Utilization of thermal water from carbonate geothermal aquifers at the outskirts of the Pannonian basin

In the geological sense, the territory of the Republic of Croatia is divided into two parts: in the north there is the Pannonian Basin, and in the south the Dinarides. The northern part of the territory of the Croatia represents the southwestern border of the Pannonian Basin, which is characterized by a high geothermal gradient - an average of 0.049 °C/m and a high surface heat flux of 76 mW/m^2 (EIHP, 2018). On the other hand, the Dinarides area has a low geothermal gradient averaging 0.025 °C/m and an average surface heat flux of 29 mW/m^2 (EIHP, 2018). The difference is due to the depth to Mohorovičić's discontinuity (Moho), the boundary between the Earth's crust and mantle. In the Dinarides, the depth to Moho varies from 32 to 46 km, and in the Pannonian Basin from 22 to 27 km (Šumanovac, 2016). Given that convection from the mantle transports heat more efficiently than in the crust, areas where the mantle is closer to the surface will have a higher heat flow, which is the main reason that the Pannonian part of Croatia has the greatest geothermal potential.

In Croatia, all groundwaters which water temperatures are higher than the average annual air temperature of the recharge area of the spring or borehole are considered thermal. According to Kovačić & Perica, (1998) geothermal waters were divided into four categories: Subthermal waters (13-20^{o}C), Hypothermal waters (20-34^{o}C), Homeothermal waters (34-38^{o}C) and Hyperthermal waters (> 38^{o}C).

However, according to this division there is a problem of the lower limit of 13^{o}C, because "cold" groundwater has the value of the average annual air temperature, and in some parts of the Republic of Croatia due to climate change the temperature rises, and thus groundwater temperature. Therefore, this division of the lowest boundary is not reliable and above mention definition is used as the lowest boundary.

In Croatia, the use of geothermal aquifers defines the legislative framework under which the state will ensure sustainable management of the geothermal resource. If geothermal resource is used for balneological, recreational, medical purposes or bottling, then the management of the geothermal resources is according to the Water Act (OG 153/09, 63/11, 130/11, 56/13, 14 / 14).

However, if geothermal resource is used for the production of electricity and/or heating, then the management of the geothermal resources is according to the Hydrocarbon Exploration and Exploitation Act (OG 52/18, 52/19). The Ministry of Economy and Sustainable Development is responsible for both legislative frameworks.

The Hydrocarbons Agency (under the authority of the above mentioned Ministry) is responsible for conducting tenders under the Hydrocarbons Exploration and Exploitation Act (OG 52/18, 52/19) while Croatian Waters (which is also under the authority of the same Ministry) performs activities under the Water Act (OG 153/09, 63/11, 130/11, 56/13, 14/14).

