

# Хидрогеолошке и хидрохемијске карактеристике појаве термоминералних вода у реону Volkovo (Скопље - Република северна Македонија)

Hristina Petrova, Katarzyna Wątor, Ewa Kmiecik, Piotr Rusiniak, Boris Vakanjac, Vesna Ristić Vakanjac, Dimitar Petrov



Дигитални репозиторијум Рударско-геолошког факултета Универзитета у Београду

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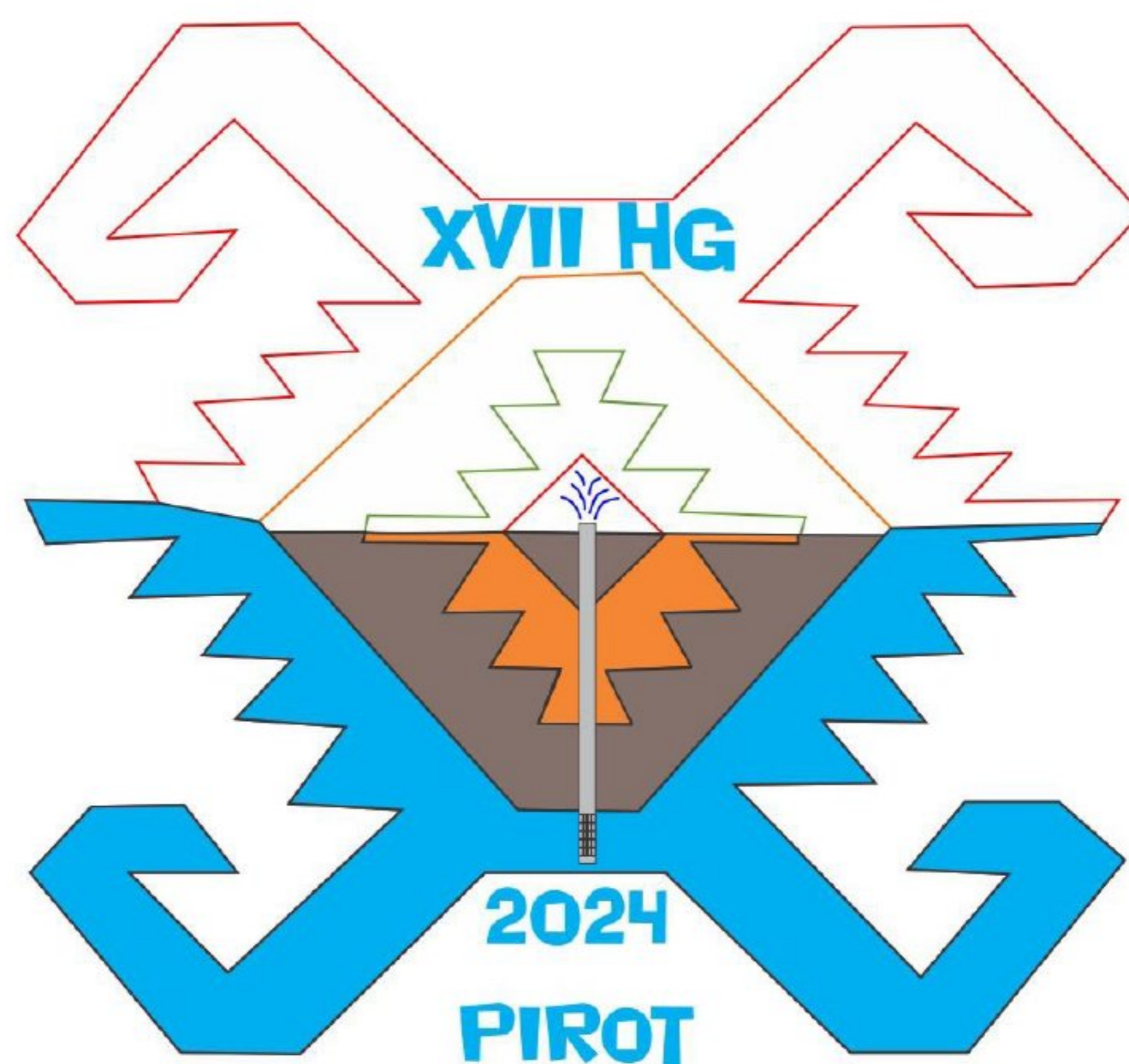
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UNIVERZITET U BEOGRADU  
RUDARSKO-GEOLOŠKI FAKULTET  
DEPARTMAN ZA HIDROGEOLOGIJU

