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Geochemical characteristics of thermal waters of Hrvatsko zagorje

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ABSTRACT

In the region of Hrvatsko zagorje there are a lot of spa localities. The study area is in the northern Pannonian part of Croatia which is characterized by a high geothermal gradient (0.049 °C/m) and surface heat flow (76 mW/m^2). Although there are a lot of thermal occurrences in the study area, only ten were taken into consideration because there was a lack of geochemical data at other locations. The thermal springs considered are: Harina Zlaka, Krapinske toplice, Tuheljske toplice, Stubičke toplice, Sutinske toplice, Šemničke toplice, Topličica (Mađarevo), Topličica (Gotalovec), Podevčevo, Vraždinske toplice. A compilation of geochemical data from different sources together with our own measurements has been used in this study. The aim of this paper is to review the thermal waters' geochemical characteristics and demonstrate how these features can be used to discern their origin and the aquifer they equilibrated with. The geochemical characteristics of thermal waters of the study area suggest that the water is in equilibrium with dolomite which means that dolomite is the thermal aquifer in the study area.

Keywords: thermal water, groundwater temperature, chemical composition, water type, Hrvatsko zagorje

1. INTRODUCTION

Hot water occurring at the earth's surface has been a subject of awe since the dawn of humankind. Ancient civilizations revered thermal springs because they were believed to have supernatural and healing powers (ROUTH et al., 1996; LAMOREAUX & TANNER, 2001). Thermal waters are increasingly being used in the world for industrial processing, agriculture production, heating, electricity production and the extraction of rare elements (ATKINSON & DAVIDSON, 2002; HELLMAN & RAMSEY, 2004; PETRACCIA et al., 2005; LUND, 2006; HAEHNLEIN et al., 2010). Moreover, with the increasing popularity of spas and the growing importance attached to the 'natural' health industry, thermal waters are becoming a valuable asset for centres of hydrotherapy (ROUTH et al., 1996; LUND, 1996; MAROVIĆ et al., 1996; HARVEY, 2007; BITUH et al., 2009). Thermal waters are thus a natural resource that could make considerable contribution to the local and regional economy. However, care should be exercised when making decisions regarding the appropriate use of thermal waters. Croatia is relatively richly endowed with thermal waters and their utilization has been a tradition for millennia.

Hrvatsko zagorje is a region situated in the north-western part of central Croatia (Fig. 1). It stretches between the Croatian-Slovenian borderline and the Medvednica and Kalnik Mountains. Most of the region is characterized by undulating relief, especially the foothills of Ivanščica Mt., populated since antiquity. A "corrugated relief" with multiple interconnected mountains and valleys has always been an obstacle for the construction of meaningful transport networks in the area. The region sees a daily workforce migration to the national capital Zagreb, but it is also a traditional recreational area for many citizens of Zagreb, who visit its numerous spa resorts (ROGLIĆ, 1974).

The number of spa localities in Hrvatsko zagorje is high, and they are densely distributed across the region. The simple indicator of this situation is the sheer number of toponyms „toplica" (singular) or „toplice" (plural), meaning ther-

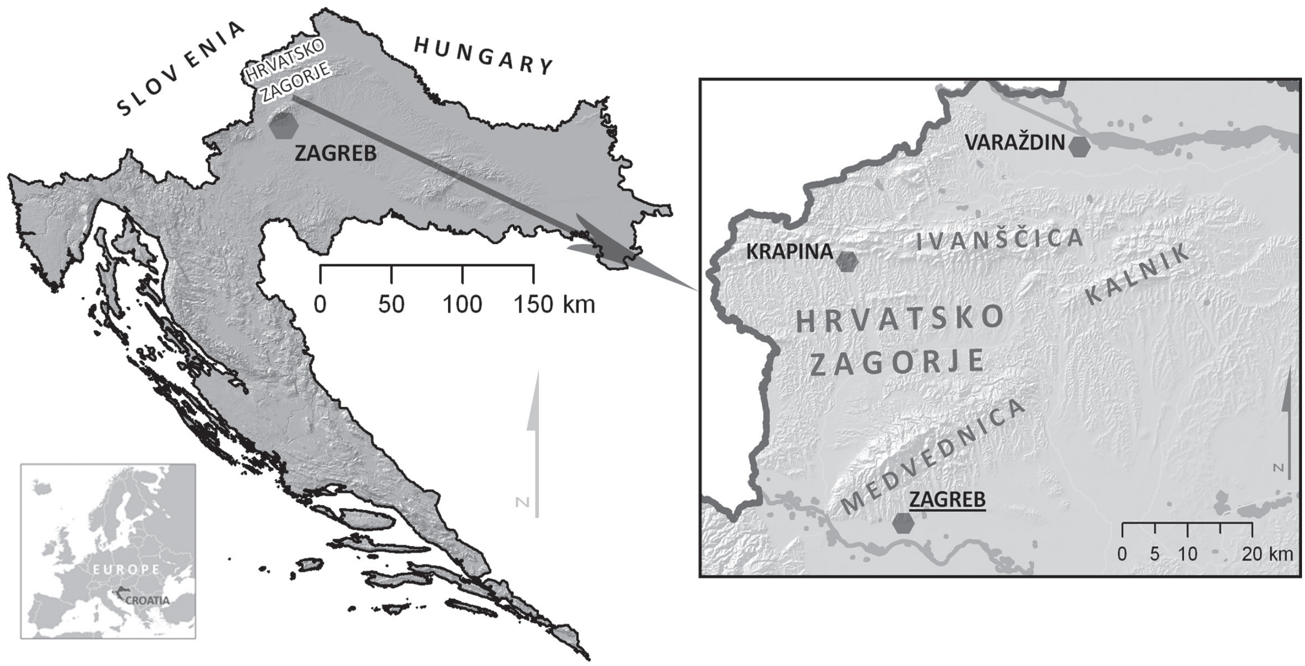


Figure 1: The location of the Hrvatsko zagorje region in Croatia.

mal water spring(s), and „topličica“ meaning little thermal water spring (with little referring to the lower temperature of the water, not its quantity). Some of the localities were utilized even in prehistoric time, and in ancient Roman time they were already established as curative destinations, especially *Aquae Iassae* (Varaždinske Toplice) with it's numerous upright archaeological remains and *Aquae Vitae* (Krapinske Toplice). Even the Roman name of the Pannonian tribe populating this area (lat. Iassi) is derived from the supposedly curative properties of thermal waters because the root ias- or iat-came from the ancient Greek language meaning to heal or cure (SCHEJBAL, 2003).