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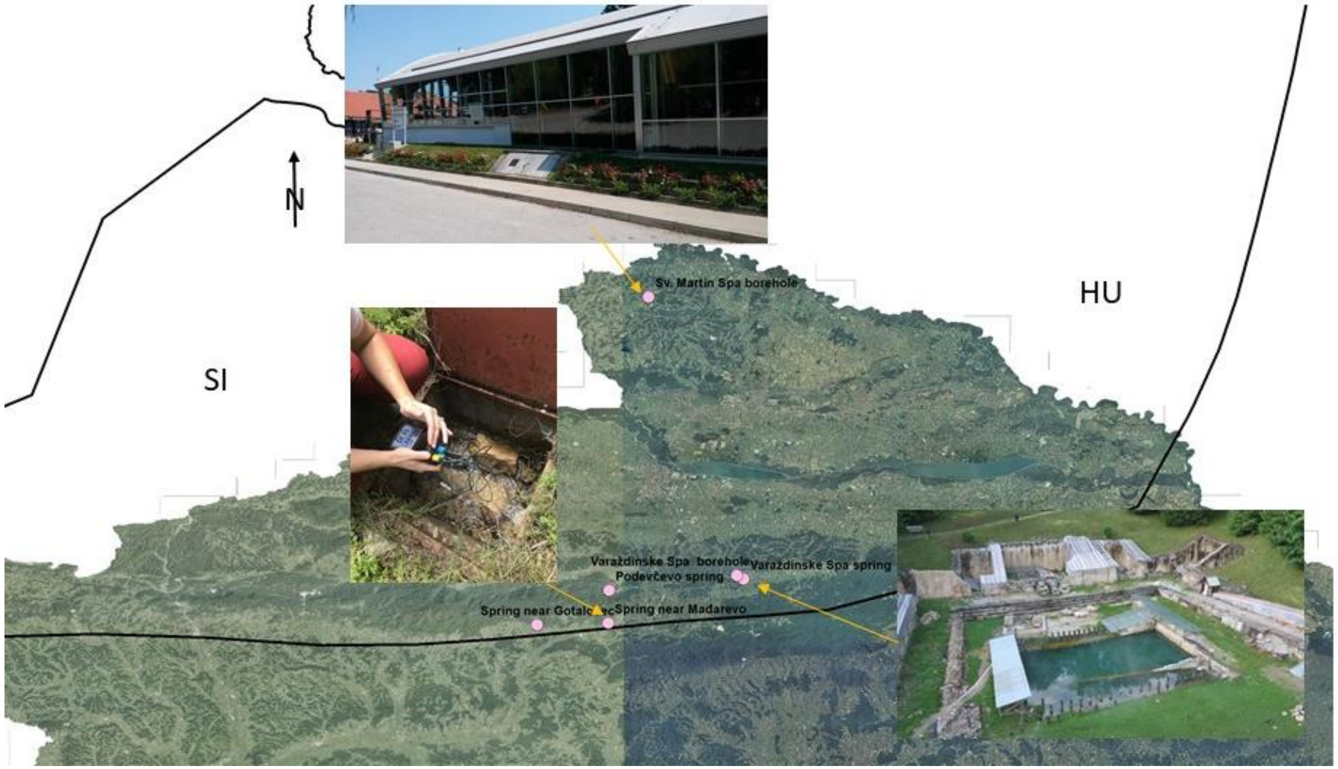

Figure 1. Position of thermal geomanifestation within the project area of Croatia

Anomalies

In the Geoconnect3d pilot area there are five appearances of thermal geomanifestations and they are shown on figure 1. They are: Topličica spring near Gotalovec, Topličica spring near Mađarevo, Podevčevo spring, springs and boreholes in Varaždin Spa area and borehole in Sv. Martin Spa.

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The Topličica spring in Gotalovec (Fig. 1) 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 eruptive and clastic sediments. The water was used until 2015 for bottling by Coca Cola Beverage Company.

The Topličica springs near Mađarevo (Fig. 1) occur at the foot of the steep slopes of the Ivanščica massif near the town Novi Marof. There are four major springs and several smaller ones. The water temperature is variable, from 21 to 23 °C indicate mixing of cold and thermal water. The aquifer is fractured dolomite. The water is used during the summer period for swimming pools and during the whole year for fish farm. The total yield of all the springs has not been measured but the yield at the right shaft was measured and it was 2-3 L/s.

In Podevčevo (Fig. 1) 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 in the contact with eruptive and clastic sediments. The total yield of both springs does not exceed 1 L/s. The spring is not used only occasionally by local people for drinking water.

Varaždinske Spa springs and boreholes (Fig. 1) are located at the foot of the steep slopes of the Kalnik massif 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 59 °C in borehole B-1 and in the largest spring Klokot from 40 to 45 ºC. The thermal waters occur in the brecciated dolomites which are covered by clastic sediments (Šimunić, 2008). Beside Klokot spring there are few smaller springs and in total 6 boreholes but only B-1 is used. There are only two users, Special Hospital for Medical Rehabilitation - Varaždinske Toplice and Bernarda Nova d.o.o. the thermal water is primarily used for medical, balneological and recreational purposes but also and space heating via a heat exchangers. Since thermal water occurring at the surface in dispersive way and from the borehole B-1, water is outflowing freely, it is very difficult to measure the total yield of spring area. The old measurements done by Baća & Herak, 1962 before drilling boreholes indicate that the Klokot spring has a yield of 18 L/s wail measurements conducted in 1997 shown that the yield was 23.14 L/s (Šimunić, 2008). During the drilling boreholes B-5 and B-6, Pranjić et al., 2000, determine that the total yield of wells is about 50 L/s and the spring is 21 L/s.

