of calcium varied from 0 to 0.5 mol l$^{-1}$. The results showed that the sorption of $^{226}$Ra by all soils decreased with increasing concentrations of dissolved calcium. The adsorption of radium is less effective under high concentrations of alkaline earth metals that compete with radium for adsorption site (Szabo 1978; Vinson *et al.* 2009).

The results of this study reveal a direct correlation between the high activity of radium in the Triassic limestone dolomite aquifer and the high concentrations of dissolved calcium and magnesium (in the Piper diagram, these waters are situated in the area dominated by calcium-sulfate-bicarbonate, see Fig. 2). In the case of the limestone dolomite aquifer, which tend to have limited sorption site, the increase in calcium (up to 268.6 mg l$^{-1}$) and magnesium (up to 63 mg l$^{-1}$) concentration, when compared to sandy clay aquifer (where calcium is up to 7 mg l$^{-1}$ and magnesium is up to 4 mg l$^{-1}$), led to a high competition with Ra for adsorption sites (Fig. 7). Consequently, higher radium concentrations (up to 1.8 Bq l$^{-1}$) have been found in limestone dolomite aquifer than the sandy clay aquifer (up to 1.1 Bq l$^{-1}$) (Figs 3 and 4C).

## Correlations between the radionuclide occurrence and the geothermal features of the area

Thermal processes can influence the migration and distribution of radionuclides in underground waters. The radon level determined in the deep thermal reservoirs (up to 34.82 Bq l$^{-1}$) was lower than that determined in the cold medium-depth (up to 106.03 Bq l$^{-1}$) and shallow (up to 110.8 Bq l$^{-1}$) aquifers (Fig. 9A). The findings can be linked to the high heat flow (90 mW m$^{-2}$) determined in the Oradea and Săcuieni area near thermal aquifers (Paraschiv & Cristian 1973; Milcoveanu 1984) (Fig. 4A). Radon is highly soluble, especially in cold water, but its
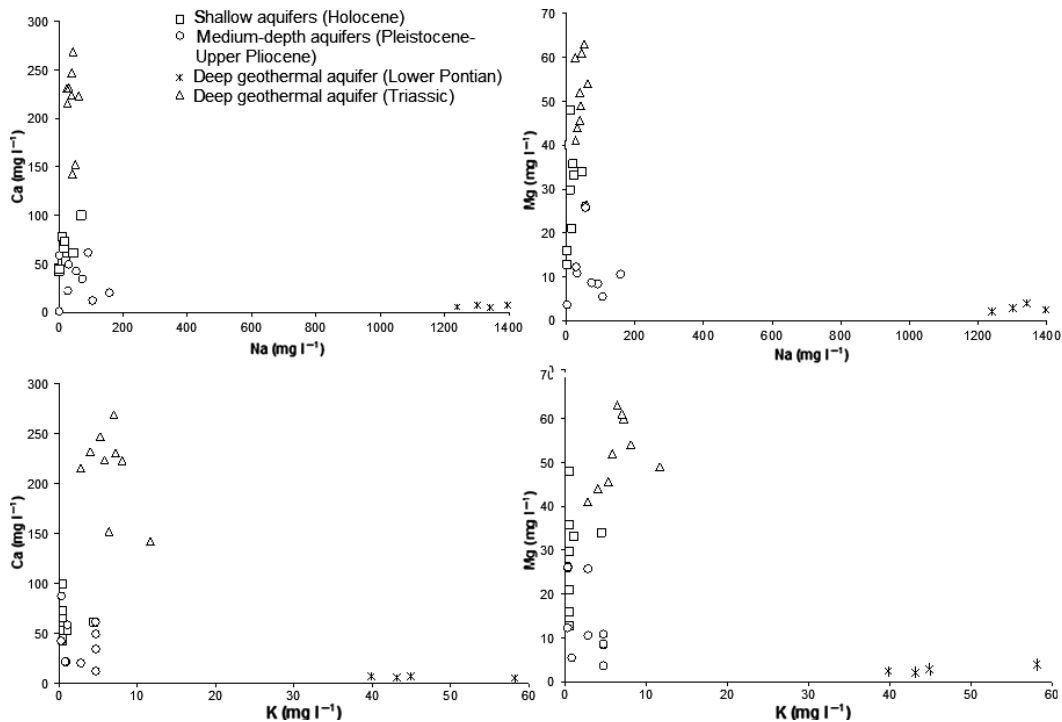