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XVII SRPSKI SIMPOZIJUM  
O HIDROGEOLOGIJI  
sa međunarodnim učešćem

**ZBORNİK RADOVA**



02-06. oktobar  
2024. godine

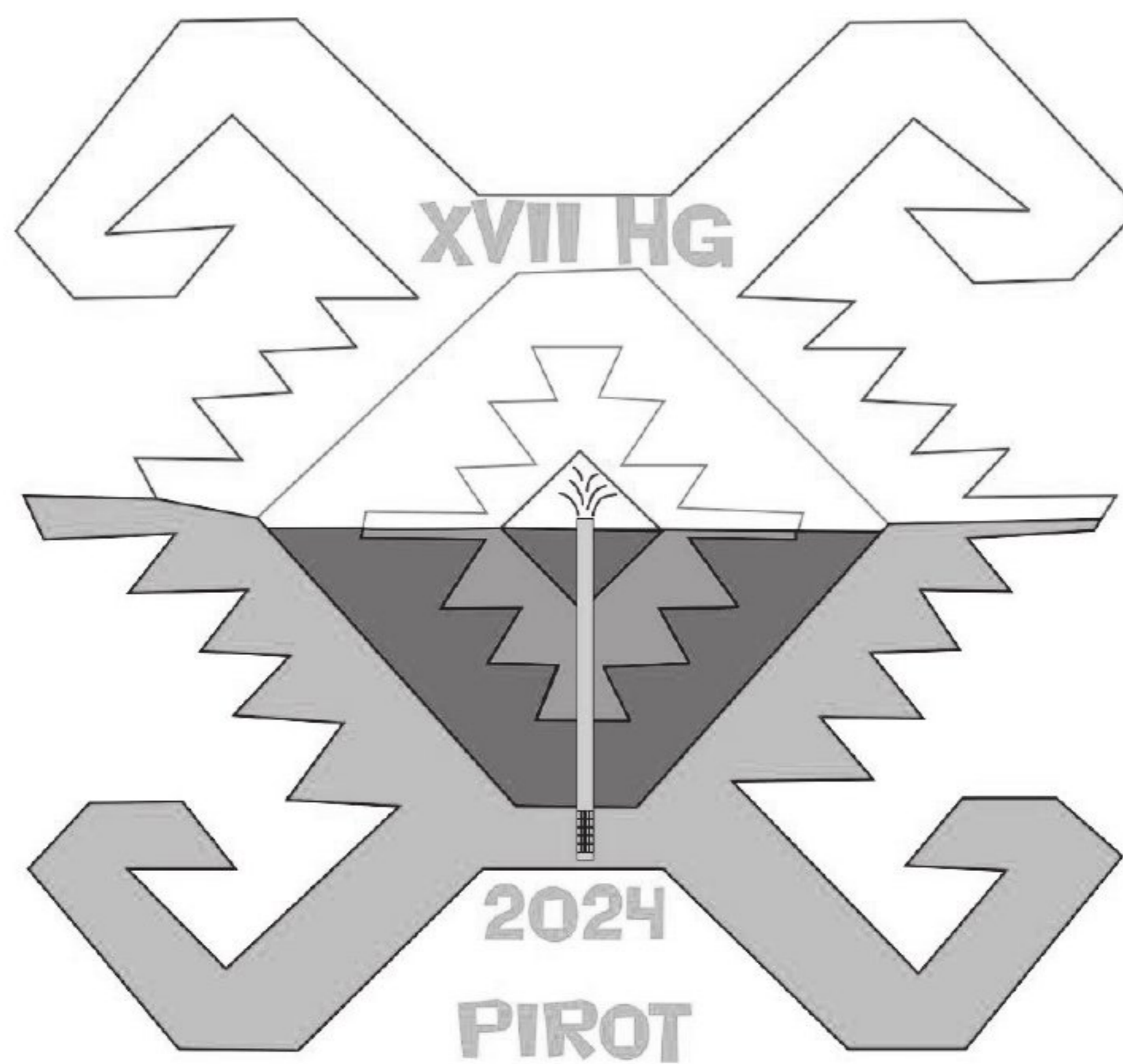


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**ZBORNİK RADOVA**

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*UNIVERZITET U BEOGRADU  
RUDARSKO-GEOLOŠKI FAKULTET  
DEPARTMAN ZA HIDROGEOLOGIJU*

*u saradnji sa*

*SRPSKIM GEOLOŠKIM DRUŠTVOM*

*SAVEZOM INŽENJERA I TEHNIČARA SRBIJE*

*DRUŠTVOM GEOLOŠKIH INŽENJERA I TEHNIČARA SRBIJE*

*NACIONALNIM KOMITETOM IAH*

*MULTILATERALNIM CENTROM, PIROT*

***POKROVITELJI:***

***MINISTARSTVO NAUKE, TEHNOLOŠKOG RAZVOJA I INOVACIJA  
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***GRAD PIROT***

***SPONZORI:***

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***TAŠ GRUPA***

***AQUA PRO ENERGY D.O.O.***

***CENTAR ZA HIDROGEOLOGIJU KARSTA***

***TURISTIČKA ORGANIZACIJA PIROT***

***IBIS-INŽENJERING D.O.O.***

***STRATING D.O.O.***

***GECO-INŽENJERING D.O.O.***

***FREATIKA***

***AGENCIJA ZA MARKETING BACKGROUND***

## Uvodna reč organizatora

Poštovane kolegice i kolege,

