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Hydrogeothermal characteristics of groundwater from Ribarska Banja spa, central Serbia

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Abstract. Ribarska Banja spa is one of the most popular balneotherapy and recreation centers in Serbia. It features several thermal groundwater sources whose temperatures range from 26 to 54 °C. The mineral content of these waters is low and their composition is of the SO_4-Na or HCO_3-Na type. Thermal water exploration has been conducted in the general area for many years, to assess the hydrogeothermal potential in order to extract larger amounts of thermal water for multiple uses. The hydrogeothermal system of Ribarska Banja spa was defined based on a synthesis of the results of comprehensive structural geology, geophysical, hydrogeological, hydrochemical and geothermal research. The primary groundwater reservoir of the hydrogeothermal system is comprised of tectonic zones (systems of faults and fractures) within Cretaceous-Paleogene metamorphosed and non-metamorphosed rocks. The overlying hydrogeological and temperature barrier is made up of a series of low metamorphosed rocks (chlorite, chlorite-sericite schists, gabbros, etc.), highly metamorphosed rocks (gneisses) and Neogene clay and sand sediments. The system is recharged by infiltration of atmospheric precipitation and surface water at the highest elevations of Mt. Jastrebac. Investigations have also shown that the system's heat source is younger granitoide intrusion spreading northwest of Ribarska Banja spa. Based on the quartz geothermometers, expected reservoir temperatures are in the range of 85–97 °C that can be expected at a depth of 1.87 km. Total energy usage at Ribarska Banja spa is 31 TJ/y with thermal capacity of 1.65 MWt and utilization factor of 0.58. Geothermal gradient is 0,051 °C/m, while heat flow density is 163.5 mW/m^2.

Key words: Thermal water, Hydrogeothermal system, Hydrogeothermal resources, Hydrogeothermal exploration, Ribarska Banja spa.

Апстракт: Рибарска Бања је једна од најпопуларнијих балнеолошко-рекреативних центара у Србији. У бањи постоји више појава истицања термалних вода са температурама у опсегу од 26 до 54 °C. Ове воде имају малу минерализацију, док су по хемијском саставу SO_4-Na или HCO_3-Na. Истраживање термалних вода у овом подручју извођена су дуги низ година, са циљем да се дефинише хидрогеотермална потенцијалност подручја и да се захвате веће количине термалних вода за вишенаменско коришћење. Хидрогеотермални систем Рибарске Бање је дефинисан на основу синтезе резултата комплексних структурно-геолошких, геофизичких, хидрогеолошких, хидрохемијских и геотермалних истраживања. Примарни резервоар хидрогеотермалног система представљају тектонске зоне (системи раседа и пукотина) у оквиру кредно-палеогених метаморфисаних и неметаморфисаних стена. Повлатну хидрогеолошку и температурну баријеру чине пакет нискометаморфних стена (хлоритски, хлоритско-серицитски шкриљци, габрови и друге стене), високометаморфних стена (гнајсеви) и неогени глиновито-песковити седименти. Прихрањивање система одвија се инфилтрацијом атмосферских и површинских вода на највишим котама планине Јастрепца. Истраживања су такође показала да извор топлоте геотермалног система је млађи гранитоидни интрузив који се пружа северозападно од Рибарске Бање. На основу кварцних геотермометара, очекивана температура резервоара је у опсегу од 85 до 97 ºC и може се очекивати на дубини од 1,87 km. Укупна енергија искоришћења Рибарске Бање је 31 TJ/y са термалним капацитетом од 1,65 MWt и фактором искоришћења од 0.58. Геотермални градијент је 0,051 °C/m, док је густина топлотног тока 163,5 mW/m^2.

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Кључне речи: термалне воде хидрогеотермални систем, хидрогеотермална истраживања, Рибарска Бања.

Introduction

Ribarska Banja spa is located in central Serbia, on the northeastern slopes of Mt. Jastrebac.

Thermal water wells, featuring water temperatures in the range from 26 to 54 °C, as well as thermal spa facilities, are situated in the Ribarska River valley, some 3 km from the village of Ribare. Intensive research of thermal waters starting in the late seventies (MILOVANOVIĆ 1978; MILOVANOVIĆ 1980; MILOVANOVIĆ 1992; MILOJEVIĆ 2004; ŠPADIJER *et al.* 2005; ŽIVANOVIĆ & ATANACKOVIĆ 2013)

The geology of the terrain was found to be highly complex and posed a major challenge for geologists (RAKIĆ *et al.* 1976; KRSTIĆ *et al.* 1980; SPAHIĆ 2006). Hydrogeological research was faced with a number of problems as it was difficult to identify the rocks and determine the rupture structures of the terrain. Drilling yielded considerable amounts of water from metamorphic rocks, characterized by increased temperatures suggesting the existence of a complex hydrogeothermal system. It was originally assumed that the system was recharged at higher altitudes of Mt. Jastrebac and that its granitoid was the cause of the elevated temperature groundwater regime at Ribarska Banja spa (MILOVANOVIĆ 1980; MILOVANOVIĆ 1992). However, recent research (ŠPADIJER *et al.* 2005; ŽIVANOVIĆ & ATANACKOVIĆ 2013), like as stable isotope analyses and chemical tests of the water samples collected from wells allowed insight into the individual contributors to the formation of the hydrogeothermal system of Ribarska Banja spa, from the source of recharge to the point of discharge.

Structural geology of the area

Geological characteristics. Due to the presence of different lithostratigraphic units and their highly complicated internal and external tectonic relationships, the zone of formation and discharge of the thermal waters of Ribarska Banja spa is characterized by an extremely complex geology. It features two large lithostratigraphic units, inversely positioned and in tectonic contact. The lower part is comprised of Upper Cretaceous and Cretaceous-Paleogene low metamorphosed rocks, overlain by pulled-over and highly metamorphosed crystalline schists (Fig. 1, Fig. 2). The Mt. Jastrebac Paleogene granitoid is emplaced in the Mesozoic-Paleogene metamorphic complex (RAKIĆ *et al.* 1976; SPAHIĆ 2006; MAROVIĆ *et al.* 2007).