The temperatures of the thermal waters in Hrvatsko zagorje vary from 16 to 65 °C. There are many available scales to classify thermal resources and thermal springs. According to all of the geothermal resource classifications (e.g. AXELSSON & GUNLAUGSSON, 1978; MUFFLER & CATALDI, 1978; UNGEMACH & ECONOMIDES, 1987; BENDERITTER & CORMY, 1990; HOCHSTEIN, 1990; NICHOLSON, 1993; SANYAL, 2005) these resources at Hrvatsko zagorje are considered low enthalpy resources. Due to their relatively low temperatures, the classifications for thermal springs are more appropriate. These classifications vary significantly, because they use different benchmark values for identifying cold, warm and hot springs. It is common to classify the springs as warm if their temperature is lower than that of the human body, and hot if it is higher (e.g. DEMING, 2002; KREŠIĆ, 2010). Some authors have also considered the lower boundary for classifying waters as thermal, taking e.g. 20 °C which is a limit for balneological purposes (HARAMUSTEK et al., 1952; IVEKOVIĆ & PEROŠ, 1981) or the temperature which disables ice formation at the rim of the spring, around 15 °C (ĐUROVIĆ, 1960). From the hydrogeological point of view however, all groundwaters with temperatures higher than the average rainwater temperature (approximately the mean annual temperature of the locality) are considered thermal, although they cannot be used in balneology. Since the climate of the investigated region is C_{fwbx}” according to the Köppen classification (GAJIĆ-ČAPKA & ZANINOVIĆ, 2008) – a temperate (C) humid (f) climate with no extremely dry periods throughout the year, and the annual mean temperature of the region varies between 7–8 °C at the highest mountains and 10–11 °C in the valleys (GAJIĆ-ČAPKA & ZANINOVIĆ, 2008) – in a hydrogeological sense all groundwaters with temperatures higher than this average are considered thermal. In this paper the waters have been categorized according to the modified balneological classification (Tab. 1). It was created on the basis of the traditional Croatian balneological classification (HARAMUSTEK et al., 1952), which actually stemmed from much earlier considerations of German and Swiss medical balneology experts (JACOBJ, 1907; HINTZ & GRÜNHUT, 1916; HARTMANN, 1925). The modification was applied to the lower part of the scale, thus including the waters where the temperature is higher than the annual mean, but lower than that required in balneology.

Table 1: Categorization of thermal localities in Croatia on the basis of water temperature (adopted from KOVAČIĆ & PERICA, 1998).

Category	SUBTHERMAL	HYPOTHERMAL	HOMEOTHERMAL	HYPERTHERMAL
Temperature	13–20 °C	>20–34 °C	>34–38 °C	>38 °C

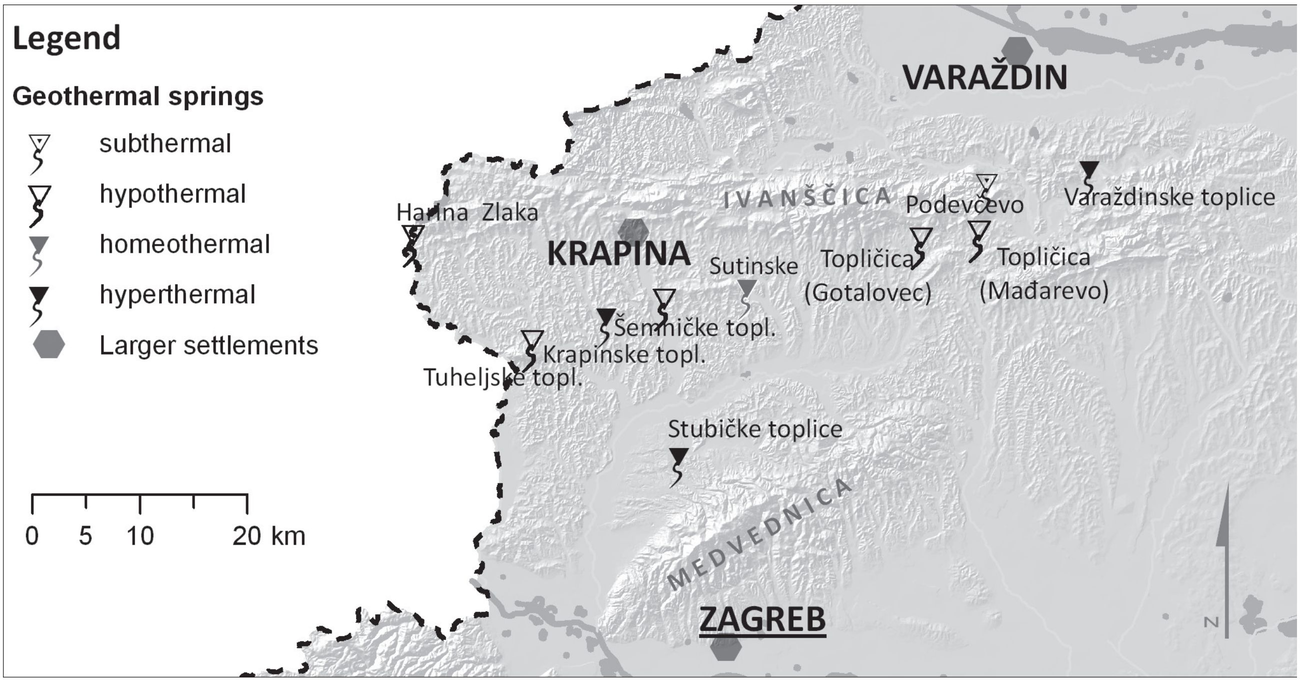


Figure 2: Locations of the thermal springs described in the paper.

The waters considered here range from subthermal to hyperthermal. The modes of utilization vary according to the temperatures, e.g. waters of the lowest temperatures are used for the public water supply, bottling and fish farming, while waters of the highest temperatures (40–65 °C) are utilized for water and space heating.