nakon samo dve godine od održavanja XVI Srpskog simpozijuma o hidrogeologiji sa međunarodnim učešćem, ponovo imamo priliku da se družimo na ovom veoma značajnom skupu za hidrogeologe. Razlog „ubrzanja“ održavanja Simpozijuma je zapravo ponovno uspostavljanje dvogodišnjeg razmaka održavanja Srpskog simpozijuma o hidrogeologiji i Geološkog kongresa Srbije. Objašnjenje za ovakav korak leži u tome da je prethodni Simpozijum, prema uspostavljenoj dinamici od 2012. godine (Zlatibor), preko 2016. godine (Kopaonik), trebalo da se održi 2020. godine, ali je usled globalne pandemije korona virusa (COVID-19), došlo do njegovog pomeranja na 2022. godinu, kada je i održan na Zlatiboru. Upravo iz iznetih razloga, a uz veliki trud i zalaganje organizatora zarad ponovnog uspostavljanja dvogodišnjeg niza sa Kongresom geologa Srbije, XVII Srpski simpozijum o hidrogeologiji sa međunarodnim učešćem se održava ove godine od 2.10.-6.10. 2024. godine u Pirotu.

Kroz XVII Simpozijum će se na neki način izvršiti retrospektiva prethodnih Simpozijuma, počevši od 1971. godine do 2024. godine, sa ciljem da se sublimira i prikaže položaj hidrogeologije kao nauke i struke, kako u Srbiji, regionu, pa i šire. Počevši od prvog Simpozijuma koji je održan u Herceg Novom 1971. godine, preko ostalih Simpozijuma održavanih širom bivših Republika Jugoslavije, kao i tad i sada je jedini usko stručni skup koji za cilj ima izlaganje naučnih i tehničkih dostignuća iz oblasti izučavanja podzemnih voda i prikaz izuzetne važnosti ovih istraživanja za sva moderna i razvijena društva.

