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THEMATIC ISSUE

# The subthermal potential of karstic groundwater of Kučaj–Beljanica region in Serbia estimated by the multivariate analysis

**Ljiljana Vasić[1] · Dragana Ž. Živojinovic[2] · Vladana Rajaković-Ognjanović[3] · Huang Fen[4,5] · Cao Jianhua[4,5]**

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## Abstract

To define the potential uses of groundwater, a detailed hydrochemical analysis was carried out in the Kučaj–Beljanica Massif at seven locations, in the eastern part of the Republic of Serbia. The hydrogeochemical analysis led to a better understanding of the hydrogeochemical processes occurring underground, as well as the existence and origin of groundwater heat sources. The chemical composition of the thermal groundwater indicates different formation conditions, the influence of different rock types and different physico-chemical processes with time and temperature variations on water quality. Better insight into the geochemical and thermal conditions of groundwater can identify the most prospective locations for geothermal applications such as indoor and outdoor space heating, sports, recreation and tourism, as well as industrial applications, with or without the additional use of heat pumps. Factor analysis (FA), especially principal component analysis (PCA) and cluster analysis (CA) were applied for the evaluation of the spatial/temporal variations of Kučaj–Beljanica thermal groundwater. It was concluded that PCA was the optimum method for explaining functional relationships between the chemical elements. After data reduction, three main factors controlling variability were identified. Hierarchical cluster analysis (HCA) was applied for sample differentiation according to sample location which resulted in the grouping of the examined location into three main groups according to their thermal or geochemical potential: Group I: lowest potential for any purpose; Group II: best thermal potential (wellness centres, agriculture and heating of different facilities and Group III: specific hydrogeochemical potential suitable for bottling or balneal tourism.

**Keywords** Thermal groundwater · Karst · Hydrochemistry · Multivariate analysis · Heat pumps · Tourism

## Introduction

Karst groundwater represents one of the most important water supply resources. Accumulated water from karst is used by 20–25% of the population, which is also the case in Serbia (Ford and Williams 1989; Stevanović et al. 2011). The Kučaj–Beljanica Massif is located in the eastern part of Serbia. It consists of two mountains, Kučaj and Beljanica, and represents one of the largest karstic mountainous regions in this part of Serbia, where significant groundwater reserves are formed (Fig. 1). This massif was also declared a natural park, with potential to become one of Serbia's six national parks. The Beljanica and Kučaj mountains represent one of Serbia's remarkably well preserved ecological environments. It is unspoiled, rich in clean water, and boasts beautiful landscapes with features such as caves, waterfalls and springs in addition to several thermal water occurrences.

Tourism development, especially international, is on the rise in Serbia. Wellness Tourism is very popular in

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✉ Ljiljana Vasić
ljiljana.vasic@rgf.bg.ac.rs

[1] Faculty of Mining and Geology, University of Belgrade, Djusina 7, 11000 Belgrade, Serbia

[2] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

[3] Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia

[4] Key Laboratory of Karst Dynamics, MLR Guangxi, Institute of Karst Geology, CAGS, Guilin 541004, Guangxi, China

[5] International Research Center on Karst, UNESCO, Guilin 541004, Guangxi, China

**Fig. 1** Geographical position of the investigated area; **a** Map of Europe, **b** Map of Central and South-eastern Europe with the main mountain ranges, **c** Map of Serbia with location of Kučaj–Beljanica massif (yellow polygons are karst terrains)

neighbouring countries (Hungary, Slovenia, Italy, Bulgaria, Romania, etc.) and development of this type of tourism shows promise for significant future growth in eastern Serbia due to the presence of a significant number of prospective groundwater geothermal sites such as those present at the Kučaj–Beljanica Massif.

Besides its potential for tourism, the Kučaj–Beljanica Massif drainage network and its large springs which are located along the rim of the massif (Fig. 2), demonstrate great potential as a regional water supply source.

Serbia has a significant number of hydrogeothermal resources with temperatures greater than 15 °C. The number of such natural thermal water sources exceeds 200 (Milenić et al. 2010). Within the massif of Kučaj and Beljanica, in its northern and western part, there are several locations where springs with thermal and sub-thermal (lukewarm) water reach the surface. The temperature of these groundwater ranges from 16 to 36 °C, where those with significantly lower temperatures ranging from 16 to 20 °C, can be additionally heated with heat pumps. Once heated this water can be used for various purposes such as wellness centres, agriculture and heating of different facilities, while groundwater with temperatures over 30 °C can be used directly.

The formation of subthermal and thermal karst groundwater usually requires an extremely long time period. The hydrogeological and geological barriers have the most significant influences on this process. Since water cannot find an outflow from the system because of the existence of barriers (which are composed of a Red Permian Sandstone overthrust in the western and Neogene basin on the northern massif edge), water percolates deeper underground, through a system of small cracks and channels. Percolating water changes chemical characteristics (Brkić et al. 2016) and temperature in contact with different types of rock and rises to the surface as subthermal or thermal water. On the Kučaj–Beljanica Massif, there are eight occurrences of subthermal and thermal groundwater (Belosavac subthermal spring, Suvi do subthermal spring, Krivovirska Banjica spring, Sisevac thermal borehole, Krupaja thermal spring, Krupaja borehole, Milanovačka Banjica spring and Krepoljinska Banjica spring) which are shown on Fig. 1.

## The geological and hydrogeological background

The Kučaj–Beljanica Massif includes rocks from the oldest, Precambrian, to the youngest, Quaternary ages. The Precambrian rocks are in the anticline core and they are mostly overlaid by Paleozoic rocks (Ordovician, Silurian and Devonian). The test area was invaded by the Middle Jurassic marine transgression, and the sedimentation cycle continued there until the end of the Lower Cretaceous (Albian). Throughout this period, thick deposits, primarily of carbonate rocks, were formed (total thickness of about 1300 m). The carbonate complex was formed mostly during the Tithonian, Valanginian, Hauterivian, Barremian and Aptian and it contains predominantly pure carbonates or magnesium carbonates. The "impure" varieties are in the lower parts, sandy limestone of the Dogger, or Oxfordian–Kimmeridgian chert–limestone (Stevanović 1991).

Paleozoic magmatic and metamorphic rocks in the anticlinorium core represent mostly aquitards or aquifuges. The karst aquifer formed in carbonate rocks of the Upper Jurassic (Tithonian) and Lower Cretaceous ages, is rich in groundwater and is recharged mainly from rainfall and from sinking flows which gravitate from higher altitudes