The crystalline bedrocks comprised of two large rock complexes: gneisses and “green schists”. The gneisses (G) are exposed in an intermittent and irregular series running in the NW-SE direction, beginning at the Village of Srndalje. They have been classified as belonging to the Proterozoic Eon (UROŠEVIĆ 1929) and are in tectonic contact with underlying green schists. To the east and northeast of Ribarska Banja spa, the gneisses are overlain by Miocene clastic sediments.

“Green schists” associated with a low-to-medium metamorphosed volcanogenic sediment formation and distinct petrographic member changes are quite extensive in the Ribarska Banja spa area. Their age was determined by the discovery of Upper Cretaceous (Upper Cretaceous-Paleogene) palynomorphs in phyllites, sericite schists and calc-schists at several locations (SPAHIĆ 2006). These schists can be grouped into three units: lower, upper and middle. The lower and middle units of metamorphic rocks are inversely positioned relative to the upper unit.

The lower unit is comprised of epidote-actinolite, epidote-chlorite and chlorite schists (Sepak) and metagabbros (ν). This unit was probably a result of gabbro rocks metamorphosing and formations of metamorphosed spilite-keratophyre association, accompanied by intensive carbonitization and serpentinization. The colors are light grayish-green to dark green.

The middle unit is made up of sericite, quartz-sericite, sericite-chlorite and quartz-muscovite schists (Sseco), calcschists and marbles (Sca). The rocks belonging to this formation are found north of Banjski Potok, in the direction of Srndalje, and their age was determined based on numerous palynomorphs as Upper Cretaceous. The middle unit features calcschist sand marbles (Sca) in the form of tectonically relocated and transported belts, along with different types of sericite schists.

The highest level of the green schists, the so-called Đulica member (K, Pg), is exposed west of Ribarska Banja spa (SPAHIĆ 2006). It is comprised of phyllites, metamorphosed sandstones, metasiltstones, and non-metamorphosed rocks (conglomerates and sandstones). These sediments were determined by exploration drilling at Ribarska Banja spa.

The Mt. Jastrebac granitoid (δγ) is located west of Ribarska Banja spa. It was created by the intrusion of a granodiorite pluton into Upper Cretaceous and Paleogene sediments, forming a periclinal dome. It is largely a homogeneous magmatic body, in places crisscrossed by veins of aplite, pegmatite, granodiorite porphyrite and latite.

Miocene sediments (M) are comprised of yellowish, semi-consolidated sandstones, sands, sandy clays and conglomerates. Quaternary sediments are found downstream from Ribarska Banja spa, in the Ribarska River alluvium, where they are comprised of gravel, sand and clay deposits (al).

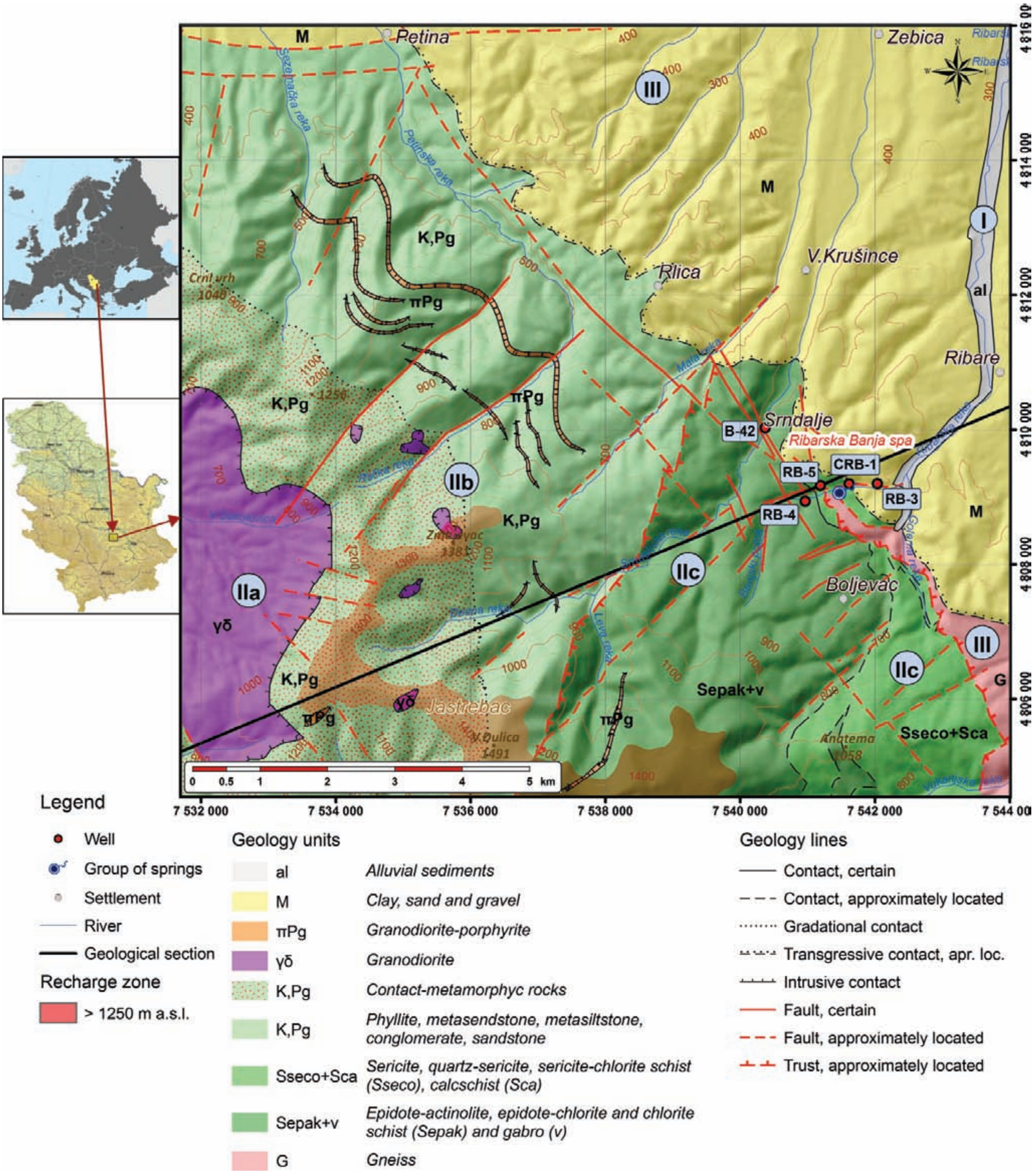

Fig. 1. Geological map of Ribarska Banja spa, according to Spahić (2006), Rakić *et al.* (1969), Krstić *et al.* (1974), modified. Legend of hydrogeological units: **I,** alluvial aquifer; **IIa,** fissured aquifer formed in granite rocks; **IIb,** fissured aquifer formed in K,Pg unit; **IIc,** fissured aquifer formed in metamorphic rocks (Sseco+Sca and Sepak+v); **III,** low permeable rocks (Gneiss and Miocene sediments)