Kao specijalni poklon Organizatora skupa, svim učesnicima skupa će na raspolaganju biti skenirani zbornici radova Simpozijuma (Sveske Hidrogeologija) od 1971. godine zaključno sa ovim poslednjim Simpozijumom koji se održava u Pirotu ove godine.

Zahvaljujući kolegama koji su do sada dali značajan doprinos, a kroz veliko zalaganje i trud u održavanju prethodnih Simpozijuma, danas je ovaj Simpozijum ponovo jedan od najznačajnijih događaja, kako hidrogeološke, tako i cele geološke struke u Srbiji i regionu.

Za ovaj XVII-ti Simpozijum, iako sa kratkim rokom za pripremu i organizaciju samog događaja i za animiranje kolega da pripreme i pošalju radove, pristigao je veliki broj radova, kako iz Srbije, tako i iz regiona, pa i šire. Na Simpozijumu će biti prezentovano više od 90 radova iz svih grana hidrogeologije, sa preko 200 autora i koautora radova, što je i dokaz uspešnosti i dobre reputacije ovog skupa, sa nadom da se tako nastavi i predstojećim godinama. Uz ove podatke, posebno je važno naglasiti da će na svečanom otvaranju ovogodišnjeg Simpozijuma biti izloženi plenarni referati kolega hidrogeologa iz svih 6 država bivše SFRJ, kao prilog i osvrt na položaj i budućnost značaja hidrogeologije.

Svi prihvaćeni radovi koji su prošli recenzentski postupak su svrstani u 6 tematskih sesija:

1. Vodosnabdevanje i upravljanje vodnim resursima
2. Zaštita podzemnih voda
3. Mineralne vode i njihovo iskorišćavanje
4. Geotermalna energija
5. Hidrogeološka istraživanja u hidrotehnici, rudarstvu i građevini
6. Studentski radovi

Podela na ovakve tematske grupe u najvećoj meri utiče aktuelnost hidrogeologije u određenim oblastima vezanim za održivo upravljanje ovim dragocenim resursom od koga zavise kako stanovništvo, tako i različite grane privrede u Srbiji i regionu, što najbolje ilustruju plenarna predavanja koja su sastavni deo Simpozijuma i zbornika radova.

Ovaj XVII-ti Srpski simpozijum o hidrogeologiji je organizovan pod pokroviteljstvom Grada Pirota i JKP „Vodovod i kanalizacija“ Pirot i uz podršku Ministarstva nauke, tehnološkog razvoja i inovacija Republike Srbije.



Takođe, veliku zahvalnost dugujemo i kompanijama koje su sponzorisale ovaj naučni skup: Departman za hidrogeologiju, BeoGeoAqua d.o.o., Taš grupa, Aqua Pro Energy d.o.o., Ibis-Inženjering d.o.o., Strating d.o.o., GECO-Inženjering d.o.o., FREATIKA, CKH, TO Pirot, Background.

Praksa koja je zaživela na XV Simpozijumu, o učestvovanju kolega iz regiona i šire i time doprinela da ovaj skup dobija i značajne međunarodne okvire, se pojačava i na ovom skupu. Izuzetno nam je zadovoljstvo da ove godine možemo poželeti dobrodošlicu u grad Pirot kolegama iz Republike Srpske i Federacije BiH, Crne Gore, Hrvatske, Slovenije, Severne Makedonije, Bugarske, Mađarske, Rusije, Poljske, SAD i Togo-a.

Veliku zahvalnost za organizovanje ovako velikog skupa u veoma kratkom vremenskom roku izražavamo Generalnom sekretaru simpozijuma prof. dr Vesni Ristić Vakanjac, Predsednici uređivačkog odbora Doc. dr Ljiljani Vasić, Članovima Organizacionog odbora: dr Branislavu Petroviću, naučnom saradniku i dr Veljku Marinoviću, naučnom saradniku. Takođe, zahvalnost izražavamo i Članovima Tehničkog odbora Srđanu Stefanoviću i Petru Vojnoviću, kao i svim dragim kolegama i studentima, članovima Tehničkog, Organizacionog i Naučnog odbora koji su pomogli da se ovaj skup održi.