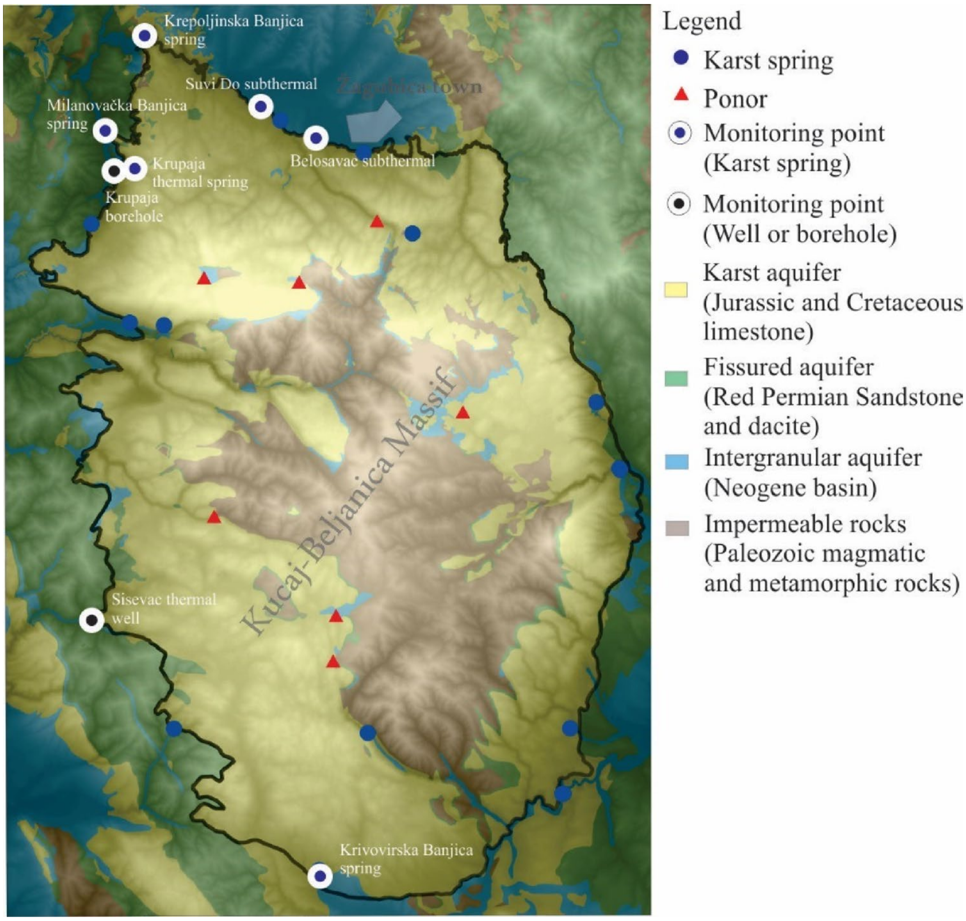


**Fig. 2** Hydrogeological map of studied area with main monitoring points

and impermeable Paleozoic rocks towards lower positioned Mesozoic limestones.

Groundwater is recharged by surface precipitation and a large number of sinkholes (Fig. 2) that are converging the entire surface of the Kučaj and Beljanica massifs. The zone of contact with the impermeable rocks, where the water, due to the specific geology, morphology of the terrain and prolonged contact, dissolves rocks and creates the conditions for underground infiltration, is of special significance.

Groundwater that percolates deeper through the system of small cracks and underground feeding channels has a higher temperature and different hydrogeochemistry, resulting from long and deep groundwater circulation induced by the dacite heat source.

## Materials and methods

To determine the most prospective location with a higher hydrogeothermal potential in relation to the water that occur on the surface, thereby defining their groundwater uses, detailed hydrogeology investigations were carried out. A total of seven locations with occurrences of subthermal and thermal groundwater were detected in the test area (Belosavac, Suvi do, Krepoljin, Milanovac, Krupaja, Krivi Vir and Sisevac) with eight different types of water, in terms of temperature: six springs with temperatures ranging from 16 to 26 °C, and two deep wells where one has a temperature of 18 °C (well depth of 400 m) and the other 36 °C (well depth of 218 m), which is the highest temperature in the test area.

This study, conducted during 1 hydrological year and within four cycles (winter, spring, summer and fall), examined the physical and chemical properties of subthermal and thermal groundwater from the Kučaj–Beljanica Massif during which seven locations were analyzed.

Basic physicochemical parameters of water were measured (temperature, pH value, conductivity, dissolved oxygen and turbidity of water) directly in the field with portable laboratory equipment (WTW, Oxi 340i/set).

Ionic composition of water ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $NO_3^{-}$, $Cl^{-}$, $F^{-}$, $SO_4^{2-}$, $HCO_3^{-}$) was determined on an ion chromatograph (IC), Dionex ICS-900, in samples that were transported to the laboratory. In addition to ionic composition, the analysis of isotope $\delta^{13}$CDIC concentration in samples was performed on a MAT253 stable isotope mass spectrometer with a precision of ± 3%. Analyses of $\delta^{13}$CDIC values were conducted on groundwater to determine groundwater residence time, since extended water–rock interaction results in water enriched with carbon of the host rock, thereby raising $^{13}$C values (Vasić 2017).

Besides the major ion composition of the summer water samples, the determination of microelements was performed to determine the origin of the geothermal heat sources, and for this purpose the elements that were identified by ICP-OES were Fe, Mn, Cr, Sr, Li, Zn, Cu, As, Ni, P and Si.

Since the objective of this study was to identify the most prospective location for obtaining hydrogeothermal energy, on the basis of hydrochemical and isotopic analyses, additional multivariant analysis was performed, through spatial hierarchical cluster analyses (HCA) and PCA analyses of variables.

The statistical data processing was performed using IBM SPSS 20 software, and a logarithmically transformed trace element concentration data set (Tabachnick and Fidell 2007).

Descriptive statistics, statistical hypothesis and dependency methods were used for the analysis of primary data. Determination of the central tendency (mean, median) and measures of variability (standard deviation) were performed in the present study. To investigate normality of data distribution, the Kolmogorov–Smirnov (K–S) test was used at a 0.05 significance level. As a measure of appropriateness of factor analysis, the Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity were performed (Živojinović et al. 2013).

Multivariate analysis of the water quality data set was performed using PCA/FA and CA. The PCA and HCA were applied for the analysis of the distribution and spatial variations of ionic impurities in different locations of the Kučaj–Beljanica Massif.

PCA is a suitable tool to reduce dimensionality of large experimental data sets and provides an easy visualization of relationships among variables (Borgese et al. 2013). PCA was used to extract a smaller number of independent factors (principal components) from intercorrelated variables, starting with the correlation matrix describing the dispersion of original variables and extracting the eigenvalues and eigenvectors. An eigenvector is a list of coefficients multiplying the original correlated variables to obtain new uncorrelated (orthogonal) principal components. Varimax rotation with Kaiser's normalization was applied to minimize the number of variables with high loading on each component and facilitates the interpretation of results. Principal components are those whose original eigenvalues exceed 1 (Kaiser 1960).

CA classifies objects (cases) into classes (clusters), so that each object is similar to the others within a class but different from those in other classes with respect to a predetermined selection criterion. Many applications of CA to water quality assessment have been reported (Ragno et al. 2007; Shrestha and Kazama 2007; Rodrigues et al. 2010).

The HCA was performed using Euclidean squared distance and Ward's linkage settings on the near total heavy element concentrations in soils to identify groups of samples which contain similar contamination levels and elements with similar geochemical affinity. The hierarchical method of the cluster analysis used in the present study has the advantage that it does not require any prior knowledge of the number of clusters, which is a prerequisite of the non-hierarchical method (Martínez-Santos et al. 2015).

## Results

Descriptive statistics of the analysed parameters data set of subthermal and thermal groundwater samples from the Kučaj–Beljanica Massif are presented in Table 1.

Table with results of physico-chemical parameters for all samples and campaigns is presented in the supplementary material as Table 1a.

Results of analysed microelements in water samples are presented in Table 2.

## Discussion

From both chemical composition and temperature, some relations and observations can be discussed. What can strongly be distinguished is that there are two types of water, in terms of temperature—subthermal and thermal. Groundwater temperature ranges from 13.8 °C at the Belosavac subthermal spring, which was the lowest measured value for that spring, and also the lowest of all subthermal and thermal springs and boreholes. The highest temperature value was measured in the Sisevac borehole, which exhibited a constant temperature range of 34–36 °C.