Tectonic assemblage. Based on numerous data about the basic elements of the assemblage (foliations, fractures, faults), which has been examined extensively to gain insight into the tectonic relationships, three distinct structural units can be recognized: lower, middle and upper structural floors. The lower structural floor is made up of Cretaceous (Cretaceous-Paleogene) metamorphosed rocks and Proterozoic gneisses, while the upper structural floor is comprised of Neogene and Quaternary sediments. The lower and middle floors are inversely positioned to each other (ŠPADIJER *et al.* 2005; SPAHIĆ 2006; MAROVIĆ *et al.* 2007).

The faults system has been studied in general, with regard to the entire region, because it was determined that these structures intersected all the structural floors. Statistical data processing revealed two distinct directions of the faults: NW–SE and ENE–WSW (ŠPADIJER *et al.* 2005; SPAHIĆ 2006).

The second fault system (ENE–WSW) is detected in the valley of stream of Banjski Potok (Banja Creek). This is a highly complex dislocation zone, marked in places by two or three faults and a crushing belt that is several meters wide. The microlocations of the thermal wells are found along this zone. The positions of the faults have been well documented by geophysical investigations, which show that the tectonic surfaces dip steeply (70–80°) from the breakout zone to the north-northeast. The fault zone was reached in wells CRB-1 and RB-2. This zone is associated with thermal water discharges (ŠPADIJER *et al.* 2005; ŽIVANOVIĆ *et al.* 2010).

Hydrogeology

The presence of diverse petrographic types, intensive tectonic and magmatic activity and the existence of rocks and sediments of varying degrees of porosity have resulted in the formation of the alluvial and fractured types of aquifers in the area of Ribarska Banja spa. Additionally, terrains poor in aquifers were identified as a separate hydrogeological unit.

The alluvial aquifer is found in loose sand-gravel deposits of the stream of Banjski Potok, with large schist and granitoid blocks whose thickness is less than 3.0 m. The groundwater levels are in direct hydraulic connection with surface water. The small areal extent and small thickness of the alluvial deposits prevents accumulation of significant groundwater reserves in this aquifer.

Fractured aquifers were formed within the rocks of the Upper Cretaceous-Paleogene metamorphosed complex and the Mt. Jastrebac granitoid. The lithological composition and the intensity of fracturing of the rock complex have led to the identification of three aquifer subtypes in the Ribarska Banja spa area (Fig. 2): fractured aquifer in granitoid rocks (IIa), fractured aquifer in the upper unit of semi-metamorphosed and non-metamorphosed clastic rocks (IIb), and fractured aquifer in the lower and middle units of metamorphosed Upper Cretaceous-Paleogene rocks (IIc).

The fractured aquifer within the upper unit of semi-metamorphosed and non-metamorphosed clastic rocks (IIb) features good hydrogeological properties. This aquifer is recharged along the edges of the Mt. Jastrebac granitoid, through infiltration of surface water and water from atmospheric precipitation (Fig. 2). A system of faults causes part of these waters to circulate towards Ribarska Banja spa, and to be heat-