U ime organizatora skupa želimo vam lep boravak u Pirotu.

U Pirotu, oktobar 2024. godine.

Predsednik Organizacionog odbora  
Prof. dr Saša Milanović



Predsednik Naučnog odbora  
Prof. dr Dušan Polomčić





## SADRŽAJ

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**HIDROGEOLOŠKE I HIDROHEMIJSKE KARAKTERISTIKE POJAVE  
TERMOMINERALNE VODE U REONU VOLKOVO  
(SKOPLJE – REPUBLIKA SEVERNA MAKEDONIJA)**

**HYDROGEOLOGICAL AND HYDROCHEMICAL CHARACTERISTICS OF  
THE OCCURRENCE OF THERMO-MINERAL WATER IN THE VOLKOVO  
REGION (SKOPJE - REPUBLIC OF NORTH MACEDONIA)**

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**APSTRAKT:** Kao rezultat tektonskog sklopa i kompleksnog litološko-geološkog sastava, na teritoriji Republike Severne Makedonije registrovan je veliki broj pojava termalnih, mineralnih i termomineralnih voda (T, M i TM voda). Dosadašnja hidrogeološka i hidrohemijaska istraživanja ovih voda vršena od strane pojedinih autora sa ciljem da se definiše njihov lekoviti faktor kao i za potrebe banjskog turizma. Sprovedena istraživanja su, dakle, bila lokalnog karaktera i bila su vezana za njihove značajnije pojave. Tokom 70-tih godina prošlog veka, Kotevski je za potrebe izrade doktorske distertacije izvršio uzorkovanje u tom trenutku dostupnih T, TM i M voda (170 pojava) sa ciljem definisanja njihovog osnovnog sastava. Cilj ovog rada je da se na primeru pojave TM voda Volkovo (Skoplje) da uporedna analiza hemijskog sastava dobijenog 1975. i rezultata analiza koje su izvršene tokom 2023. godine. Pored uporedne analize osnovnog hemijskog sastava, u radu će biti date i mikrokomponente ovih voda kao i njihov lekoviti faktor.

**Ključne reči:** termomineralne vode, hidrohemijske karakteristike, lekoviti faktor voda, Volkovo, Republika Severna Makedonija

**ABSTRACT:** As a result of the tectonic structure and lithological-geological composition, a large number of occurrences of thermal, mineral, and thermomineral waters (T, M, and TM waters) have been registered in the territory of the Republic of North Macedonia. Previous hydrogeological and hydrochemical research on these waters was carried out by individual authors with the aim of defining their healing properties and promoting spa tourism. The conducted research was, therefore, of a local character and was related to more significant phenomena. During the 1970s, Kotevski, for his doctoral dissertation, sampled all T, TM, and M waters available at that time (170 occurrences) to define their basic composition. The idea of this paper is to provide a comparative analysis of the chemical composition obtained in 1975 and the results of analyses carried out during 2023 using the example of TM water from Volkovo (Skopje). In addition to the comparative analysis of the basic chemical composition, the microcomponents of these waters as well as their healing properties will be presented in the paper.

**Key words:** thermomineral waters, hydrochemical characteristics, healing factor, Volkovo, Republic of North Macedonia

## INTRODUCTION

Mineral waters represent a significant economic potential for every country. In general, the average age of residents in the Balkans and Europe is getting higher and higher. In Republic of North Macedonia, according to the 2021 census, the average age is 40.08 years (<https://www.danas.rs/svet/u-severnoj-makedoniji-zivi-18-miliona-stanovnika/>), while the average age of EU residents is 43 years (<https://www.danas.rs/svet/prosecna-starost-stanovnika-u-eu-oko-43-godine/>). Additionally, the lifestyle and dietary habits based on fast food have led to various health problems among the majority of residents, including excessive obesity, high blood pressure, and high blood sugar. Physical therapy, mountain tourism, and particularly balneotherapy and balneotourism, can yield good results in the prevention and reduction of these health issues. In the future, thermal, mineral, and thermomineral (T, M,

and TM) waters will be valuable resources for investment to ensure the population can utilize them unhindered. Macedonia and Serbia are small in area but are extremely rich in the number and variety of these occurrences based on their composition and healing properties. This raises the question of how renewable these resources are, considering their geological, hydrogeological, geochemical, or isotopic characteristics.