The electrical conductivity of the subthermal and thermal water all vary in range from 468 to 569 µS/cm, except for Milanovačka Banjica. The parameters for this location exhibit higher values than those obtained for other locations. The electrical conductivity varies from 714 to 802 µS/cm, which indicates a higher concentration of ionic impurities.

The pH value is within the narrow range from 7.0 to 7.5 for all the analysed locations; therefore, it is not a parameter of interest for statistical analysis.

The concentration of dissolved oxygen in the water samples varies from 1.13 mg/l at the Krupaja thermal spring, up to 7.7 mg/l at the Belosavac subthermal spring. Such low values indicate a prolonged subterranean residence time, leading to the conclusion, based on the concentration levels of dissolved oxygen, that the oldest groundwater are those that occur at the Krupaja thermal spring (1.13–2.61 mg/l), Suvi Do subthermal spring (1.7–2.35 mg/l) and the Sisevac thermal borehole (2.6–4.55 mg/l), while the youngest are at the Krivovirska Banjica Spring (max 7.5 mg/l) and the Belosavac subthermal spring (max 7.7 mg/l).

A stable isotope value of $\delta^{13}C$ indicates older and younger components in groundwater. Water that was recently recharged from precipitation or surface water will have higher negative values, while those water which spend a longer time in interaction with the host rock (limestone) will have lower negative values. From the results shown in Table 1, the wide range of $\delta^{13}C$ values for all the springs indicates a strong mixing influence between older and younger groundwater during low and high discharge periods. The lowest $\delta^{13}C$ values are recorded at the Krupaja thermal spring (−2.69 to −5.32 ‰). The highest $\delta^{13}C$ value at the Krupaja thermal spring is observed during the spring period, when strong mixing of the high infiltration of surface and rain water with old groundwater occurs in the shallower part of the aquifer. Lower values are observed at the Sisevac thermal borehole, Krepoljinska and Milanovačka Banjica, as well as at the Suvi Do subthermal spring. Constantly higher values are observed at the Belosavac subthermal spring and Krivovirska Banjica, which indicate that those groundwater are youngest and do not percolate deep into the ground as other subthermal and thermal groundwater.

Groundwater turbidity is usually low. This value confirms that the water spends long periods of time underground and that it has been exposed to the autopurification process of the aquifer. Low oxygen and turbidity values are indicators of pure groundwater, where microbiological contamination can be excluded. Usual turbidity values are up to 2 NTU, while higher values are observed at the Belosavac subthermal spring and Milanovačka Banjica. The highest value of 10.56 NTU at Belosavac subthermal spring was observed during spring which is a consequence of surface water influence. Milanovačka Banjica has higher turbidity when compared to other springs due to a small lake reservoir in the soil that forms in the discharge zone.

The chemical groundwater composition is shown in a Piper's diagram (Fig. 3), which is comprised of data collected in the summer period, used to better understand the relative abundance of common ions in large number of water samples on one plot (Fernández-Martínez et al. 2019). The chemical analysis identifies two groups of subthermal and thermal water that can be distinguished (Table 1), on the basis of major ions analysis ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $NO_3^{-}$, $Cl^{-}$, $F^{-}$, $SO_4^{2-}$, $HCO_3^{-}$):

(i) $Ca–HCO_3$ composition for all samples collected from the springs (Belosavac, Suvi Do, Krivovirska Banjica, Sisevac, Krepoljinska Banjica), and from one borehole (Krupaja) and

**Table 1** Descriptive statistics of the analysed parameters data set

| | Ca | Mg | Na | K | F | $HCO_3$ | Cl | $SO_4$ | $NO_3$ | TDS | Temp | pH | Cond | DO | Turbidity | $\delta^{13}C$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 38.3184 | 8.37841 | 13.88906 | 1.44778 | 0.21727 | 167.181 | 5.18427 | 22.7231 | 3.43923 | 260.779 | 21.575 | 7.22563 | 557.031 | 4.28938 | 1.71474 | 6.86625 |
| Standard error | 1.83559 | 0.8508 | 3.318997 | 0.17471 | 0.07203 | 6.01971 | 1.14566 | 3.93752 | 0.26392 | 12.0136 | 1.08085 | 0.0237 | 15.1373 | 0.35475 | 0.38935 | 0.42761 |
| Median | 38.115 | 6.8785 | 5.532 | 1.1125 | 0.0684 | 163.073 | 2.4349 | 15.1563 | 3.23645 | 239.484 | 19.7 | 7.2 | 540 | 4.14 | 1.025 | 6.225 |
| Mode[a] | #N/A | 6.604 | #N/A | #N/A | 0.0632 | #N/A | #N/A | #N/A | #N/A | #N/A | 18.4 | 7.2 | 516 | 1.7 | 1.2 | 5.91 |
| Standard deviation | 10.3837 | 4.81284 | 18.77508 | 0.98828 | 0.40748 | 34.0526 | 6.48083 | 22.274 | 1.49293 | 67.9591 | 6.11424 | 0.13409 | 85.6295 | 2.00678 | 2.20248 | 2.41891 |
| Sample variance | 107.821 | 23.1634 | 352.5037 | 0.9767 | 0.16604 | 1159.58 | 42.0011 | 496.131 | 2.22885 | 4618.44 | 37.3839 | 0.01798 | 7332.42 | 4.02717 | 4.85092 | 5.85115 |
| Kurtosis | 3.3398 | −0.4349 | 4.310704 | 3.95131 | 7.21384 | −0.8537 | 2.23797 | 4.05976 | −1.1252 | 1.67687 | 0.4693 | −0.2316 | 3.50503 | −1.2442 | 7.97552 | −0.3733 |
| Skewness | 1.24497 | 0.70552 | 2.285202 | 2.19457 | 2.87508 | 0.54528 | 1.88206 | 2.28501 | −0.0496 | 1.35437 | 1.13427 | 0.40943 | 2.08001 | 0.20293 | 2.65027 | 0.51458 |
| Range | 51.51 | 16.308 | 71.891 | 3.7743 | 1.6213 | 115.595 | 21.8689 | 82.5177 | 5.1208 | 283.467 | 21.4 | 0.5 | 337 | 6.57 | 10.38 | 9.74 |
| Minimum | 22.69 | 1.572 | 1.389 | 0.6747 | 0.018 | 120.475 | 1.1262 | 8.0642 | 0.6117 | 175.068 | 13.8 | 7 | 465 | 1.13 | 0.18 | 2.69 |
| Maximum | 74.2 | 17.88 | 73.28 | 4.449 | 1.6393 | 236.07 | 22.9951 | 90.5819 | 5.7325 | 458.534 | 35.2 | 7.5 | 802 | 7.7 | 10.56 | 12.43 |
| Sum | 1226.19 | 268.109 | 444.45 | 46.3288 | 6.9526 | 5349.8 | 165.897 | 727.138 | 110.055 | 8344.92 | 690.4 | 231.22 | 17,825 | 137.26 | 54.8718 | 219.72 |
| Count | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 |
| Confidence level (95.0%) | 3.74372 | 1.73521 | 6.769139 | 0.35631 | 0.14691 | 12.2773 | 2.33659 | 8.03063 | 0.53826 | 24.5019 | 2.20442 | 0.04834 | 30.8727 | 0.72352 | 0.79408 | 0.87211 |