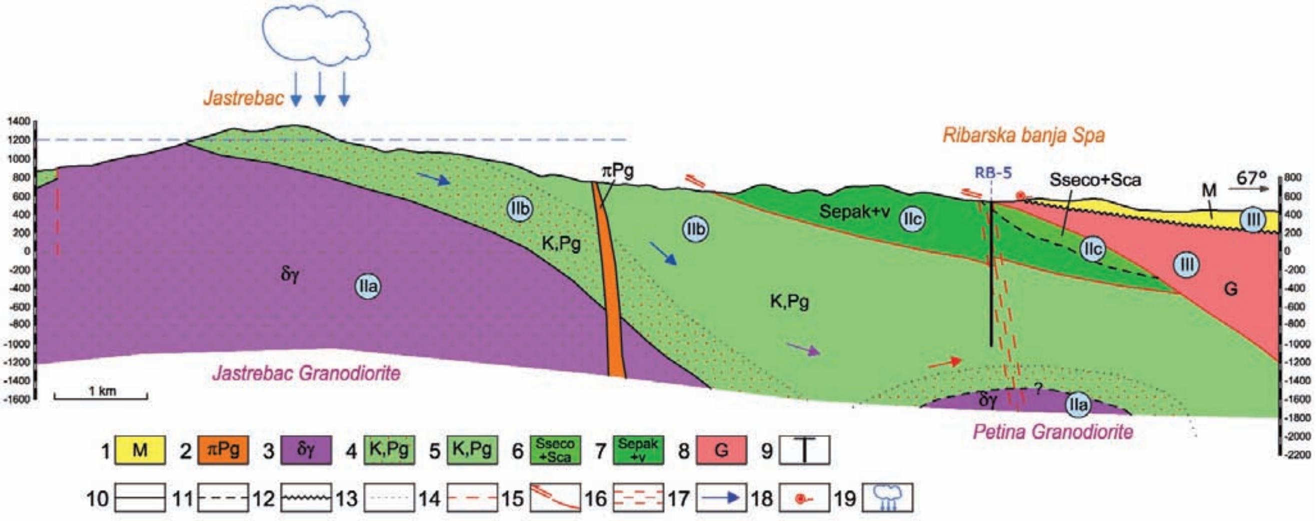

Fig. 2. Geological and hydrogeological section. Legend: **1,** Miocene sediments (clay, sand and gravel); **2,** Granodiorite-porphytite; **3,** Granodiorite; **4,** Contact-metamorphic Cretaceous-Neogene rocks; **5,** Cretaceous-Neogene rocks (phyllite, metasendstone, metasiltstone, conglomerate, sandstone); **6,** Sericite, quartz-sericite, sericite-chlorite schist (Sseco), calcschist and marble (Sca); **7,** Epidote-actinolite, epidote-chlorite and chlorite schists (Sepak) and gabbro (v); **8,** Gneiss; **9,** Well; **10,** Contact, certain; **11**, Contact, approximately located; **12,** Transgressive contact; **13,** Gradational contact; **14,** Fault, approximately located; **15,** Trust; **16,** Fault zone; **17,** Groundwater direction; **18,** Thermal spring; **19**, Recharge area. Hydrogeological units: **IIa,** fissured aquifer formed in granite rocks; **IIb,** fissured aquifer formed in K,Pg unit; **IIc,** fissured aquifer formed in metamorphic rocks (Sseco+Sca and Sepak+v); **III,** low permeable rocks.

ed along the way. The part of the aquifer below the local base of erosion (the stream of Banjski Potok) was previously drained via thermal springs featuring temperatures up to 38 °C. These springs were active until wells were drilled and these wells now drain the aquifer.

Fractured aquifers formed in granitoid rocks (IIa) and those formed in the lower and middle units of metamorphosed Upper Cretaceous-Paleogene rocks (IIc) feature poorer hydrogeological properties than those of the upper unit. Groundwater occurs at shallow levels of these rocks and the fracture porosity, and thus the water-bearing capacity, decreases with depth. Generally speaking, relative to the groundwater in the fractured aquifer of the upper unit (IIb), the granitoid rocks (IIa) constitute an underlying barrier while lower and middle units (IIc) constitute a barrier for the upward movement of groundwater whose temperature is generally elevated.

Low permeable rocks are comprised of Precambrian gneisses and Miocene sediments, spreading east and northeast of Ribarska Banja spa. The gneisses tend to be highly fractured and degraded near the ground surface, and may locally feature aquifers poor in groundwater. At some places, these aquifers are discharged via springs whose yield is less than 0.01 l/s. They often dry out during longer summer periods. In general, based on its hydrogeological properties, this rock complex is a barrier to the flow of groundwater from fractured or alluvial aquifers, and may be classified as impermeable or semi-permeable terrains.

In the vicinity of Ribarska Banja spa, Miocene sediments are mostly composed of clays with low water-bearing potential. Still, further east of the study area, exploratory drilling revealed artesian groundwater in the Miocene complex.

Hydrogeothermal resources of Ribarska Banja spa

According to the data available from previous research (LEKO *et al.* 1922; PROTIĆ 1995) thermal waters in Ribarska Banja spa were previously discharged naturally via a series of springs distributed along the stream of Banjski Potok, until the year 1969. The yield of these springs varied (0.05–1.5 l/s), as did the water temperature (16–38 °C). The main, hypsometrically lowest spring featured a water temperature of about 38 °C. The total yield of all thermal springs was some 2 l/s, which was insufficient for the needs of the "Special Hospital". This led to the drilling of several exploratory boreholes/production wells, from which thermal water has been exploited since 1970.

Boreholes are drilled in the zone of thermal water discharge along the route of one of the gravity faults (ŽIVANOVIĆ *et al.* 2010): RB-1 was 100 m deep (later replaced by well RB-5), RB-2 was 125 m deep and RB-3 was 278 m deep. All featured thermal water, pressures of 0.45, 2.75 and 3.2 bar, outflow capacities of 2.0, 9.0 and 7.0 l/s and exit water temperatures of 21 °C, 32 °C and 27 °C, respectively. Well CRB-1 was drilled nearby borehole RB-2, with a water temperature between 38 and 42 °C. The artesian flow of the well was 15 l/s and the initial water temperature was 41 °C. Once the exploitation of the well started in 1971, all the small springs in the stream of Banjski Potok valley dried out. Exploratory borehole RB-4 was drilled to a depth of 852 m. Water from this well is 41.5 °C. The well is used to fill the pools of the new Thermal Spa Center. Deepest well in the Ribarska Banja spa is RB-5 which was drilled at the location of the former shallow borehole RB-1, to a depth of 1543 m. Initial artesian flow was 10 l/s, featuring a water temperature of 54 °C and hydrostatic pressure of 5.85 bars.

Hydrodynamic research during the period from 2003 to 2013 included exploratory/production wells CRB-1, RB-3, RB-4 and RB-5 (Table 1). It should be noted that the thermal waters of RB-4 and RB-5 are in direct hydraulic contact. The table shows the artesian flows when all wells are operating.

Table 1. Hydrogeothermal resources of Ribarska Banja spa based on hydrodynamic tests conducted from 2003 to 2009 (ŽIVANOVIĆ & ATANACKOVIĆ 2013).

Well	Depth (m)	Max outflow capacity (l/s)	Temperature (°C)
CRB-1	163	9.5	38.7
RB-3	278	5.5	26.0
RB-4	852	3.3	41.5
RB-5	1543	9.2	54.0
		27.5	

Utilization of thermal water

All the four wells are in service: CRB-1 is used to fill balneotherapy pools, RB-3 and RB-4 to fill the pool of the new Thermal Spa Center, and RB-5 to heat the entire resort.

At its maximum capacity of 9.2 l/s, the heat energy of RB-5 is 0.89 MWt (for a temperature reduction by ΔT=23 °C). At the average annual rate of discharge of 5.8 l/s, 17.60 TJ/y is utilized. The utilization factor is 0.63. Similar utilization factors are calculated for other exploitation wells (Table 2). Total energy utilization at Ribarska Banja spa is 31.42 TJ/y, while the thermal power at current outlet temperatures is estimated to be 1.65 MWt. This amount of heat replaces 750.45 tons of oil equivalent, or 1072 tons of coal equivalent. The relatively high outlet temperature and relatively low utilization (capacity) factor indicate that the thermal water potential is not completely

Table 2. Utilization of geothermal energy for direct heat. Applied equations: Capacity (MWt) = Max. flow rate (l/s) x [inlet temp. (°C) - outlet temperature (°C)] x 0.004184; Energy use (TJ/y) = Ave. flow rate (l/s) x [inlet temp. (°C) - outlet temperature (°C)] x 0.1319; Capacity factor = [Annual energy use (TJ/y) x 0.03171] / Capacity (MWt)

Well	**T (°C)**		**Flow rate (l/s)**		**Capacity (Mwt)**	**Energy use (TJ/y)**	**Capacity Factor**
	Inlet	**Outlet**	**Maximum**	**Average**			
CRB-1	38.7	28.0	9.5	6.0	0.43	8.47	0.63
RB-5	54.0	31.0	9.2	5.8	0.89	17.60	0.63
RB-4	41.5	25.0	3.3	1.4	0.23	3.05	0.42
RB-3	26.0	21.0	5.5	3.5	0.12	2.31	0.64
Sum/Avr					**1.65**	**31.42**	**0.58**

exploited and that additional geothermal energy usage can be achieved by cascaded water utilization.