The last thermal occurrence is situated in the Upper Međimurje area near the border with Slovenia. In this area are important boreholes which were drilled during the hydrocarbons exploration, and they are responsible for the development of the Sv. Martin Spa. The beginning of the development of the Sv. Martin Spa is related to the healing properties of the thermo-mineral water, which exploitation began in 1913 when borehole E-17 was drilled. The water temperature was 33 °C and it was self-overflowing, under the influence of the "gas-lift" system. In 1971, borehole Vučkovec-2 (Vuč-2) was drilled, which had a yield of about 1.7 L/s, and the water temperature measured after drilling was 40 ºC. Today, the yield is increased to 2 L/s, and the temperature is 36 ºC and spa uses this borehole for balneological and recreational purposes. The borehole ended in the Badenian sediments – limestone and sandstone.

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The studied thermal waters belong from CaMg-HCO_3 type (springs in Gotalovec and Mađarevo), CaNa-HCO_3SO_4 (Varaždinske Spa and Podevčevo) to Na-Cl type (Sv. Matin Spa) (Fig 2). The highest mineralization/electrical conductivity (EC) was measured as over 10 000 μS/cm (Fig 3) in water in Sv. Martin Spa (Vuč-2) because it contains high concentrations of ammonium (from 20 to 23.8 mg/L), fluorine (from 4 to 8.7 mg/L), chloride (from 2500 to 4300 mg/L), sodium (from 2700 to 2800 mg/L), iodine (from 3 to 3.7 mg/L) and hydrocarbonate over 4500 mg/L. Comparing chemical analyzes from the 70s when the borehole was drilled and today there are no changes in the chemical composition indicating that there are no changes in the hydrothermal system. Thermal waters from Varaždin Spa follow the above mentioned water and have electrical conductivity over 1000 μS/cm (Fig 3) and contain high concentrations of H_2S over 12 mg/L, also ammonium and fluorine are present in concentrations from 0.4 to 0.9 mg/L for NH_4^+ and 0.3 to 0.9 for F^-. The highest concentrations are of calcium over 120 mg/L, magnesium over 25 mg/L, sodium over 90 mg/L and sulfate over 150 mg/L. The lowest EC values have waters from springs in Mađarevo, Gotalovec and Podevčevo. The values are in range from 437 to 637 μS/cm. All three waters do not contain NH_4^+ and H_2S. Spring waters in Mađarevo and Gotalovec contain very low concentrations of sodium and sulfate (1-3 mg/l Na^+ and 13-14 mg/L SO_4^{2-}) (wail spring water in Podevčevo has a little bit higher concentration in comparison to them (22 mg/l Na^+ and 80 mg/L SO_4^{2-})).