[a] N/A: not available

**Table 2** The concentration of microelements in subthermal and thermal groundwater

| Concentration, µg/L | Sample location | | | | | | |
|---|---|---|---|---|---|---|---|
| | Suvi Do spring | Sisevac borehole | Krivovirska Banjica spring | Krepoljinska Banjica spring | Milanovačka Banjica spring | Krupaja thermal spring | Krupaja borehole |
| Fe | < 0.5 | < 0.5 | 66.5 | < 0.5 | 18.5 | < 0.5 | < 0.5 |
| Mn | 0.75 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| Cr | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |
| Sr | 139.3 | 212.3 | 177.3 | 111.3 | 459.7 | 341.3 | 169.3 |
| Li | < 16 | < 16 | < 16 | < 16 | 33 | < 16 | < 16 |
| Zn | < 0.03 | 2.27 | < 0.03 | < 0.03 | < 0.03 | < 0.03 | < 0.03 |
| Cu | < 0.25 | < 0.25 | < 0.25 | < 0.25 | < 0.25 | < 0.25 | < 0.25 |
| As | 9.6 | 14.1 | 9 | 7.9 | 3.3 | 22.7 | 14.7 |
| Ni | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |
| P | 24 | 20 | 35 | 21 | 12 | 21 | 24 |
| Si | 9200 | 9700 | 10,700 | 8000 | 21,900 | 19,400 | 10,200 |

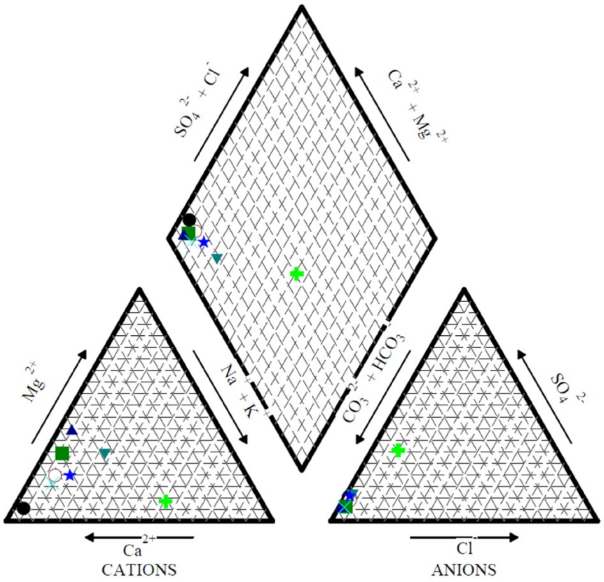


**Fig. 3** Piper diagram (Piper 1944) for thermal and sub-thermal summer water from Kučaj–Beljanica. Filled circle Belosavac subthermal spring, open circle Suvi do subthermal spring, ■ Krivovirska Banjica spring, filled triangle Sisevac thermal borehole, ▼ Krupaja thermal spring, ★ Krupaja borehole, ✚ Milanovačka Banjica spring, x Krepoljinska Banjica spring

(ii) Na–Cl composition for the borehole—Milanovačka Banjica location.

The hydrochemical evaluation of the thermal water reveals that groundwater has a hydrochemical facies caused by water–rock interactions or discharge of pollution (Yurteri and Simsek 2017; Banks et al. 1998). In this research, thermal water has hydrochemical facies of Ca–$HCO_3$ in the drainage region and Na–Cl type only at Milanovačka Banjica which confirms that groundwater from this spring was formed under different hydrogeochemical conditions and is most probably the consequence of marine transgression.

The variation for:

- $Cl^-$ ions within cycles has been significant for Milanovačka Banjica (from 13 to 22 mg/l) and Krivovirska Banjica (around from 3 to 21 mg/l). Measured values for all other samples vary from 1.0 to 4.0 mg/l.
- $SO_4^{2-}$-ions within cycles has been significant for Milanovačka Banjica (from 65 to 90 mg/l) and Krupaja thermal spring (around from 16 to 24 mg/l); measured values for all other samples vary from 8.0 to 17.0 mg/l.
- $NO_3^-$-ions within cycles has not been significant. All measured values vary from 0.6 to 4.0 mg/l, except for Belosavac and Krepoljinska Banjica (around 5 mg/l);
- $HCO_3^-$-ions within cycles has been significant for thermal springs, Sisevac, Krupaja and Krivovirska Banjica, as well as for Milanovačka Banjica, which is a reflection of higher temperature; other measured values vary from 130.0 to 150.0 mg/l.
- $F^-$-ions within cycles has not been significant, except for Milanovačka Banjica. The measured values vary from 0.06 to 1.6 mg/l, which is higher than the maximum concentration recommended by World Health Organization (WHO);
- $K^+$-ions within cycles has not been significant, except for Milanovačka Banjica. The measured values vary from 3.0 to 4.0 mg/l;
- $Na^+$-ions within cycles has not been significant, except for Milanovačka Banjica and Krupaja thermal spring. The measured values vary around 60 mg/L for Milanovačka Banjica, and around 17 mg/l for Krupaja thermal spring;
- $Mg^{2+}$-ions within cycles has been significant for the thermal springs of Sisevac, Krupaja and Krivovirska Banjica.

The values for other samples vary around 17 mg/l. The concentration of $Mg^{2+}$-ions increases with higher temperature.

- $Ca^{2+}$-ions within cycles has been significant for the thermal springs of Sisevac and Krupaja. The measured values for other samples vary from 27 to 43 mg/l. The concentration of $Ca^{2+}$-ions decreases with higher temperature.

The concentrations of analysed microelements in water samples show higher values of strontium, arsenic, phosphorus and silicon, but still all values are below the maximum allowable values. Concentrations of Mn, Cr, Cu and Ni are below the detection limits in all analysed water samples. Results of analysed microelements in water samples are presented in Table 2.

The concentration of Sr is detected in all groundwater samples and this element usually occurs together with calcium. As stated by Stojković (2013) ionic radius of strontium is similar to ionic radius of calcium and potassium, and strontium can be found in the crystal lattices of many major and accessory minerals, the exchange of these two microelements is very frequent.

Strontium concentrations in subthermal groundwater ranges from 111.3 in Krepoljinska Banjica to 177.3 µg/l in Krivovirska Banjica, while the highest values are recorded on the thermal water at the Sisevac borehole (212.3 µg/l), Krupaja (341.3 µg/l) and Milanovačka Banjica, which have a maximum value of up to 459.7 µg/l. On this basis, it is concluded that the concentration of Sr increases with increasing temperature, and the lowest is in subthermal groundwater, while the highest values were observed in thermal water. Since Sr concentration is not the highest in groundwater with the highest temperature, it can also be concluded that concentration of Sr in groundwater depends on the depth of the groundwater circulation and its prolonged contact with the host rock.

Lithium concentrations of 33 µg/l were detected only at the Milanovačka Banjica thermal spring. Lithium shows similarity with magnesium in its ionic radius size and it often replaces magnesium in the crystal lattices of minerals (Hitchon 1999; Reimann and Birke 2010; Stojković, 2013). Because of this, Milanovačka banjica groundwater has lower magnesium values (5.9 mg/l), compared to other thermal springs.

Generally, Li concentrations in Milanovačka banjica groundwater could be related to modern volcanism that took place in the Carpathian–Balkanides during the Tertiary, but very high concentrations of sodium and chloride, which also occur in these water together with Li concentrations may indicate the inflow of groundwater that originates from much greater depths.

Arsenic was detected in all the analysed samples, and the lowest values were found in the Milanovačka Banjica spring (3.3 µg/l). In most of the samples, As values were up to 10 µg/l, except for the samples from borehole SIS-1 (14.1 µg/l) and borehole B – 1 (14.7 µg/l), and a maximum value of 22.7 µg/l was recorded at Krupaja thermal spring.