Thermal and mineral springs are created under specific geological conditions, resulting from the interaction between water and the geological environment in both the near and distant past, and continue to form today. Throughout the history of human civilization, this resource was initially recognized for maintaining personal hygiene (basic physiological needs), and later for its medicinal properties (bathing, treatment, therapy), and even for religious rituals (Porowski, 2019). According to the same author, archaeological findings confirm that mineral and thermal waters were used for bathing during the Bronze Age (12,000 - 3,000 years BC) and that people formed their settlements near these sources at that time. For example, remains of such settlements in Japan date back to around 11,000 years BC.

As certain sciences developed, chemists and doctors began to study the chemical properties and medicinal benefits of these waters. This led to the development of balneology and the publication of scientific and professional works on the topic. One of the first doctoral dissertations on this subject related to the territory of the Republic of North Macedonia was by Kotevski, who defended his dissertation in 1979, entitled 'Hydrogeology of Mineral, Thermal, and Thermomineral Waters in the Territory of the Republic of Macedonia,' which includes 170 occurrences in the territory of Macedonia. The dissertation presents general data on springs, dug or drilled wells, as well as their geological and hydrogeological characteristics, including chemical analyses that formed the basis for the reclassification and categorization of these waters. However, microcomponents were examined in only 34 occurrences.

One of the sampled locations is the thermal mineral waters of Volkovo, which belong to the Skopje basin. Sampling of these waters was initially carried out in 1975. After 48 years, in 2023, a two-day sampling campaign of thermal, mineral, and thermomineral waters in the eastern part of the Republic of North Macedonia was conducted, resulting in a total of 15 samples. For the purposes of this manuscript, the thermal mineral water of the Volkovo locality was chosen for the reason that only this locality experienced changes in water chemistry.

## RESEARCH METHODOLOGY

The Republic of North Macedonia is rich in thermal, mineral, and thermomineral waters, thanks to its geological structure and the hydrogeochemical processes that have occurred throughout its history. Each source has its specific characteristics and a unique regime of quantitative and qualitative parameters. Understanding these regimes is essential for the rational use of these waters. In 2023, 15 samples of mineral and thermomineral water were collected from springs, dug wells, and drilled wells in the eastern part of Macedonia. These 15 occurrences belong to two geotectonic units: the Vardar Zone and the Serbian-Macedonian Massif. The aim of this research was to determine the physical and chemical characteristics of mineral and thermomineral waters, with an emphasis on the presence of microelements and their healing properties.

The samples were collected in polyethylene bottles. In situ measurements were performed in the field, including water temperature (T), electrical conductivity (EC), and pH. After collection, the samples were protected from environmental influences and transported to the Hydrogeochemical Laboratory of the Department of Hydrogeology and Engineering Geology at the Faculty of Geology, Geophysics, and Environmental Protection, AGH University of Krakow. Laboratory analyses included measurements of the major ions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), as well as trace elements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sr, Ti, Tl, V, Zn, Zr).