According to its geothermal characteristics, Croatia can be divided into two parts where the mean values of the important geothermal parameters vary significantly. The northern Pannonian part is characterized by a high geothermal gradient (0,049 °C/m) and surface heat flow (76 mW/m^2), while the southern Dinaric part has a low average geothermal gradient (0,018 °C/m) and surface heat flow (29 mW/m^2) (BOŠNJAK et al., 1998). In accordance with these characteristics, many locations where thermal springs exist are located in the northern part of Croatia where the groundwater receives enough heat from its surroundings.

Attempts to explain the appearance and origin of the thermal springs in Croatia date back as far as the 18th century. Many geologists at those times were studying the warm springs of Hrvatsko zagorje owing to their unusual density in the region, and they postulated a number of different hypotheses to explain their occurrence. For example, in the beginning of 20th century Dragutin Gorjanović-Kramberger was convinced that the thermal waters of north-western Croatia were of volcanic origin with magma chambers heating the waters and deep faults, so called "thermal lines", bringing them to the surface. The main shortcoming of this hypothesis is that there are no recent magmatic bodies to supply heat, but because of Gorjanović-Kramberger's authority it still has a fair number of supporters (ŠIMUNIĆ, 2008). The idea that thermal waters could be of meteoric origin and then heated during circulation through the subsurface first appeared in the works of Gjuro Pilar at the end of 19th century and is still supported by all the evidence. Until now, it has been proven that all significant thermal springs in the Pannonian part of Croatia are located in the tops of anticlines which were fractured by faults of SW – NE or N – S strike. The intersections of faults and folds usually represent a strongly fractured environment of high permeability which enables the upwelling of heated water at depth to the surface (ŠIMUNIĆ, 2008). The geochemical studies of HORVATINČIĆ et al. (1991; 1996) proved that the thermal waters of the Hrvatsko zagorje area are of meteoric origin. In other papers, the geochemical characteristics of some springs in the research area have been studied and all data point to a meteoric origin (MIHOLIĆ, 1940a, 1952, 1959; MAROVIĆ et al., 1996; MARKOVIĆ & KOVAČIĆ, 2006; BITUH et al., 2009; POLANČEC, 2011).

The aim of this paper is to review the thermal waters' geochemical characteristics and demonstrate how geochemical features of thermal waters can be used to discern their origin and the aquifer they equilibrated with. Although there are lots of thermal occurrences in the study area, only ten were taken into consideration because there was a lack of geochemical data at other locations. The thermal springs considered are: Harina Zlaka, Krapinske toplice, Tuheljske toplice, Stubičke toplice, Sutinske toplice, Šemničke toplice, Topličica (Mađarevo), Topličica (Gotalovec), Podevčevo and Vraždinske toplice (Fig. 2).

2. HYDROGEOLOGICAL SETTINGS

In Harina Zlaka (Fig. 2) there was a natural thermal spring with a water temperature of 32.8 °C (MIHOLIĆ, 1940a). The spring dried up after 1966, following exploitation of thermal water from the well on the opposite bank of the Sutla River for the Atomske toplice spa in Podčetrtek, Slovenia. The well is drilled in the carbonate sediments (dolomites). In 1998, near the dried up spring, the well HZL-1 was drilled, also in dolomites. It has been tested with a yield of 45 L/s, and the water temperature at the wellhead was 19–20 °C (MRAZ & KRSNIK, 2005).

Thermal springs of Krapinske toplice (Fig. 2) occur in a narrow valley of the Topličica stream and there are three main springs and a few springs of lower yield. The main occurrence of thermal springs is in the area of Pučke and Jakobove kupelji. The total measured yield of all springs in Krapinske toplice, according to BAĆ & HERAK (1962), ranges from 69 to 81 L/s. The majority of springs occur along the boundary between the dolomite and limestone. In 1985 a deep well was drilled about 250 m north from the thermal springs. The well passed through limestone and dolomite before it ended up in calcarenites and shale at a depth of 861 m (ŠIMUNIĆ, 1986). The well was tested with a yield of 30 L/s and the water temperature was 45 °C. Thermal waters in Krapinske Toplice are used for recreation, balneotherapy, space heating and sanitary water.

Tuheljske toplice springs (Fig. 2) are located nearby at the Krapinske toplice thermal water source, 4.5 km to the southeast. The surrounding area of Tuheljske toplice consists of limestone, dolomite, sandstone, marl, clay, gravel and sand. Thermal springs are ascending springs and they occur in several places, from which the most important are the Dadino vrelo and Vrelo u bari springs. The total yield of the thermal springs was 85 L/s (BAĆ & HERAK, 1962) and the temperature varies from 32.5 to 33.1 °C. These thermal waters have so far only been used for recreational purposes.

Stubičke toplice springs (Fig. 2) are located on the northern side of Medvednica Mt. They had consisted of two major and several smaller springs, but they dried up when deep wells were drilled and put into operation. Spring water temperature varied from 30 to 49.8 °C and the water in the wells has a temperature of 65 °C. The yield of the springs was 18 L/s (BAĆ & HERAK, 1962). The surrounding area of the Stubičke toplice springs comprises clastic carbonate sediments, dolomite, alluvial, proluvial-deluvial deposits and siliciclastic rocks. Today thermal water from the wells is used for recreation, balneotherapy, water and space heating, sanitary water and greenhouse heating, and it is the locality with most diversified utilization of geothermal waters in Croatia (BOROVIĆ & MARKOVIĆ, 2015).

Thermal springs of Sutinske toplice (Fig. 2) are located in the canyon of the Sutinska stream. Water temperature ranges from 30 to 37.4 °C and the water emerges from fractured dolomites. In 1988 a well was drilled in the southern exit of Sutinska canyon and a dolomite aquifer was detected in the interval between 75 – 385 m. A pumping test was carried out resulting in a yield of 112 L/s and the water temperature at the wellhead varied from 38 to 39 °C (BRITVIĆ, 1988). The water had been used for a swimming pool during the summer, but it was closed in the summer of 2013.

The Šemničke toplice springs (Fig. 2) are located near to the Krapinske toplice thermal water source, 9 km to the northwest. The yield of the thermal spring is 0.5-1.0 L/s and the water temperature ranges from 31 to 33.1 °C. The well was drilled in the vicinity of the springs and carbonates were found. The well was pumped with the yield of 20 L/s, and the water temperature varied from 33 to 36°C (CAPAR, 1982). The thermal water of Šemničke toplice is not currently being utilized.