The concentration of phosphorus was also detected in all the analysed samples and the values are generally above 20 µg/l, with the exception of Milanovačka banjica, whose concentration is 12 µg/l. A value of 34 µg/l was found in the water of Krivovirska Banjica spring. The origin of phosphorus in the water is due to the various forms of calcium-phosphate, which usually occurs in sedimentary rock. Since phosphorus is not present in high concentrations, it excludes the possibility of pollution sources.

In subthermal groundwater, the silicon concentration ranges from 8 to 10.7 mg/l, indicating prolonged water–rock interaction. The highest silicon values were observed at Milanovačka Banjica spring (21.9 mg/l) and Krupaja thermal spring (19.4 mg/l), which, besides the silica from sedimentary rocks, may also indicate that younger volcanic rock may be considered as the source of the silicon.

## Principal component analysis/factor analysis (PCA/FA)

In the first step of the statistic evaluation, Ryan–Joiner or Kolmogorov–Smirnov test (the significance level $\alpha$ was 0.05) was initially used to test the distribution of each analysed parameter. This test revealed that the original data set deviated from normal distributions to different extents. In contrast, the log-transformed data were normally distributed for all analysed parameters. Hereupon, all data analyses were performed using log-transformed data.

The data set of the concentration measurements were subjected to principal component analysis (PCA) to reveal relationships between the parameters. With PCA, data reductions were performed by transforming the data into orthogonal components that were a linear combination of the original variables. First, the data matrix was tested to remove outliers from the data set by applying the Grubbs test (Grubbs 1969). These values were discarded from PCA modelling. No outliers were found in the log-transformed data set. The correlation matrix of 14 elements or physico-chemical parameters obtained by PCA is presented in Table 3.

The following criteria was adopted: a significant correlation is considered to be one that has correlation coefficient value greater than 0.50 and a strong correlation is one that is greater than 0.70 (Varol et al. 2012).

Significant and strong positive correlations were observed between $Cl^-$, $Na^+$, $K^+$, $SO_4^{2-}$, $F^-$, conductivity and TDS ($r = 0.65$ to 0.860). These ions are responsible for water mineralization. $Mg^{2+}$ was positively correlated with temperature and $C^{13}$ determining the groundwater age in deeper

**Table 3** Pearson correlation matrix of the physico-chemical parameters in groundwater samples

| | Correlation matrix | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | log C$l_3$ | Ca | Mg | Na | K | F | $HCO_3^-$ | Cl | $SO_4$ | TDS | Temperature | Conductivity | Oxygen | Turbidity |
| log C$l_3$ | 1.000 | 0.441 | −0.556 | −0.477 | −0.521 | −0.506 | −0.465 | 0.000 | −0.233 | −0.397 | −0.644 | −0.270 | 0.432 | −0.045 |
| Calcium | 0.441 | 1.000 | −0.332 | −0.296 | −0.279 | −0.312 | 0.358 | 0.053 | −0.191 | 0.237 | −0.373 | −0.294 | 0.175 | 0.080 |
| Magnesium | −0.556 | −0.332 | 1.000 | 0.268 | 0.118 | 0.216 | 0.549 | 0.035 | −0.153 | 0.274 | 0.828 | 0.003 | −0.380 | −0.343 |
| Sodium | −0.477 | −0.296 | 0.268 | 1.000 | 0.918 | 0.848 | 0.363 | 0.803 | 0.833 | 0.722 | 0.276 | 0.854 | −0.283 | 0.357 |
| Potassium | −0.521 | −0.279 | 0.118 | 0.918 | 1.000 | 0.802 | 0.355 | 0.725 | 0.859 | 0.749 | 0.280 | 0.860 | −0.192 | 0.528 |
| Fluoride | −0.506 | −0.312 | 0.216 | 0.848 | 0.802 | 1.000 | 0.382 | 0.629 | 0.758 | 0.679 | 0.275 | 0.809 | −0.416 | 0.313 |
| Bicarbonate | −0.465 | 0.358 | 0.549 | 0.363 | 0.355 | 0.382 | 1.000 | 0.267 | 0.153 | 0.829 | 0.596 | 0.196 | −0.460 | 0.085 |
| Chloride | 0.000 | 0.053 | 0.035 | 0.803 | 0.725 | 0.629 | 0.267 | 1.000 | 0.737 | 0.670 | −0.021 | 0.732 | −0.055 | 0.443 |
| Sulphate | −0.233 | −0.191 | −0.153 | 0.833 | 0.859 | 0.758 | 0.153 | 0.737 | 1.000 | 0.644 | 0.072 | 0.862 | −0.184 | 0.509 |
| TDS | −0.397 | .237 | 0.274 | 0.722 | 0.749 | 0.679 | 0.829 | 0.670 | 0.644 | 1.000 | 0.432 | 0.649 | −0.360 | 0.398 |
| Temperature | −0.644 | −0.373 | 0.828 | 0.276 | 0.280 | 0.275 | 0.596 | −0.021 | 0.072 | 0.432 | 1.000 | 0.172 | −0.458 | −0.173 |
| Conductivity | −0.270 | −0.294 | 0.003 | 0.854 | 0.860 | 0.809 | 0.196 | 0.732 | 0.862 | 0.649 | 0.172 | 1.000 | −0.188 | 0.423 |
| Oxygen | 0.432 | 0.175 | −0.380 | −0.283 | −0.192 | −0.416 | −0.460 | −0.055 | −0.184 | −0.360 | −0.458 | −0.188 | 1.000 | 0.238 |
| Turbidity | −0.045 | 0.080 | −0.343 | 0.357 | 0.528 | 0.313 | 0.085 | 0.443 | 0.509 | 0.398 | −0.173 | 0.423 | 0.238 | 1.000 |

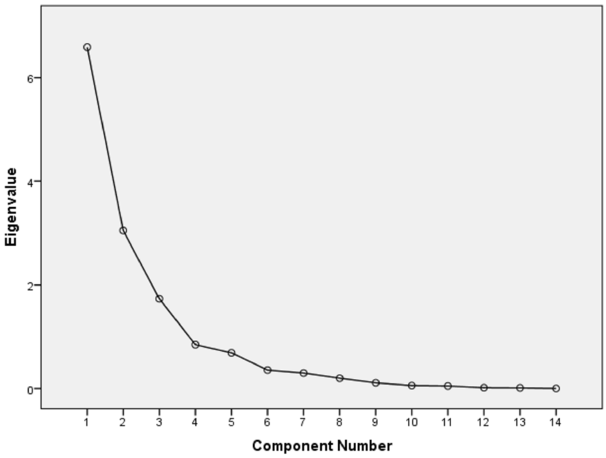


**Fig. 4** Scree plot of Eigen values of the principal components

layers indicating a common link between increased temperature and increased concentrations of $Mg^{2+}$ in subthermal and thermal water, which may be due to the release of ions from $Mg^{2+}$ dacite (minerals, biotite and hornblende) at increased groundwater temperatures. Also, increased values of $^{13}C$ confirm that groundwater with higher temperature and $Mg^{2+}$ content indicate a greater water–rock interaction time. Dissolved oxygen has a negative correlation with those parameters, which is expected, because the concentration of dissolved oxygen decreases with increasing water temperature. A strong positive correlation was observed among $Ca^{2+}$ and $HCO_3^-$. These parameters are responsible for limestone deposits.

From the shape of the scree plot, shown in Fig. 4, the number of important components that will be used in further calculations can be observed.