Water temperature to 54 °C, can be used for ponds, soil heating, melting snow, the production of alcohol, food, for greenhouses, for manufacturing furniture, cleaning wool and metal.

Methods

Chemical analyses of thermal waters sampled from wells RB-4, RB-5 and CRB-1 were performed in 2011 at the Federal Institute for Geosciences and Natural Resources (BGR) laboratory in Hannover. The samples were stored in polyethylene terephthalate (PET) bottles (0.5 L) with PET caps, filled completely. Chemical analyses were performed in the laboratories of the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover. The following techniques were used for the analyses: ICP-AES inductively coupled plasma atomic emission spectroscopy (Ca, K, Mg, Na, SiO_2), IC ion chromatography (Cl, F, SO_4), titration (HCO_3).

Well RB-3 was not available for sampling, so data from analysis performed at the Institute of Chemistry, Technology and Metallurgy (IHTM) laboratory in Belgrade in 2004. UV-VIS spectrophotometry was applied for SO_4, volumetric method for HCO_3, CO_3 and Cl, while AAS spectrophotometer was used for cations. For all samples, pH and temperature were determined in the field, and electroconductivity (EC) was determined by conductometric method. Results of chemical analysis are shown in Table 3.

Geothermometer calculations were made to assess rock temperatures within the reservoir. Silicon and cation geothermometers were used for the four deep wells: RB-3, RB-4, RB-5 and CRB-1 (Table 4).

Stable isotopes ^{2}H and ^{18}O were determined at the Technical University in Dresden on a mass spectrometer in 2011 (Table 5). V-SMOW2 and SLAP2 standards were applied.

RAD7 instrument was used for determining ^{222}Rn concentrations in the water samples. The activity concentrations of ^{226}Ra in the thermal water samples were also measured by the gamma-spectroscopy method and the results are shown in Table 5 (NIKOLOV *et al.* 2014).

Results and discussion

Hydrogeochemical properties of thermal waters. The thermal water samples at Ribarska Banja spa were found to be alkaline with a low EC (Table 3). According concentration of anion, it is apparent that the SO_4 and HCO_3 concentrations were roughly the same (in % eq), but that the deep wells (RB-4 and RB-5) featured higher SO_4 than HCO_3 concentrations, while HCO_3 was dominant over SO_4 in well CRB-1 and RB-3. Obviously at greater depths there are considerable inputs of SO_4, while closer to the surface HCO_3 dominates. Sulfur is widely distributed in reduced form as metallic sulfides (HEM 1985). Pyrite (FeS_2)

Table 3. Chemical analyses and stable isotopes of thermal water samples.

Sample	pH	EC (µS/cm)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	HCO_3 (mg/l)	CO_3 (mg/l)	SO_4 (mg/l)	Cl (mg/l)	SiO_2 (mg/l)	F (mg/l)
RB-4	9.1	417.0	88.5	1.5	1.9	0.03	111.0	6.0	92.9	1.78	43.6	2.05
RB-5	9.2	426.0	88.4	1.5	2.0	0.01	97.0	8.0	95.8	1.78	43.4	2.04
CRB-1	8.4	424.0	82.0	2.0	8.67	1.7	149.0	3.0	73.8	2.64	38.6	1.49
RB-3	8.0	360.0	72.5	1.6	18.4	4.0	165.0	3.6	65.1	10.7	35.0	

was found in a wide area around Ribarska Banja spa, which explains the high concentration of SO_4 in the groundwater there. Additionally, the cooler water samples were richer in Ca and Mg than those collected from the deep wells.

High concentrations of fluoride indicate the groundwater circulation through joints and faults in metamorphic and igneous rocks (PETROVIĆ *et al.* 2012). The geological source of fluoride in groundwater is related to the mineral composition of fluorite, fluoroapatite, cryolite, amphibolites and micas (DANGIĆ & PROTIĆ 1995; CHAE *et al.* 2007).

The chemical composition of Ribarska Banja spa water, make this water healing. Water is used in balneotherapy as a treatment aid for locomotor system disorders and conditions (such as rheumatism, bone and joint injuries, bone fractures and bone and joint surgery).

Solute geothermometry. The geothermometers applied (Table 4) indicated that higher temperatures may be expected in the geothermal reservoir than those detected to date in the deep wells. Chalcedony geothermometers suggested that the temperatures within the system were from 55 to 67 °C, closely matching the temperatures measured inside the well. Such temperatures were also indicated by the Na-K geothermometer (according to ARNÓRSSON *et al.* 1983). Temperatures calculated by Na-K geothermometers are not acceptable in this case because of the higher pH values and the groundwater temperatures below 100 °C. Results obtained by Na-K-Ca geothermometers are also not acceptable because of low compound of Ca and groundwater temperature. Significant temperature difference between shallower (CRB-1, RB-3) and deeper boreholes (RB-4 and RB-5) indicates the inflow of colder waters rich with Ca in the shallow boreholes.

It is generally believed that chalcedony, cristobalite and amorphous silica can control the solubility of silicon at low temperatures (FOURNIER 1977), although this is not always the case. All quartz geothermometers showed roughly the same temperatures (from 85 °C to 97 °C), regardless of the applied method. The reliability of quartz geothermometers is generally the highest at temperatures from 120 to 250 °C (ARNÓRSSON 2000), although if water has been in contact with rocks over a long period, quartz may control the solubility of silicates at temperatures below 100 °C (CHELNOKOV 2004). According to these geothermometers, the highest temperature was expected in wells RB-5 and RB-4 (about 95 to 97 °C).