The Topličica springs in Mađarevo (Fig. 2) occur at the foot of the steep slopes of the Ivanščica massif near Novi Marof. There are four major springs and several smaller ones. The water temperature is inconsistent: during the summer it varies from 18 to 22.5 °C, and during winter temperatures are lower. Significant fluctuations in temperature and yield indicate mixing of cold and thermal water. The total yield of all the springs has not been measured. Thermal water is used for heating a fish farm nearby and for recreation in the summer.

The Topličica spring in Gotalovec (Fig. 2) is located on the southern slopes of the central part of the Ivanščica massif. The yield of the spring ranges from 15 to 18 L/s and the water temperature is from 25 to 26 °C. The spring occurs at the contact between the fractured dolomite aquifer and eruptives and clastic sediments. The water is being used for bottling as natural spring water.

In Podevčevo (Fig. 2) there are two thermal springs, with variable temperatures, from 16.3 to 20.0 °C depending on the hydrological cycle. The aquifer is fractured dolomite. The total yield of both springs does not exceed 1 L/s. The springs are not used.

Varaždinske toplice springs (Fig. 2) are located in the north-eastern corner of the study area, nearby the town of Varaždin. They are among the best known, are the largest spas in Croatia and have been used for the longest time. The water temperature varies from 56.5 to 57.5 °C and the yield ranges from 45 to 50 L/s. The thermal waters occur in the brecciated dolomites which are covered by clastic sediments (ŠIMUNIĆ, 2008). The largest spring in Varažidnske toplice is Klokot, accompanied by three smaller hypothermal springs with temperatures of 24–25 °C. There are also a lot of wells. Thermal waters from the spring and wells are used for recreation, balneotherapy, water and space heating (BOROVIĆ & MARKOVIĆ, 2015).

3. MATERIALS AND METHODS

A compilation of geochemical data from different sources has been used in this study, including chemical analyses by MIHOLIĆ (1952) and JURŠIĆ-MITROVIĆ (2001), and chemical analyses performed during research for the Basic Hydrogeological Map sheets Rogatec and Varaždin in October 2009. From a total of 32 analyses, 10 analyses were performed by MIHOLIĆ (1952), 10 by JURŠIĆ-MITROVIĆ (2001) and 12 analyses were performed in the scope of the research for the Basic Hydrogeological Map. The samples taken during research for hydrogeological map were analysed at the Hydrochemical laboratory of the Department of Hydrogeology and Engineering Geology of Croatian Geological Survey. Prior to sampling, the electrical conductivity (EC), pH and temperature (T) were determined using portable WTW probes. Total alkalinity was measured by titra-

Table 2: Mean, minimum and maximum values of physicochemical parameters in observed thermal waters.

		Harina Zlaka	Krapinske toplice	Tuheljske topliice	Stubičke toplice	Sutinske toplice	Šemničke toplice	Topličica Mađarevo	Topličica Gotalovec	Podevčevo	Varaždinske toplice
EC(µS/cm)	mean	635	519	623	627	515	532	568	422	675	1206
	min	597	438	620	610	510	522	539	403	672	1176
	max	655	566	627	653	520	545	596	440	678	1235
T(°C)	mean	24.2	41.8	32.8	53.9	34.9	32.7	23.0	25.6	17.7	54.2
	min	19.8	40.2	32.5	47.0	34.0	32.5	22.5	25.5	16.0	51.2
	max	32.8	45.0	33.1	65.0	35.7	33.1	23.4	25.7	19.4	57.2
pH	mean	7.4	7.1	7.3	7.0	7.2	7.4	7.3	7.3	7.8	6.7
	min	7.4	7.0	7.3	6.7	6.9	7.4	7.3	7.2	7.6	6.6
	max	7.5	7.3	7.4	7.3	7.5	7.5	7.3	7.3	8.0	6.8
Na^+(mg/l)	mean	7.2	11.4	11.3	25.3	5.0	9.7	3.2	4.3	26.1	86.2
	min	2.8	9.1	10.9	20.8	3.8	6.3	2.4	3.4	22.6	76.8
	max	14.0	17.0	11.8	28.5	6.2	11.8	4.0	5.2	29.6	95.6
K^+(mg/l)	mean	2.3	3.3	3.0	6.3	1.7	3.0	1.6	1.9	9.4	32.1
	min	2.0	2.8	2.9	4.6	1.6	2.9	0.9	1.0	9.3	23.2
	max	2.9	3.5	3.1	7.3	1.8	3.1	2.2	2.8	9.6	40.9
Ca^{2+}(mg/l)	mean	68.7	54.9	63.8	66.9	65.2	61.5	62.3	60.9	58.8	126.2
	min	61.9	52.4	63.2	61.0	53.7	57.6	53.7	55.8	56.6	125.1
	max	75.3	58.2	64.6	71.7	76.6	63.7	70.9	65.9	60.9	127.3
Mg^{2+}(mg/l)	mean	36.0	30.7	36.9	25.4	29.8	39.0	30.4	24.7	32.8	28.3
	min	31.8	27.8	34.9	23.1	26.6	37.9	26.8	21.6	29.6	27.3
	max	44.1	35.1	38.0	30.2	33.0	41.0	33.9	27.8	36.0	29.2
HCO_3^- (mg/l)	mean	362.0	296.3	367.9	281.8	288.1	355.6	328.2	292.1	341.3	454.4
	min	333.8	280.6	364.8	262.3	288.0	330.9	298.0	288.2	338.0	445.3
	max	407.5	330.9	371.0	300.4	288.2	371.0	358.3	296.0	344.7	463.5
SO_4^{2-} (mg/l)	mean	25.7	37.3	37.6	88.3	31.3	40.6	20.6	14.7	71.0	168.6
	min	15.6	35.3	35.2	80.2	27.9	38.2	15.8	13.1	61.9	155.8
	max	39.7	39.7	39.4	97.9	34.8	44.2	25.4	16.3	80.0	181.5
Cl^-(mg/l)	mean	7.7	3.1	3.5	12.1	3.9	3.6	3.4	6.1	14.3	82.8
	min	3.4	2.5	2.6	9.6	1.5	2.6	3.1	5.9	12.5	79.0
	max	10.7	3.7	5.0	13.9	6.2	5.3	3.7	6.4	16.2	86.6
Number of samples		3	5	3	4	3	3	3	3	2	3

tion with 1.6 N H_2SO_4 using phenolphthalein and bromcresol green – methyl red as indicators. Anions (SO_4^{2-} and Cl^-) were measured by ion chromatograph (LabAlliance Ltd) and dissolved cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) by atomic absorption spectrophotometer (Perkin Elmer Analyst 700).