PCA revealed the presence of three components with characteristic values exceeding 1, explaining 47.1, 21.8 and 12.4% of the variance. Kaiser's criterion was adopted, according to which there are three major components that explain 81.3% of the total variance. Based on the Catel criteria (see scree plot) (Manly 2000), three components will be used in further explanations of variances. This three-component solution explained a total of 82% of the variance, which is in agreement with Kaiser's criterion of eigenvalues. According to the Kaiser criterion (Kaiser 1960), only the first three principal components were retained, because the subsequent eigenvalues were all less than one.

For deeper insight into the structure of the data, the correlation matrix for principal component analysis was subjected to the varimax orthogonal rotation (shown in Fig. 5).

The loading plot for the first two components is presented in Fig. 5. Through the loading plot the similarities and correlations between elements can be observed. The elements with small loadings located near the origin have

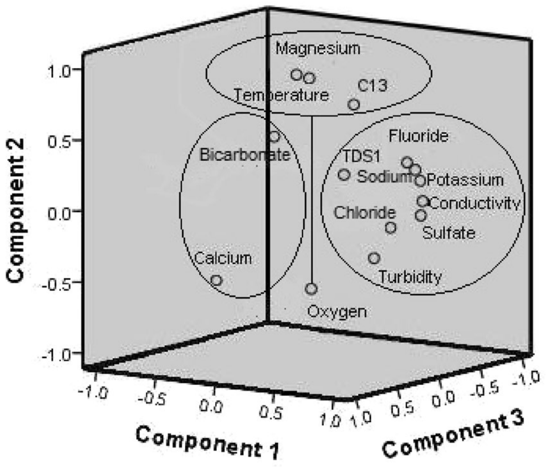


**Fig. 5** Loading plots, in rotated space, of elements data in groundwater samples

little influence on the data structure, whereas the elements with high loadings represent those elements with the greatest influence on the grouping and separation of samples. A close relation was observed between the concentrations of these parameters:

I. $Na^+$, $Cl^-$, $K^+$, $SO_4^{2-}$, $F^-$, conductivity, turbidity and TDS;
II. $Ca^{2+}$ and $HCO_3^-$;
III. $Mg^{2+}$, temperature and $C^{13}$.

From the data presented in Fig. 5, three significant factors were observed. These factors are related to the sources of the elements in the studied samples. The first factor comprises of $Na^+$, $K^+$, $Cl^-$, $SO_4^{2-}$, $F^-$, conductivity and TDS with high values of loadings, from 0.75 to 0.94. $Mg^{2+}$ and temperature, $C^{13}$ and oxygen are components of second factor values of loadings from 0.65 to 0.90. Negative loadings for dissolved $O_2$ and $C^{13}$ were observed for the second factor. The third factor is composed with a combination of calcium and hydrogen-carbonate with high factor loadings 0.91, and 0.69. Some parameters, such as TDS, turbidity and $HCO_3^-$, have a low or medium presence in more than one factor, indicating the existence of more than one significant source.

According to cluster analyses, the resulting dendrogram consists of three main clusters (Fig. 6). These were further divided into subclusters. Milanovačka Banjica spring is a cluster which has been isolated from the other clusters based on the variables and confirmed by hydrochemical analysis. The first cluster represents all the subthermal springs divided into subclusters, primarily according to their temperature similarity and sampling period. The second cluster consists of two subclusters which contain the Krupaja thermal spring and the Sisevac borehole data. It is clear and understandable that this cluster groups groundwater with the highest temperatures. Higher salinity and temperature corresponds to longer residence times and deeper circulation (Celati et al. 1991).

It can be observed that cluster analysis provides information which can be used to identify future geothermal locations with the highest potential. For the first cluster, groundwater samples from subthermal springs were grouped and these springs represent locations which have the smallest potential to receive groundwater with higher geothermal potential.

For the second cluster, thermal groundwater samples were grouped which already represent the locations with the highest temperature. Tapping groundwater from much greater depth would lead to the best achievement of geothermal potential in this region.

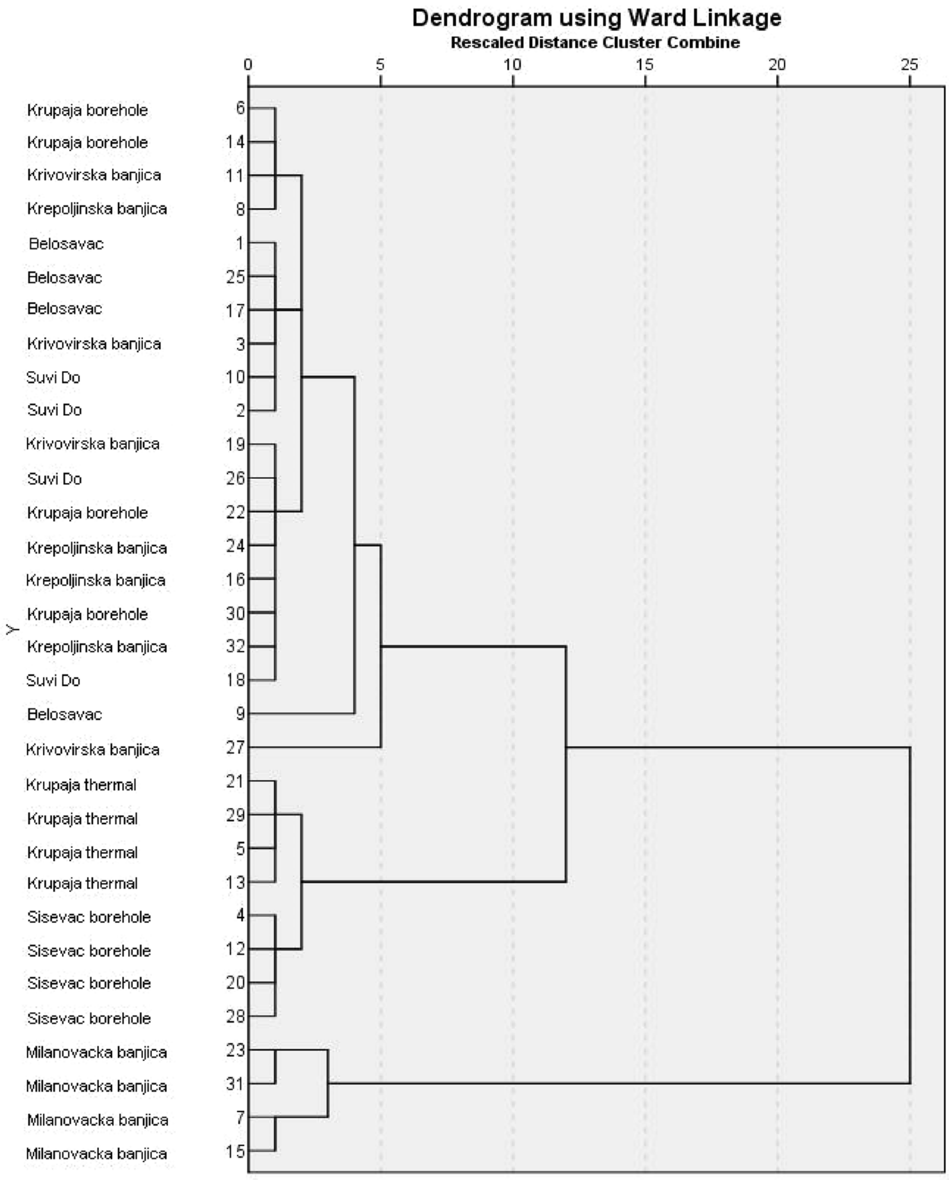
The third cluster that only extracted and recognized Milanovačka Banjica also represents potential for tourism development. This water has the potential use, not only for receiving heat from higher temperature groundwater, but also as having balneological properties, which is reflected in the high values of Na, Cl and $SO_4^{2-}$, as well as some microelements.