Isotopic properties of thermal waters ($\delta^{18}O$, δ^2H, ^{222}Rn, ^{226}Ra). The isotopic composition were determined as between $\delta^2H = -77.12‰$ and $-77.43‰$, and $\delta^{18}O = -10.85‰$ and $-11.01‰$ (Table 5). Stable isotopes were used to determine the recharge of water. The stable isotope values of the wells at Ribarska Banja spa were distributed along the global meteoric water line, GMWL (CRAIG 1961), indicating recharge by atmospheric precipitation (Fig. 3).

Based on isotope values for geothermal water of Serbian Crystalline Core (PETROVIĆ PANTIĆ 2014), recharge zone of Ribarska Banja spa thermal water is defined above 1000 m a.s.l. The highest peak of Mt. Jastrebac-Đulica is at 1492 m a.s.l., suggesting that the geothermal system of Ribarska Banja spa is

Table 4. Determination of aquifer temperature by geothermometers (index q-quartz, ch-chalcedony). a) SiO_2 geothermometer (FOURNIER 1977); b) SiO_2 geothermometer (FOURNIER 1977); c) SiO_2 geothermometer (FOURNIER & POTTER 1982); d) SiO_2 geothermometer (FOURNIER & POTTER 1982); e) SiO_2 geothermometer (ARNORSSON *et al.* 1983); f) SiO_2 geothermometer (FOURNIER 1977); g) Na-K geothermometer (GIGGENBACH 1988); h) Na-K geothermometer (NIEVA & NIEVA 1987); i) Na-K geothermometer (FOURNIER 1979); j) Na-K geothermometer (ARNORSSON *et al.* 1983); k) Na-K-Ca geothermometer (FOURNIER & TRUESDELL 1973);

Well	T (°C)	T_q^a (°C)	T_q^b (°C)	T_q^c (°C)	T_q^d (°C)	T_{ch}^c (°C)	T_{ch}^f (°C)	T_{Na-K}^g (°C)	T_{Na-K}^h (°C)	T_{Na-K}^i (°C)	T_{Na-K}^j (°C)	$T_{Na-K-Ca}^k$ (°C)
CRB-1	38.7	90.1	92.4	90.6	91.0	61.4	59.4	140.2	108.9	119.9	84.9	62.7
RB-3	26.0	85.9	88.7	86.4	86.8	57.2	54.9	134.9	103.6	114.5	79.0	41.4
RB-4	41.5	95.5	97.1	95.9	96.2	66.8	65.1	121.6	90.3	100.8	64.4	86.6
RB-5	54.0	95.3	96.9	95.8	96.0	66.6	64.9	121.7	90.4	100.9	64.5	85.5

Table 5. Content of $\delta^{18}O$, δ^2H, ^{222}Rn, ^{226}Ra in Ribarska Banja spa water.

Sample	$\delta^{18}O$ (‰)	δ^2H (‰)	Activity concentration of ^{222}Rn (Bq/L)	Activity concentration of ^{226}Ra (Bq/L)
RB-4	–10.99	–77.33	42 ± 7	0.32 ± 0.19
RB-5	–11.01	–77.43	54 ± 8	0.48 ± 0.18
CRB-1	–10.85	–77.12	104 ± 15	0.26 ± 0.08

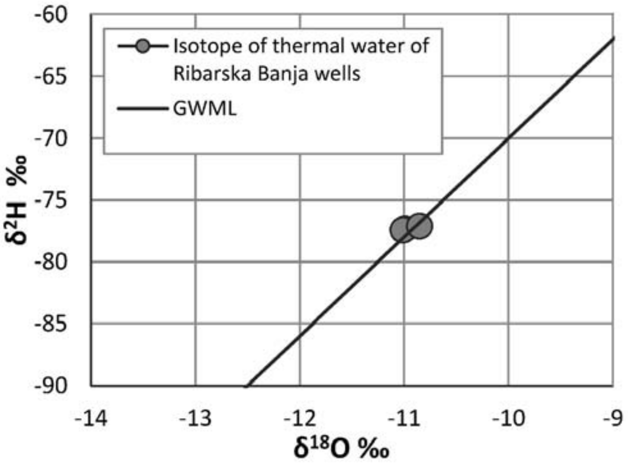

Fig. 3. The ^{2}H versus ^{18}O diagram for thermal water of Ribarska Banja spa (wells RB-4, RB-5 and CRB-1). Global world meteoric line GWML (CRAIG 1961).

recharged on Mt. Jastrebac within K–Pg contact metamorphic rocks. This is also confirmed by the low concentrations of ^{18}O and ^{2}H because low isotope concentrations are related to waters recharging in the winter months at high attitudes (HADŽIŠEHOVIĆ *et al.* 1995; KEBEDE *et al.* 2005).

Water from shallow well CRB-1 in Ribarska Banja spa has the highest concentration of ^{222}Rn, and the lowest concentration of ^{226}Ra. Opposite of this sample is sample from well RB-5 with the highest Ra and the lowest ^{222}Rn. ^{222}Rn is appear in fault and this is a reason why their concentration is highest from CRB-1 which is from fault zone in schist. High concentration of ^{222}Rn could indicate an active fault zone, as well known that area of Ribarska Banja spa is marked with neotectonic movement.

Geothermal potentiality. Based on temperature log at borehole RB-5 (H=1178 m), temperature gradient is 0,051 °C/m. The heat flow density is 163.5 mW/m^2 (PETROVIĆ PANTIĆ 2014) and heat conductivity of schist has been found to be 3.21 W/mK (MILIVOJEVIĆ & PERIĆ 1990). A significant geothermal potential of Ribarska Banja spa is indicated by the average value of geothermal gradient in the world ranging 0.025 to 0.03 °C/m (DICKSON & FANELLI 2004) and average Earth heat flow density of 91.6 mW/m^2 (DAVIES & DAVIES 2010).