The NETPATH-WIN program (EL-KADI et al., 2010) was used to calculate saturation indices of the observed waters with respect to the calcite and dolomite mineral phases and CO_2 partial pressure (pCO_2).

4. GEOCHEMICAL CHARASTERISTICS

In Table 2 the minimum, maximum and mean values of observed geochemical parameters in thermal waters of ten investigated water sources are given.

The mean water temperatures ranged from 19.2 to 54.2 °C. The highest value is observed in Varaždinske toplice and the lowest in the water of Podevčevo spring (Tab. 2). According to the temperature categorization by KOVAČIĆ & PERICA (1998), the spring water in Podevčevo is subthermal; water from Sutinske toplice is homeothermal; waters from Harina Zlaka, Tuheljske toplice, Šemničke toplice, Topličica (Mađarevo) and Topličica (Gotalovec) are hypothermal and waters from Stubičke toplice, Krapinske toplice and Varaždinske toplice are hyperthermal.

The mean pH values ranged from 6.7 to 7.8 (Tab. 2). The lowest value is observed in the waters from Varaždinske toplice (acid) and the highest is observed in the water of Podevčevo spring (alkaline). In Stubičke and Krapinske toplice lower pH values in waters are also observed. The pH is controlled by dissolution of gases (such as CO_2, H_2S, NH_3, CH_4) which are entering the aquifer system and geochemical processes such as the synthesis and mineralisation of biomass, redox processes etc. in the aquifer. The higher the amount of dissolved gases in the aquifer system, the lower the pH value will be. From the water quality monitoring of the Special Hospital for Medical Rehabilitation Varaždinske toplice (SPECIAL HOSPITAL, 2014) a high amount of H_2S (10.4 mg/l) in thermal waters has been observed. Furthermore, in the waters from Stubičke toplice a high content of CO_2 is observed - 101.49 mg/l (HOSPITAL STUBIČKE TOPLICE, 2014) and H_2S is also detected in the water from Krapisnke toplice (HOSPITAL KRAPINSKE TOPLICE, 2014). Also, the contribution of H^+ ions during the geochemical processes in the aquifer should not be dismissed. For example during the redox process H^+ ions occur, e.g. $FeS_2 + 3.75\ O_2 + 1.5\ H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+$ (pyrite oxidation).

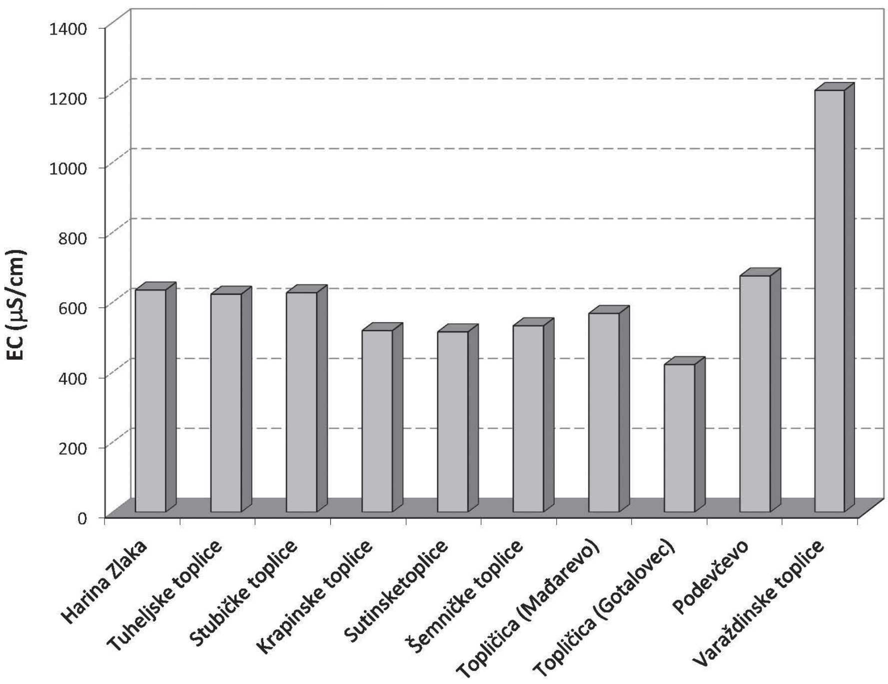


Figure 3: Distribution of mean EC values.