By grouping variables (Fig. 7) within the thermal and subthermal water of Kučaj–Beljanica Massif, three clusters were distinguished. Within the first cluster, $Na^+$, $K^+$, $SO_4^{2-}$, $F^-$, conductivity, $Cl^-$ and TDS were the variables. Within the first cluster at the smallest distance, the best correlation is given for $Na^+$, $K^+$, $SO_4^{2-}$, $F^-$ and conductivity, while at a greater distance, with a smaller correlation to the previous elements are $Cl^-$ and TDS with the greatest distance for turbidity (Fig. 7). This cluster grouped most of the macro elements together with electrical conductivity and TDS, indicating what is typical for defining water quality, the relationship between ions, TDS and conductivity. These ions are responsible for water mineralization, as well as for defining conductivity.

The second cluster is characterized by temperature, $Mg^{2+}$, $^{13}C$, temperature and $HCO_3^-$. At the minimum distance are groups of $Mg^{2+}$ and temperature, indicating a common link where an increase in temperature increases the concentration of $Mg^{2+}$in subthermal and thermal water, which indicates the release of $Mg^{2+}$ions from dacite (minerals, biotite and hornblende) at the increased temperature of groundwater. At a greater distance than Mg and temperature presented in the diagram, are the parameters $^{13}C$ and $HCO_3^-$, the correlation of which indicates that groundwater with longer residence time and longer water–rock interaction is enriched with carbonate from the carbonate host rock.

In the third cluster are $Ca^{2+}$, $NO_3^-$, pH and $O_2$. If the value of $O_2$ and $NO_3^-$ are highly correlated, this may indicate pollution, where concentrations of $NO_3^-$ increased and concentrations of dissolved oxygen decreased.

**Fig. 6** The dendogram from cluster analysis using Ward linkage

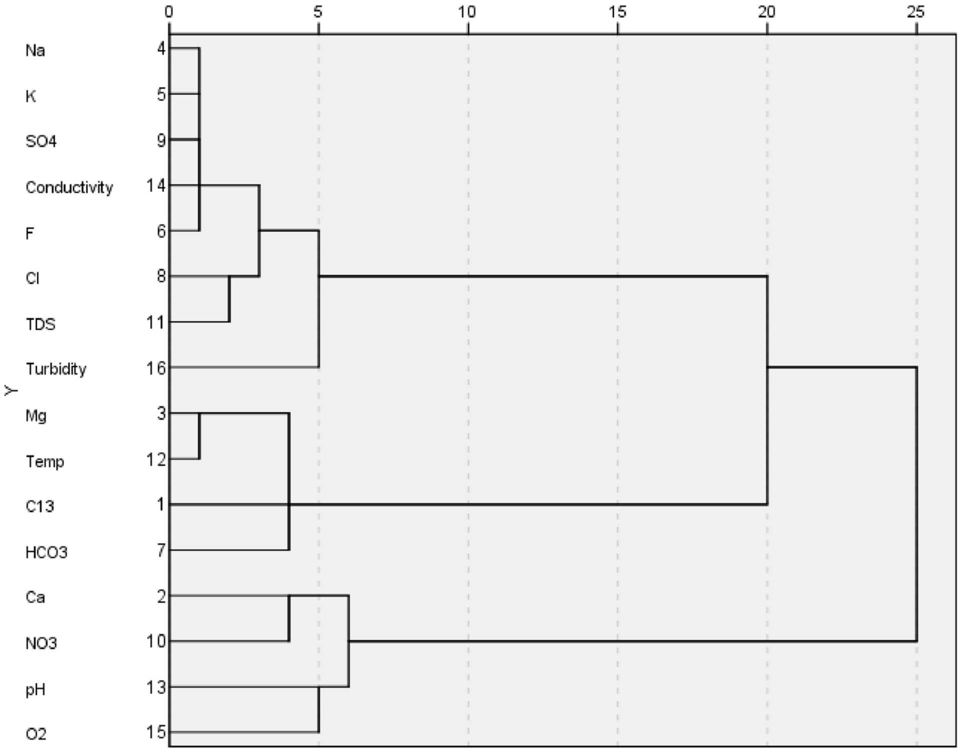


However, the karst water of the Kučaj–Beljanica Massif do not exhibit this type of pollution. The infiltration/percolation of atmospheric water from the surface into the groundwater during high rain periods (spring and fall) can enter nitrates into underground, when we also have a reduced concentrations of $Ca^{2+}$ in the thermal water and small increases in $O_2$ and $NO_3^-$, which can be the result of young water inflow into deep siphonal circulation channels. pH value is not of great importance itself, but is associated with Ca, $NO_3$ and $O_2$ as it affects the form and balance of these parameters (Ca system – carbonate/bicarbonate).

## Spatial interpolation of some parameters from Kučaj–Beljanica Massif

When the parameters of temperature, magnesium, sodium and stable $^{13}C$ isotopes are inserted into ArcGIS 9.1 program and the spatial interpolation of these parameter values for the monitored sites have been implemented, the extracted areas with elevated levels of these parameters can clearly be observed, and therefore, prospective locations can be defined based on the different aspects and purposes for utilizing these water.

**Fig. 7** The dendogram obtained by grouping variables using Ward linkage



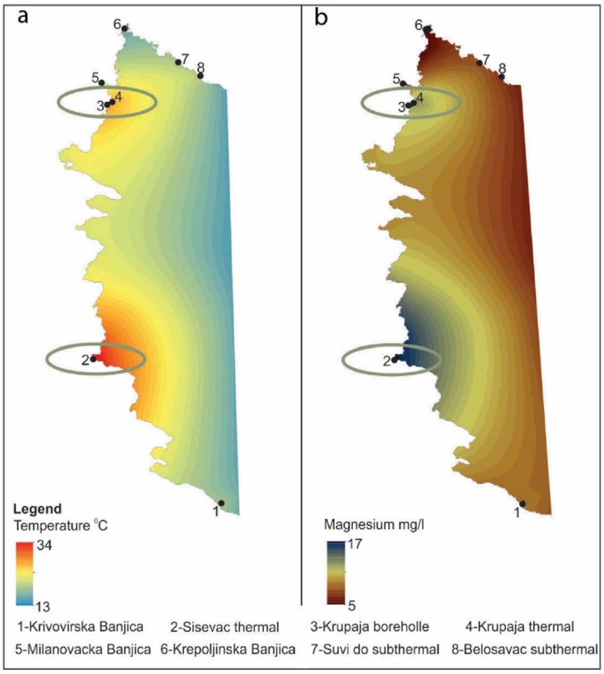


**Fig. 8** Locations with high: **a** temperature and **b** magnesium concentration in groundwater on Kučaj–Beljanica Massif

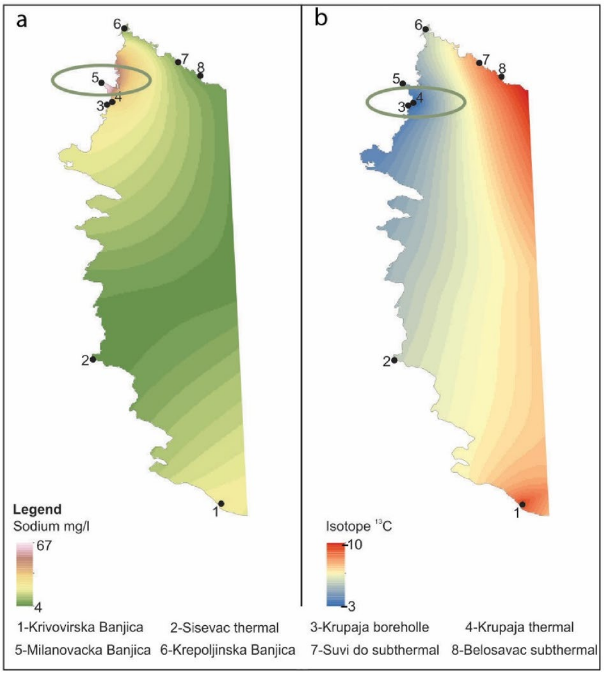


**Fig. 9** Extracted locations with high **a** sodium and **b** stable isotope $^{13}$C concentration in groundwater on Kučaj–Beljanica Massif

Therefore, the temperature and concentration of magnesium in water clearly identifies two prospective locations (Fig. 8). The location of the Krupaja phenomena (thermal spring and borehole), as well as the location in Sisevac, comprised of a borehole with the highest recorded water temperature.