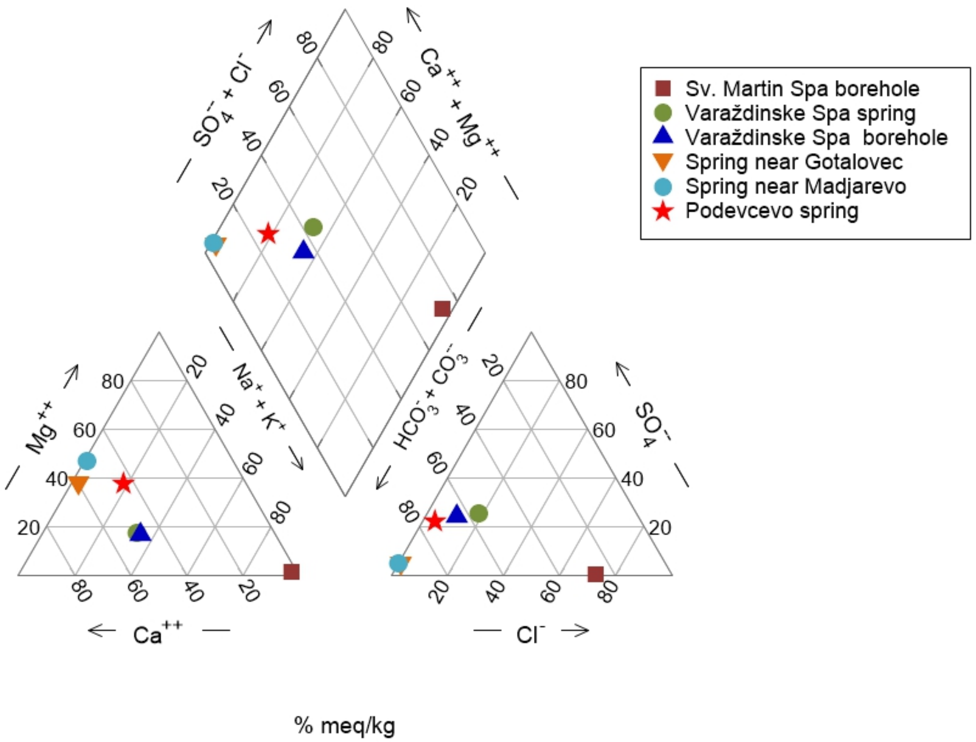

Figure 2. Piper diagram of thermal waters

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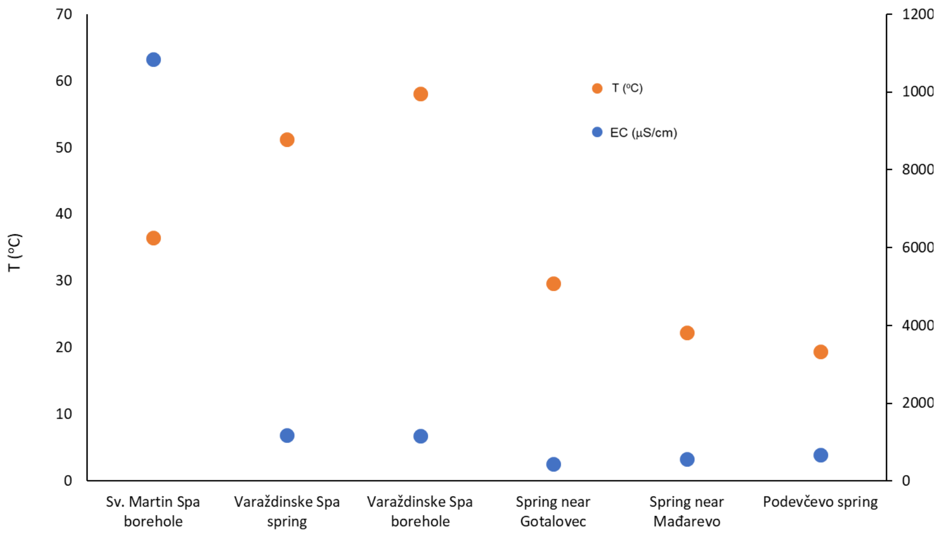