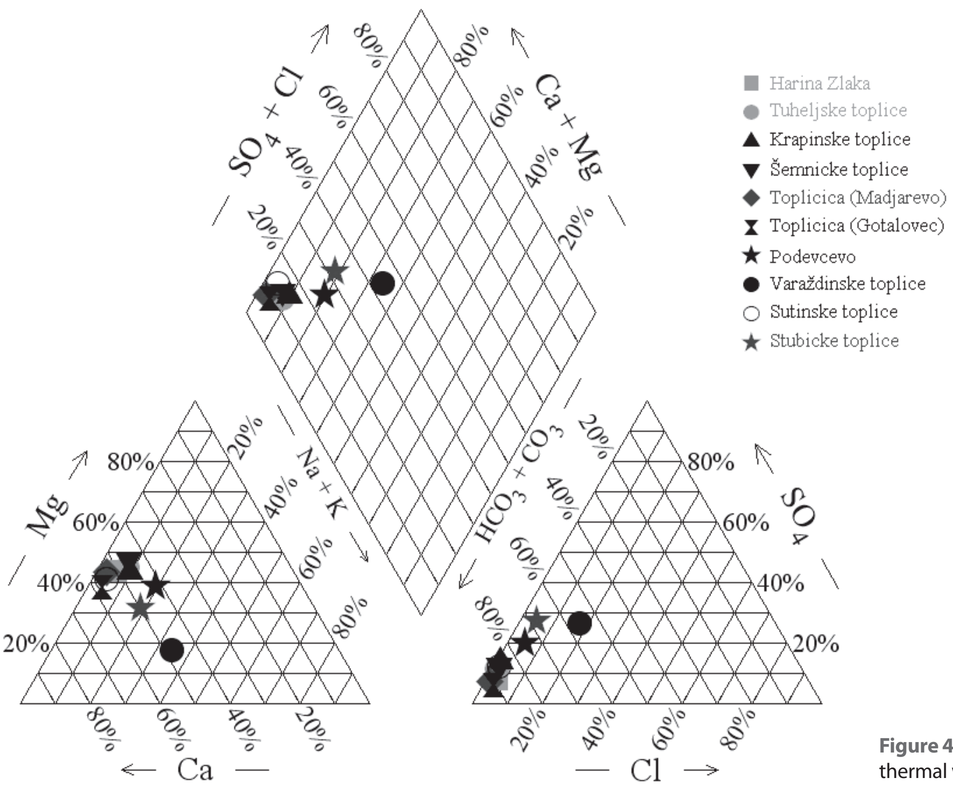
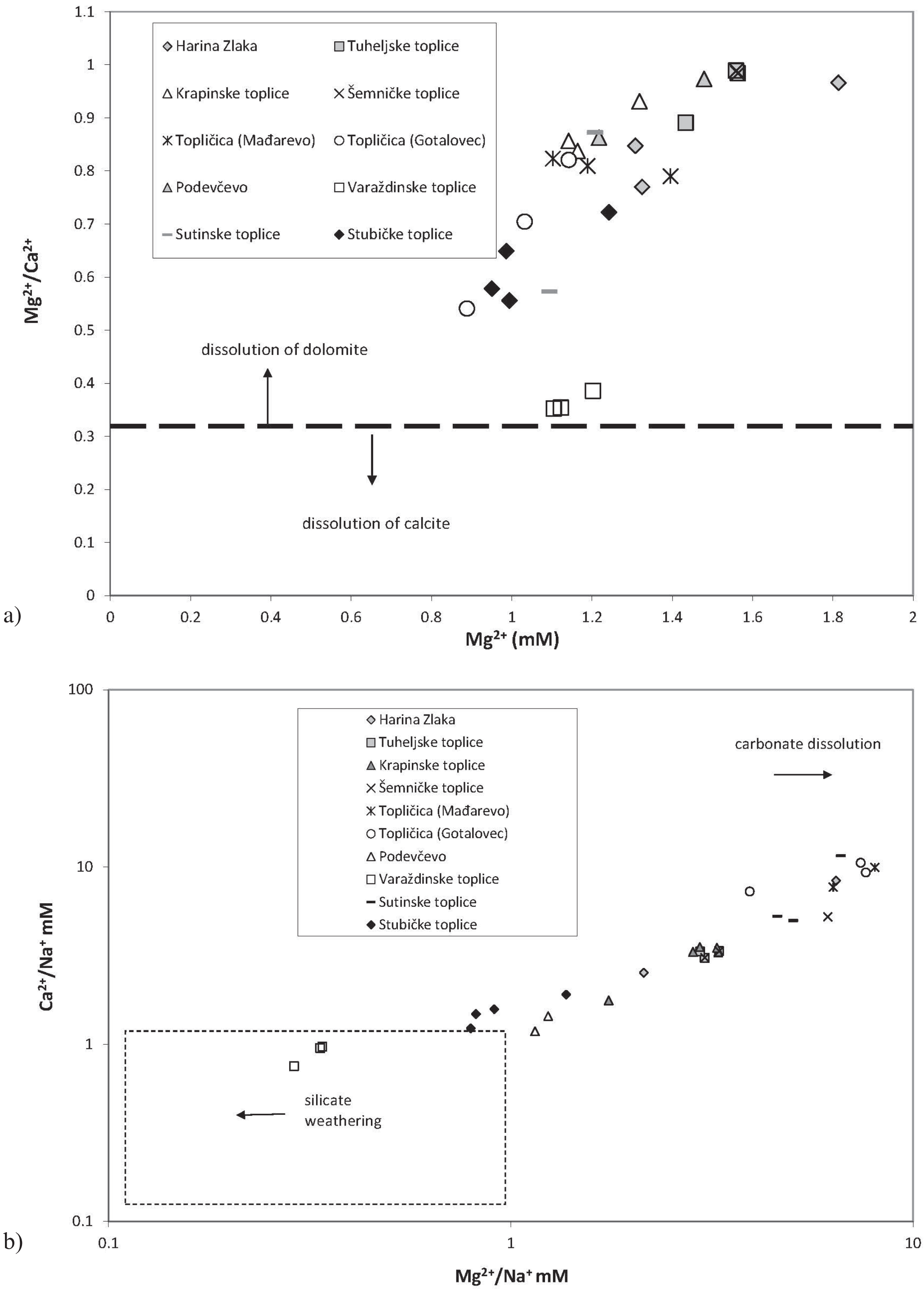


Figure 4: Piper diagram of major constituents in thermal waters.

The highest EC value is observed at the Varaždinske toplice springs, with a mean value of 1205 μS/cm, while the lowest value is observed at the Topličica (Gotalovec) spring, with a mean 422 μS/cm (Fig. 3). It is visible from Fig. 3 that some of the waters have similar EC values, e.g. waters from Harina Zlaka, Tuheljske and Stubičke toplice. In the next group there are waters from Sutinske, Krapinske and Šemničke toplice, with Topličica (Mađarevo) close to them. Podevčevo spring waters lie between the last group and the highest EC value. The EC value is influenced by the amount of dissolved solids in the water. If the water contains a high amount of dissolved solids, the EC values will be higher, and vice versa. The amount of dissolved solids in the water is controlled by numerous factors. The type of rock mass which constitutes the catchment area of the spring is one of the important factors. If a rock mass of high solubility (e.g. limestone, volcanic ash) constitutes the catchment area, then the EC will be higher. Waters which contain high concentrations

Figure: 5 a) Molar ratios of magnesium and calcium ions in thermal waters; **b)** Bivariate mixing diagram of Na^+-normalized Ca^{2+} versus Na^+-normalized Mg^{2+}.



of CO_2 and H_2S gases, resulting in high concentrations of dissolved CO_2 and H_2S, facilitate the dissolution of carbonate and silicate rocks (YOSHIMURA et al., 2004) and consequently, such waters have higher EC values. Moreover, higher water temperature and a more fractured aquifer in combination with low pH values of the water also facilitate dissolution of carbonate rocks and sediments (BERTRAM et al., 1991; GAUTELIER et al., 1999; MORSE & ARVIDSON, 2002) resulting in high EC values.