At the area of Ribarska Banja spa 36 boreholes (from 20 to 100 m) were drilled (MILOVANOVIĆ 1978) in order to define thermal properties of rocks (PEROVIĆ *et al.* 1978) as well as the geothermal gradient and heat flow density of the wider area.

The map of heat flow density (Fig. 4) shows that the highest values of heat flow are observed south of the spa. The resulting value of the density of heat flow in the well RB-5 of 163.5 mW/m^2 corresponds to the density of heat flow in the area of the spa defined by interpolation of values from boreholes up to 100 m.

The depth of thermal water circulation can be determined based on the temperature at which groundwater is circulating (defined using geothermometers) and the geothermal gradient determined for a given area (ALLEN *et al.* 2006). Reliability of this method depends on selected geothermometers and reliability of temperature log.

The value of the geothermal gradient of 51 °C/km for Ribarska Banja spa is determined in the borehole RB-5. The temperature of 95.3 °C calculated on the basis of quartz geothermometers can be expected at the depth of 1.87 km. Borehole RB-5 is drilled to 1543 m, with a registered maximum temperature of about 80 °C, and therefore the depth of the thermal waters circulation of 1.87 km is quite realistic.

Hydrogeothermal system of Ribarska Banja spa. The Mt. Jastrebac granitoid has generally been identified in the literature as the heat source of the geothermal system of Ribarska Banja spa (MILOVANOVIĆ 1980). The reason for this is the location of the granitoid relative to the locations of the thermal springs, such that the hydrogeothermal system of Ribarska Banja spa is often referred to as the Mt. Jastrebac hydrogeothermal system. Based on K/Ar analyses, the granitoid was found to be of an Eocene age of 37 million years (ČERVENJAK *et al.* 1963). Numerous occurrences of vein rocks in the extended area of Mt. Jastrebac are indicative of the granitoid beneath sedimentary strata.

Geomagnetic investigations conducted in the Petina area northwest of Ribarska Banja spa have detected a large geomagnetic anomaly of an elliptical shape. The anomaly was caused by a granitoid intrusion at a depth of about 2000 m, below Upper Cretaceous-Paleogene and Neogene sediments. This intrusion was emplaced in the Post-Paleogene period, or in the final stage of magmatism (VUKAŠINOVIĆ 2005). As this is a young granitoid and given that overlying sediments prevent heat dissipation, it was assumed that the intrusive body was the heat source of the geothermal water. This assumption has been supported by negative values of gravitational anomalies (MILOJEVIĆ 2004) from Petina to Ribarska Banja spa, as a result of deposition of the tectonically fractured granitoid in a trench or, more likely, of undetected apophyses that may be part of the Mt. Jastrebac granitoid.

In magmatic areas, heat is most often transferred through contact-metamorphosed rocks or hard magmatic rocks. Based on the measured heat conductivity of 3.87 W/m°C (PEROVIĆ *et al.* 1978), contact-metamorphosed Upper Cretaceous rocks are the best heat conductors. In addition to this function, the complex also serves as a reservoir, such that thermal groundwater is stored within the faults and fractures of contact-metamorphosed rocks, from where they circulate to Ribarska Banja spa. Considerable amounts of water were found to be present in these fractures and faults. Water temperatures at the point of discharge measured

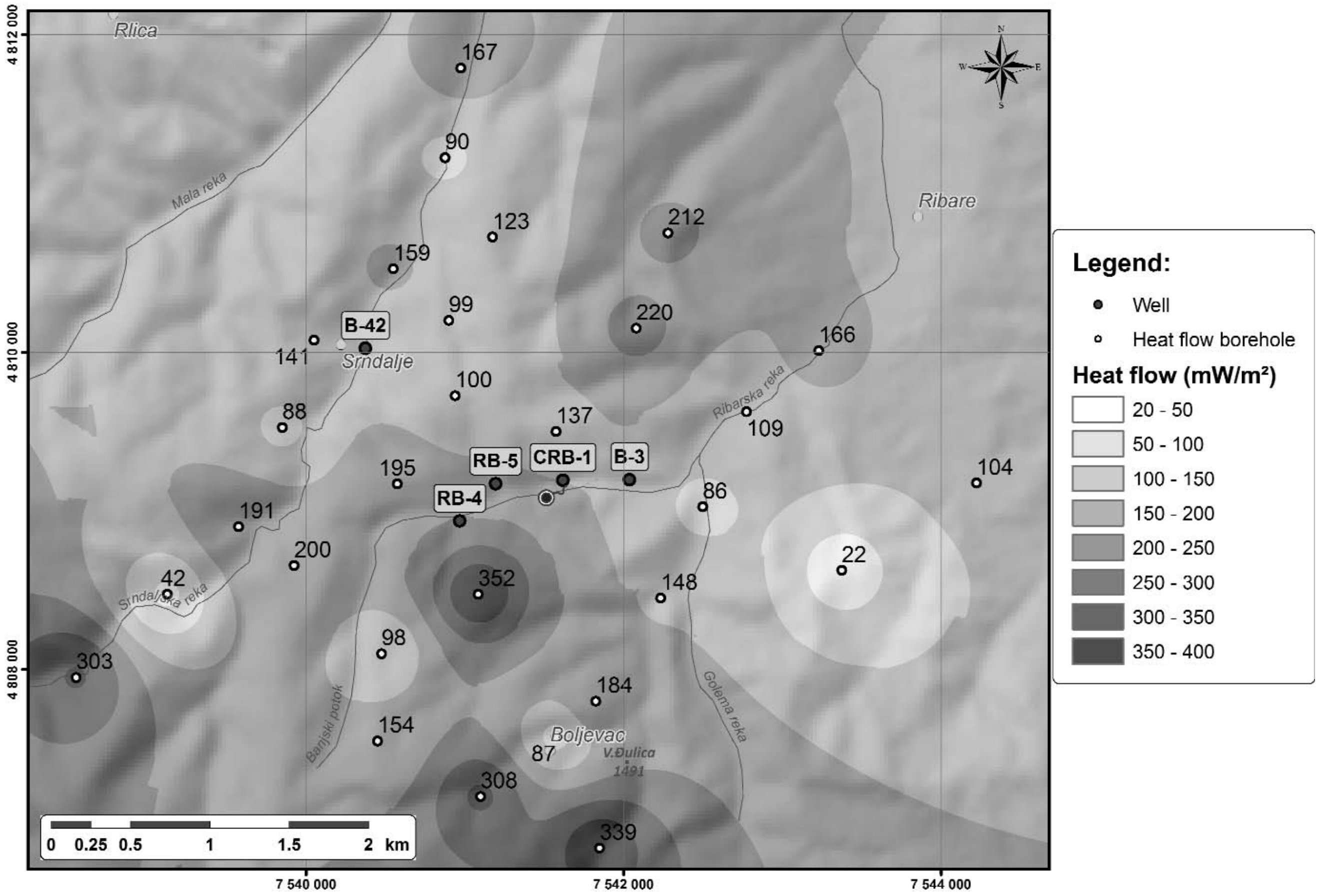

Fig. 4. Interpolated heat flow density map created using Inverse Distance Weighting (IDW) method (according to MILOVANOVIĆ 1978).