On the other hand, looking at the sodium concentration in the water, the only location with elevated levels of this element is Milanovačka Banjica spring (Fig. 9a), which in addition to this element, also has a higher concentration of certain trace elements, such as Sr, Li and Si. The specific hydrochemical regime of this spring indicates that groundwater from this location may be used for therapeutic purposes. The borehole drilled next to Milanovačka Banjica is up to 150 m deep with water displaying hydrochemical parameters similar to those of Milanovačka Banjica thermal spring, including the higher temperature, which means that at greater depths, or by crossing the fault, much higher water temperatures and possibly higher micro- and macro-component concentrations can be found.

Although the borehole on Krupaja has not reached a water temperature higher than that of the natural thermal spring (26 °C) at a depth of 400 m, a temperature of 25 °C was detected at the borehole bottom, which is due to strong mixing in the shallower part of the aquifer (around a depth of 130–160 m) with cold fresh water lowering it to 18 °C. According to the stable $^{13}$C isotope values (Fig. 9b), this location has been identified as the location with the highest values, indicating that these water exhibit a significantly longer water–rock interaction compared to the other investigated subthermal and thermal phenomena. Values obtained in the summer period were used as the most representative for purposes of spatial interpolation also taking into consideration that mixing of thermal water with cold water in the drainage zone is minimized during this period. Therefore, it can be concluded that higher groundwater temperatures cannot be obtained in the Krupaja springs zone, or that drilling of much deeper boreholes may be required. In general, taking into account the geothermal gradient, groundwater temperatures up to 35 °C (ideal for various uses) may be expected at a depth of ~ 697 m.

To detect fault zones and identify future well locations, it is necessary to conduct a detailed geophysical survey, but generally, the research zone should be relocated north of Krupaja springs, closer to the zone of the Tertiary volcanic rock intrusions.

Specific locations can achieve higher water temperatures with the use of a heat pump without drilling (Table 4), for example, according to Eq. (1), Suvi do subthermal spring has an average capacity of 15 l/s with a water temperature of 20 °C can be heated up to 30 °C with the energy of $Q1 = 628.5$ kWh, which is the lowest water temperature necessary for low-temperature heating systems (panel systems) (Milenić and Vranješ 2015) and toplification of greenhouses, or to 35 °C with the energy of $Q2 = 942.75$ kWh, which is ideal for sports and recreation tourism. The use of a water–water heat pump, with a coefficient of performance 3 (Milenić and Vranješ, 2015; Luo et al. 2015; Piscagliaa et al. 2016), the consumed energy is reduced on $Q1 = 209.5/Q2 = 314.25$ kWh. Although, the use of heat pumps represents a good and cost-effective solution for achieving higher water temperatures in the aforementioned locations, this solution presents a problem at other locations (Belosavac, Krupaja, Krepoljinska Banjica and Milanovačka Banjica) due to insufficient water quantities (optimally 20–30 l/s per location) where drilling would be necessary.

$$Q = m \times c \times \Delta T, \tag{1}$$

where $Q$ is the heat energy. $m$ is the quantity of water (kg). $c$ is the thermal conductivity (4190 j/kg, K). $\Delta T$ is the difference between the actual temperature and the temperature to be achieved (K).

It was actually the multivariate analysis which led to the best selection of borehole positioning locations in accordance with the prevailing underground geochemical conditions which are of great importance for the formation of temperature and chemical groundwater characteristics.

## Conclusion

The results obtained by analysis of thermal and subthermal water in the Kučaj–Beljanica Massif area have shown that the chemical composition of the analysed locations is relatively similar to the cold karst spring water. The differences in their temperature and micro and macro components indicate deeper, siphonal circulation. The groundwater temperature differences indicate zonality in circulation and differences of karstification in the vertical profile within

**Table 4** Additional energy needed to heat groundwater at a certain temperature

| Location | $Q$ (l/s) | $T$ (°C) | $Q1$ (kWh) to heat water on $T = 30$ °C | $Q2$ (kWh) to heat water on $T = 35$ °C | Heat pump water–water (COP 3) $Q1/Q2$ (kWh) |
|---|---|---|---|---|---|
| Belosavac | 9 | 15 | 565.65 | 754.2 | 188.55/251.4 |
| Krepoljinska Banjica | 7.2 | 16.5 | 407.27 | 558.37 | 135.76/186.12 |
| Suvi do banjica | 15 | 20 | 628.5 | 942.75 | 209.5/314.25 |
| Milanovačka Banjica | 3.8 | 22 | 127.38 | 206.99 | 42.46/68.99 |
| Krupaja thermal | 2 | 26 | 33.52 | 75.42 | 11.17/25.14 |
| Krupaja boreholle | 5 | 18 | 251.4 | 356.15 | 83.8/118.72 |

the massif. The subthermal and thermal water in this area, according to their hydrogeochemical characteristics, are not classified as spa water, but due to their temperature, they are ideal for indoor and outdoor heating, toplification of greenhouses, sports and recreation tourism as well as industrial purposes.

The location which can be recommended as the most ideal for different purposes is Sisevac, since it has the highest groundwater temperature at a depth of 217 m. Another prospective location is Krupaja, where, with a newly drilled 600 m borehole, groundwater with temperatures greater than 35 °C can be extracted. Without new drilling, the thermal water of 26 °C in Krupaja can be additionally heated with the use of a heat pump, and the addition of 33.52 kWh of electrical power, the groundwater temperature can be raised to 30 °C, and with 75.42 kWh of electrical power the temperature can be raised to 35 °C, which is ideal for sports and recreation tourism, but the problem is the spring's low capacity requiring additional groundwater quantities.

The location with the highest balneological potential is Milanovačka Banjica. In addition to a higher groundwater temperature of 22 °C, it is also characterized by its very specific micro and macro composition and its high concentrations of sodium, chloride and bicarbonate. The chemical composition of this groundwater is very different from the chemical composition of typical karst water, and it can be concluded that this groundwater originates from the deepest underground aquifer and drilling deeper boreholes could bring to surface mineral-rich geothermal groundwater that can be used for spa tourism and balneology.

Other springs also can be used for sports-recreational and tourism purposes, but since they have much lower temperatures, it can be assumed that the investment in their reheating or drilling from great depth boreholes (more than 1000 m) could not be profitable.

The general conclusion is that detailed hydrochemical investigation together with the use of multivariate analysis and spatial interpolation can give significant insight on the most prospective and profitable locations for different purposes.

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