The thermal water source of Varaždinske toplice has the highest concentrations of sodium, potassium, sulphate and chloride (Tab. 2). It is followed by the thermal springs of Stubičke toplice, the spring in Podevčevo and the thermal water source of Krapinske toplice (Tab. 2). The lowest values are observed in the springs of Topličica in Gotalovec and Mađarevo. Higher concentrations of sodium, potassium, sulphate and chloride ions are the consequence of the dissolution of magmatic rocks and siliciclastic (including pyroclastic) sediments in the areas surrounding the thermal water sources. While some 55 ionic species have been reported in ash leachates (WITHAM et al., 2005) the most abundant species usually found are the cations Na^+, K^+, Ca^{2+} and Mg^{2+}

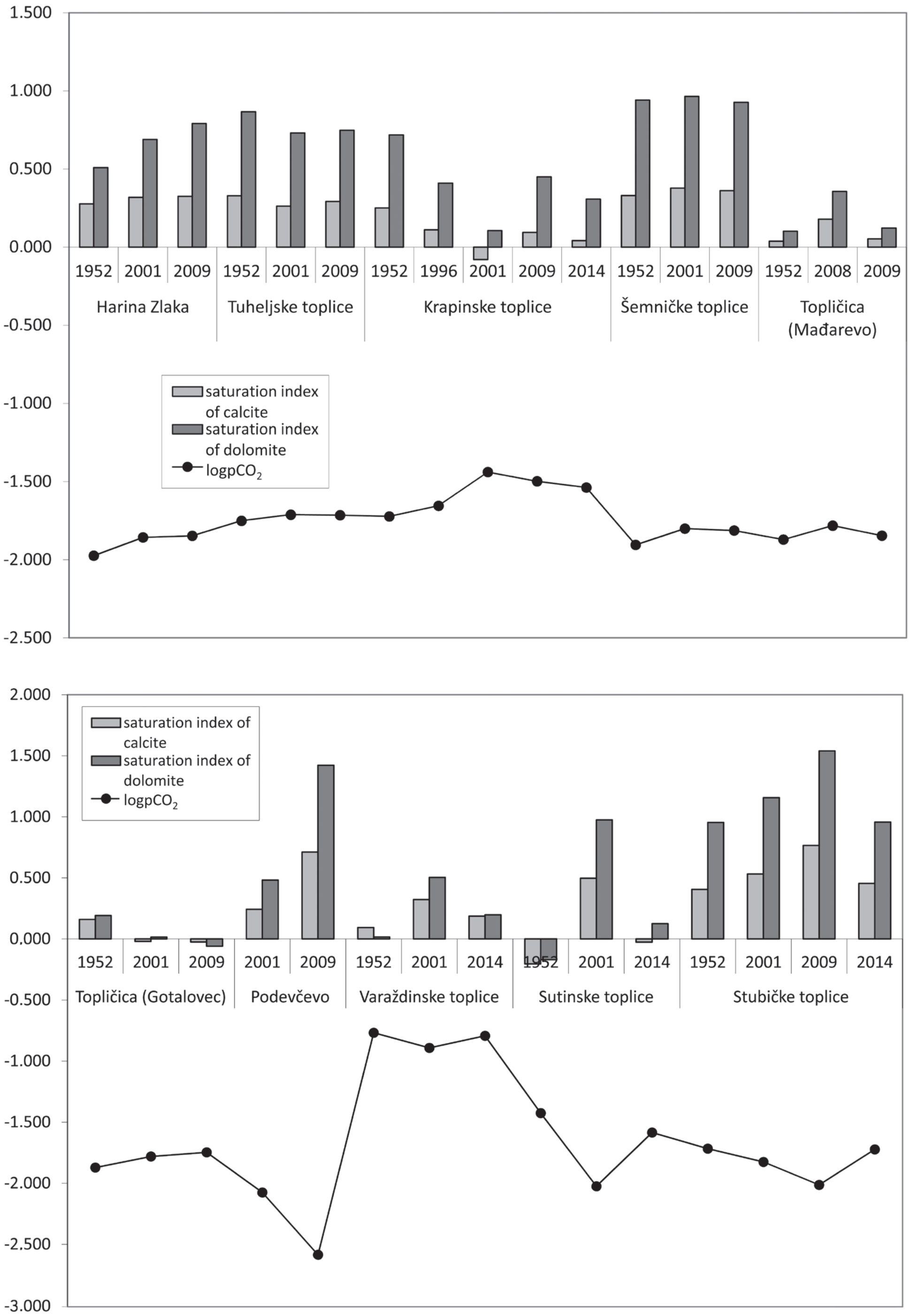


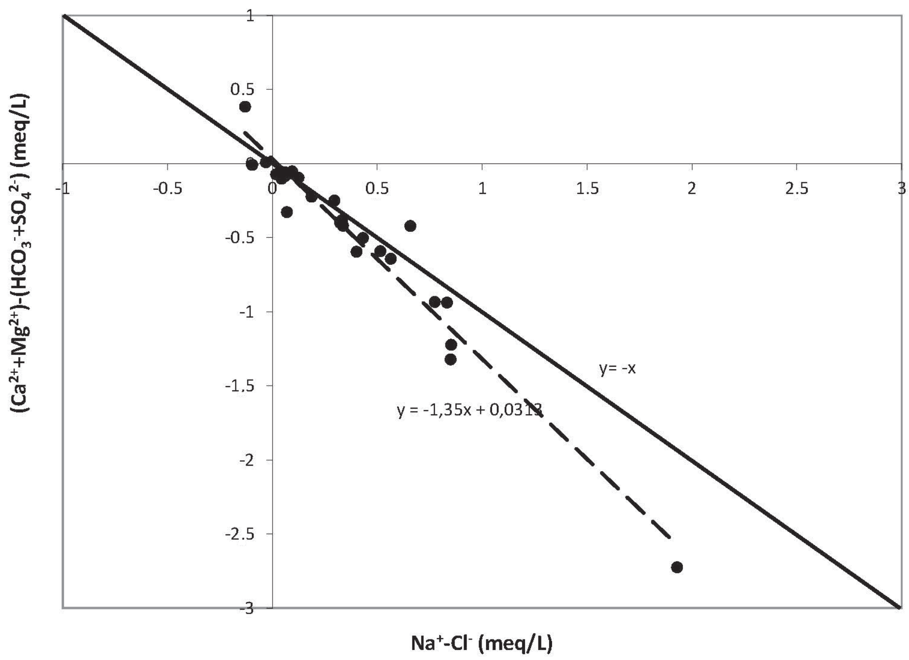
Figure: 6 Saturation index and logpCO_2 calculations **a)** in waters of Harina Zlaka, Tuheljske toplice, Krapinske toplice, Šemničke toplice and Topličica Mađarevci **b)** in water of Topličica (Gotalovec), Podevčevo spring, Varaždinske toplice, Sutinske toplice and Stubičke toplice