from 26 to 54 °C, while inside the reservoir, according to quartz geothermometer are expected to be up to 97 °C.

The overlying and lateral barriers of the hydrogeothermal system of Ribarska Banja spa are comprised of Lower and Middle Cretaceous-Paleogene rocks and gneisses. The heat conductivity of these rocks has been found to range from 2.14 to 3.18 W/mK (PEROVIĆ *et al.* 1978).

Based on research conducted to date, the main features of the hydrogeothermal system of Ribarska Banja spa may be defined as follows (Fig. 2):

- The system is recharged at Mt. Jastrebac, within K-Pg sediments, through precipitation infiltration;
- Contact-metamorphosed Upper Cretaceous rocks are good heat conductions of this system;
- Tectonic zones/systems of faults and fractures within the Upper Cretaceous contact-metamorphosed rocks are the reservoirs of the system;
- Lower and Middle Cretaceous-Paleogene rocks, gneisses and Neogene sediments constitute the system's hydrogeologic and temperature barrier;
- A granitoid intrusion at Petina, emplaced in the final stage of magmatism, is the heat source.

Conclusion

The hydrogeothermal system of Ribarska Banja spa was defined on the basis of structural geology, geophysical, geothermal, hydrogeological, hydrodynamic and hydrochemical research conducted in the narrow and extended zones of thermal water discharges. The research project reported in this paper has shown that the heat source is a younger granitoid intrusion in the Petina area, emplaced in the final stage of magmatism. The recharge zone is at high altitudes of Mt. Jastrebac, made up of Upper Cretaceous-Paleogene clastic rocks. Waters originating from atmospheric precipitation and small surface streams are infiltrated and circulate to Ribarska Banja spa along faults perpendicular to this rock complex. The upper hydrogeological and temperature barrier is comprised of metamorphosed rocks dominated by chlorite and chlorite-sericite schists, gneisses and overlying Neogene formations.

The resources of the hydrogeothermal system of Ribarska Banja spa amount to 27.5 l/s. Based on their chemical composition, these are oligomineral waters, where Na is the dominant cation. With regard to the anion composition, waters closer to the surface are of the HCO_3 type and with increasing depth they become

SO_4-HCO_3. In addition to balneotherapy and recreation, the quantity and quality of the hydrogeothermal resources can support heating of thermal spa facilities. Current energy utilization is 31 TJ/y, but estimated thermal capacity of 1.65 MWt and energy utilization factor of 0.58 indicates that additional geothermal energy can be used. Expected reservoir temperatures of about 97 ºC, can be expected at a depth of 1.87 km. Geothermal gradient is 0.051 ºC/m, while heat flow density is 163.5 mW/m^2.

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Резиме

Хидрогеотермалне карактеристике подземних вода Рибарске Бање, централна Србија

Рибарска Бања се налази у централном делу Србије, на северо-источним падинама Великог Јастребца. У геолошкој грађи терена доминирају зелени шкриљци. Западно од Рибарске Бање утиснут је Јастребачки гранитоид, док се северо-источно пружају миоценски седименти. У хидрогеолошком погледу издвајају се следеће издани: алувијална и пукотинска. Највеће количине вода добијене су из пукотинске издани формиране у горњем пакету слабо метаморфисаних стена кластичног карактера.

У бањи тренутно постоје четири бушотине (од 163 до 1543 m) из којих се експлоатишу подземне воде, максималаног капацитета 27,5 l/s, температуре од 26 до 54 °C. Применом кварцних геотермометара, очекивана температура резервоара подземних вода је у опсегу од 85 до 97 °C и та температура се може очекивати на дубини од 1,87 km. По хемијском саставу воде су маломинерализоване, алкалне, SO_4-Na или HCO_3-Na са повишеним садржајем флуора. У раду су примењене и изотопске анализе. На основу изотопа δ^2H и $\delta^{18}O$ прихрањивање подземних вода се врши падавинама и отапањем снежног покривача на висинама изнад 1000 м.н.в, што одговара планини Велики Јастребац. Највиша концентрација ^{222}Rn одређена је у води из бушотине ЦРБ-1 где је вода захваћена из раседне зоне.

Проучавањем геотермалног потенцијала Рибарске Бање, само у бушотини РБ-5, добијена вредност геотермалног градијента износи 0,051 °C/m, док је густина топлотног тока 163,5 mW/m^2. У раду је дефинисан хидрогеотермални систем Рибарске Бање, тако са су дати следећи елементи система:

- прихрањивање се врши на планини Јастребац, у оквиру K-Pg седимената, инфилтрацијом атмосферских вода;
- добри проводници топлоте у систему су контактно-метаморфне стене горње креде;
- тектонске зоне, системи раседа и пукотина у оквиру контактно-метаморфних стена горње креде представљају резервоаре система;

- баријеру система (хидрогеолошку и температурну) представљају стене доњег и средњег кредно-палеогеног комплекса, гнајсеви и неогени седименти;
- извор топлоте представља гранитоидни интрузив код Петине (северо-западно од бање), утиснут у последњој фази магматизма.

Термалне воде се вишенаменски користе, за пуњење базена, за загревање објеката, као санитарна топла вода. Укупна енергија искоришћења Рибарске Бање је 31,42 TJ/y са термалним капацитетом од 1,65 MWt и фактором искоришћења од 0,58.