**Fig. 8.** The correlations between the major monovalent and divalent dissolved cations identified in the investigated aquifers.
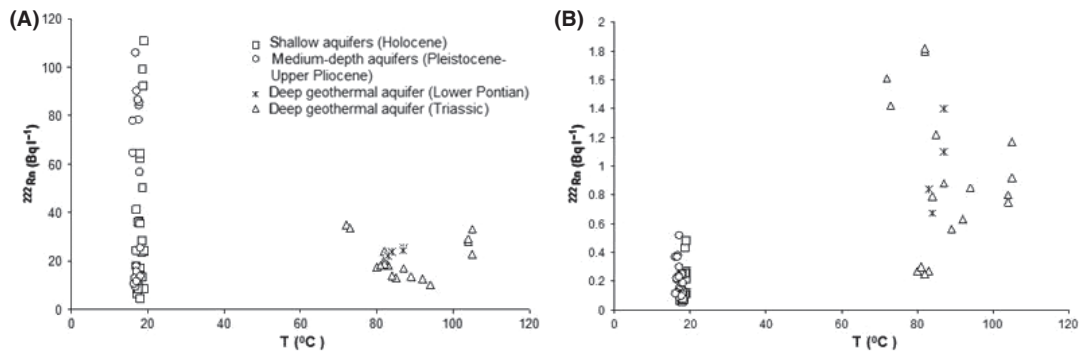
**Fig. 9.** Radon (A) and radium (B) concentration versus water temperature.

solubility decreases with the increase in temperature. As a result, high radon levels correspond to low water temperatures. The high temperatures registered in the analyzed geothermal waters (50–85°C for Săcuieni and 70–105°C for Oradea) enhance radon escape from solution, while the low temperatures (16–19°C) of the shallow and medium-depth aquifers increase the water solubility of radon (Table 1).

However, thermal processes can also enhance the migration and distribution of radium in groundwater. The presence of high heat flow in the area surrounding thermal aquifers leads to high water temperatures that enhance the dissolution of radioactive minerals including radium minerals. As a result, in geothermal aquifers, which have higher temperatures, the radium level is considerably higher than that in cold water aquifers (Fig. 9B).

## CONCLUSIONS

(1) The high radionuclide levels recorded in the southeast (North Apuseni Mountains) of the study area are a consequence of the proximity of uranium-rich geological formations.

(2) The low radon level from the shallow and medium-depth aquifers located in the northern part of the study area, along Crişul Repede River, is correlated with the presence of the impermeable, thick, clay deposits, through which radon gas cannot easily pass to the surface.

(3) The differences between the radon and radium content of the two thermal aquifers reflect their hydrodynamic features. The high radionuclide concentrations from Oradea aquifer are the consequence of the dynamic character of this aquifer, compared to Săcuieni thermal aquifer that has a closed system with low recharge.

(4) The availability of surface adsorption sites, because of the clay content of Săcuieni aquifer rocks, and the presence of neutral and alkaline conditions (water with pH = 7.55–8.15) represent important constraints for radium activity in sandy clay aquifers, because they enhance the sorption of radium onto clay minerals in exchange for sodium.

(5) In the case of the limestone dolomite aquifer, which tend to have limited sorption site, the abundance of dissolved calcium (up to 268.6 mg $l^{-1}$) and magnesium (up to 63 mg $l^{-1}$) led to a high competition with Ra for the adsorption sites. Consequently, in the limestone dolomite aquifer, higher radium concentrations were found than those in the sandy clay aquifer.

(6) The decrease in radon activity with depth of the investigated aquifers is correlated with the presence of high heat flows in the deep geothermal aquifers area. Radon solubility in water decreases with the increasing temperature; as a consequence, radon escapes from solution and migrates to upper and cold aquifers.

(7) The increase in temperature enhances the dissolution of Ra-bearing minerals. As a consequence, the investigated deep geothermal aquifers have considerably higher radium content than the cold shallow and medium-depth aquifers.

(8) The present study indicates that radon and radium occurrence in groundwater is not only limited to the uranium and thorium water content and that there are also secondary controls because of the hydrogeochemical and geothermal features of the area. To investigate in detail the mechanism responsible for the secondary control, a larger study with more sampling areas is required.

## ACKNOWLEDGEMENTS

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