and the anions Cl^-, F^- and SO_4^{2-} (JONES & GISALSON, 2008; WITHAM et al., 2005).

According to the major ionic composition, water from Varaždinske toplice belongs to a NaCaMg-HCO_3SO_4 mixed type; Podevčevo and Stubičke toplice waters belong to a CaMgNa-HCO_3SO_4 mixed type; while the rest of thermal waters (Harina Zlaka, Tuheljske toplice, Krapinske toplice, Topličica (Mađarevo), Topličica (Gotalovec), Sutinske toplice and Šemničke toplice) belong to the CaMg-HCO_3 type (Fig. 4).

Hydrochemical facies, as recognised from water chemistry data, are a consequence of the chemistry of the recharging water, and water–aquifer matrix interactions (e.g. cation exchange), as well as groundwater residence time within the aquifer. Two general processes contribute solutes to groundwater: carbonate dissolution and silicate weathering (GARRELS & MACKENZIE, 1971). The chemistry of the evolving water depends not only on the bulk chemistry of the matrix, but also on the rate of weathering. MEYBECK (1987) commented that weathering rates of limestone and dolomite are up to 80 times and 12 times, respectively, faster than silicate weathering rates. From Fig. 5a it can be observed that the groundwater chemistry is primarily controlled by the dissolution of carbonate rocks (dolomite and lime-

Figure 7: Bivariate plot of (Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-}) against (Na^+ - Cl^-).



stone). In addition, the saturation indices of the observed thermal waters with respect to calcite and dolomite mineral phases indicate the dissolution of carbonate rocks (Figs. 6 a, b). Generally, it can be stated that the waters of all observed thermal sources were saturated with respect to calcite and dolomite (Figs. 6 a, b). It was observed that the saturation index with respect to dolomite was higher than with respect to calcite. The chemistry of waters from Varaždinske toplice, Podevčevo and Stubičke toplice is also influenced by the dissolution of carbonates. However, on the bivariate mixing diagrams (Fig. 5b) of Na^+-normalized Ca^{2+} versus Na^+-normalized Mg^{2+}, the samples from Varaždinske toplice, Podevčevo and Stubičke toplice tend to fall within the silicate weathering domain. This suggests that incongruent leaching of the siliceous volcanic rocks is present in the aquifer. The diagram (Fig. 5b) also shows that carbonate dissolution is dominant in waters of the thermal sources of the Harina Zlaka, Krapinske toplice, Tuheljske toplice, Sutinske toplice, Šemničke toplice, Topličica (Mađarevo) and Topličica (Gotalovec).

Also, partial pressure of CO_2 (pCO_2) of observed waters were calculated. It was observed that the pCO_2 values in all sampled waters, were in disequilibrium with respect to the atmosphere ($10^{-3.5}$ or $logpCO_2$= -3.5). The highest partial pressure was observed in the thermal waters of Varaždinske toplice and Krapinske toplice (Figs. 6 a, b) as a consequence of gas influence.

The influence of cation exchange was evaluated by an equivalent bivariate plot of corrected bivalent cations versus corrected Na^+ (Fig. 7). Concentrations of bivalent cations (Ca^{2+} and Mg^{2+}) that may have been involved in exchange reactions were corrected by subtracting equivalent concentrations of associated anions (HCO_3^- and SO_4^{2-}) that would be derived from other processes (e.g. carbonate or silicate weathering). Similarly, Na^+ that may be derived from the aquifer matrix can be accounted for by assuming that Na^+ contributions of meteoric origin would be balanced by equivalent concentrations of Cl^- (MCLEAN & JANKOWSKI, 2000). For active cation exchange taking place in the aquifer, the slope of this bivariate plot should be -1 (i.e. y = -x) (JANKOWSKI et al., 1998). Due to small number of samples, all were included in a single diagram. The slope of -1.35 for the observed samples indicates cation exchange (Fig. 7).

The mixed cation exchange-mineral weathering might be a reflection of the longer residence time of thermal water in the subsurface. Although a bivariate plot (Fig. 7) shows influence of exchange processes and the bivariate mixing diagram (Fig. 5b) indicates silicate weathering, the majority of the analyzed samples tend to fall closer to the carbonate composition than to the silicate composition which means that dolomite is the dominant geothermal aquifer in the study area.

5. CONCLUSION

In the region of Hrvatsko zagorje there are a lot of spa localities. In this part of Croatia geothermal characteristics are favourable. The water temperatures of thermal springs vary from 16 to 65 °C, i.e. from subthermal to hyperthermal. The highest water temperatures are observed in Varaždinske and Stubičke toplice water sources and the lowest in the Podevčevo spring. Lower pH values are observed in the waters from Varaždinske, Stubičke and Krapinske toplice and the highest is observed in the water of the Podevčevo spring. Low pH values are the consequence of H_2S and CO_2 gas dissolution.

According to the major ionic composition, the waters belong to types ranging from mixed NaCaMg-HCO_3SO_4 to the CaMg-HCO_3 type. The geochemical characteristics of the observed thermal waters indicate that the waters are in equilibrium with dolomite which means that dolomite is the geothermal aquifer in the study area. However, during the movement of thermal water toward the surface, it comes into contact with limestone and volcanic clastic sediments and processes of cation exchange and silicate weathering take placet. The influence of those processes is recognized in the waters of the Gotalovec, Varaždinske toplice, Podevčevo and Stubičke toplice thermal water sources.

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