Figure 3. Temperature and EC values of thermal waters

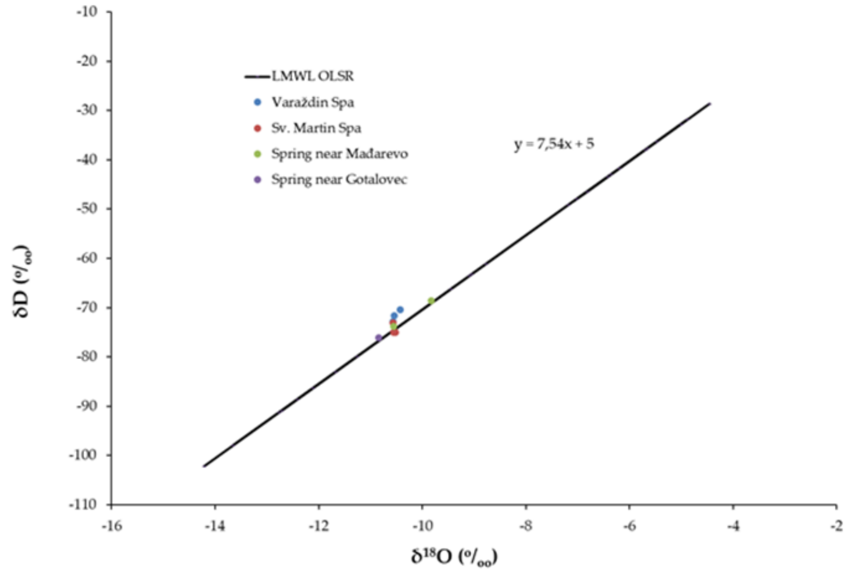

Figure 4. Distribution of groundwater $\delta^{18}O$ (°/oo) and $\delta^{2}H$ (°/oo) values around the local meteoric water line (LMWL) Varaždin (Marković et al., 2020).

The measured stable isotope ($\delta^{18}O$ (°/oo) and $\delta^{2}H$ (°/oo)) values in thermal waters are distributed around the local meteoric water line (LMWL) of Varaždin (Marković et al., 2020), indicating the meteoric origin of the thermal waters. Although, some values are high above LMWL indicating infiltration of precipitation during the colder periods of the Earth history. Nevertheless, values of waters from springs in Mađarevo, Gotalovec and Podevčevo lie on the line indicating recharge and/or mixing thermal waters with fresh groundwaters.

According the bivariate plot of Mg^{2+} versus Ca^{2+} all studied thermal waters are originating from dolomite carbonate aquifers because ratios Mg^{2+}/Ca^{2+} in all waters are higher than 0.33. Mg^{2+}/Ca^{2+} values below 0.33 are characteristic for dissolution of limestones and values above for dissolution of dolomite.

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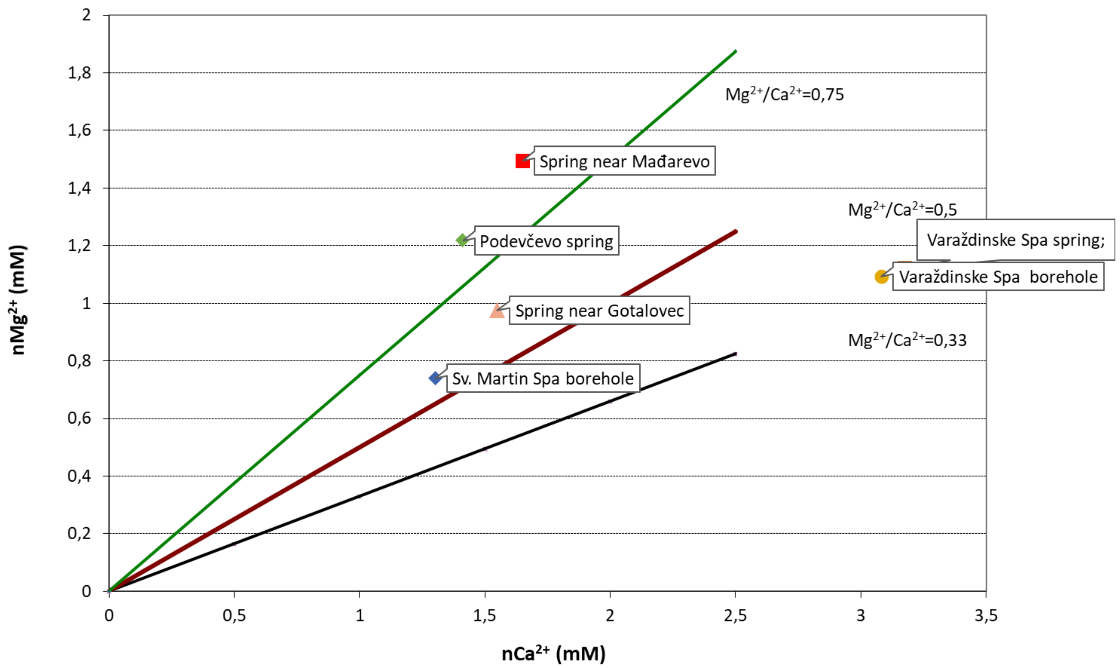

Figure 5. Bivariate plot of Mg^{2+} versus Ca^{2+} to identify the prevailing minerals weathering in thermal waters

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