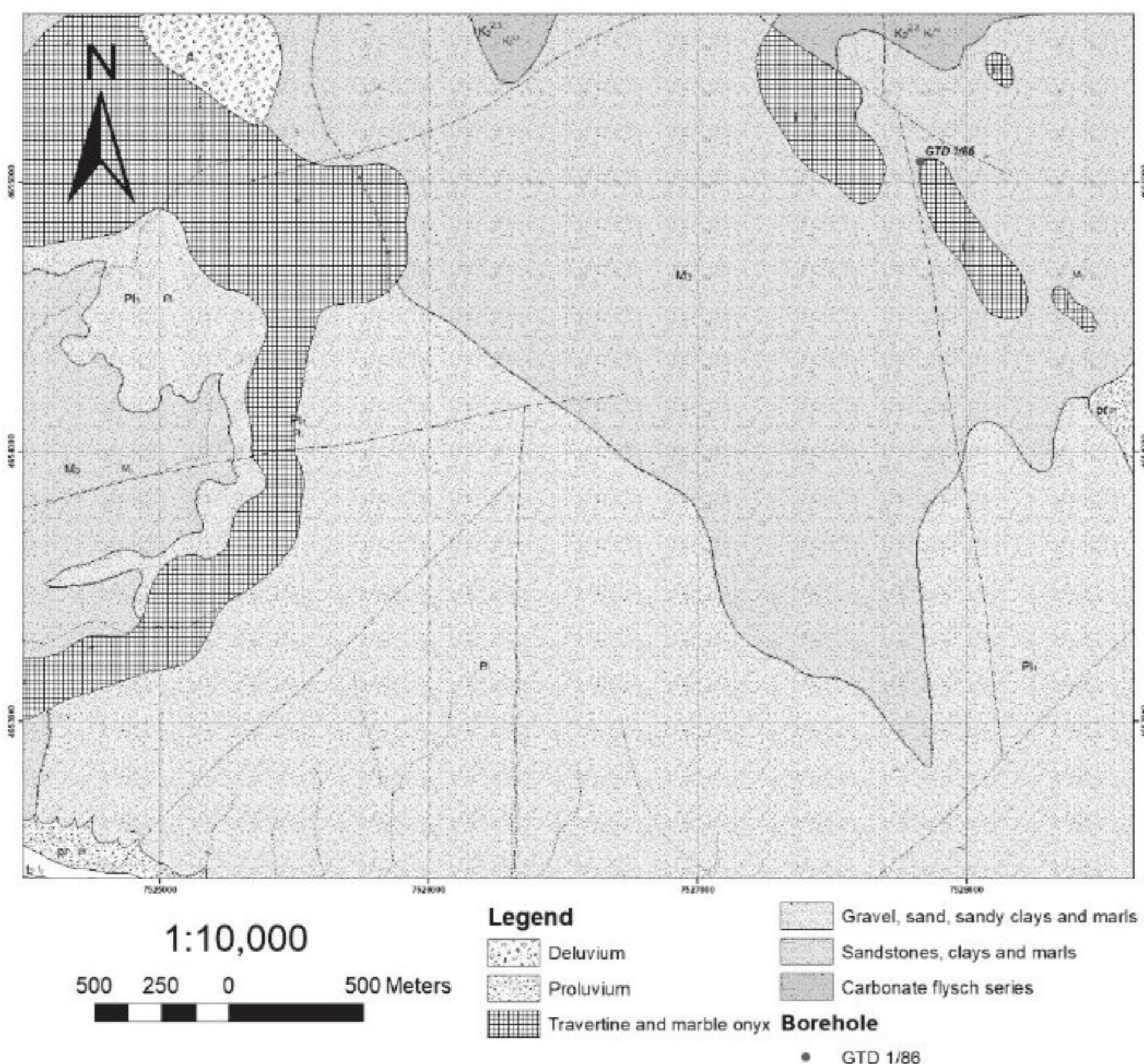
## RESULTS

The analyzed sampled thermal mineral water from Volkovo is located in the western part of the territory of the capital, Skopje. Today, Volkovo is an urban and modern settlement in the Skopje basin, with an average annual temperature of about 12.4°C. Summers are long, dry, and hot, while winters are cold with many foggy days. Geomorphologically, the terrain represents the transition from the Skopje Basin to the Skopska Crna Gora. As the transition is gradual, the relief is slightly inclined towards the basin. It is essentially a plain between the rivers Vardar and Lepenec.

The location of this phenomenon is at the contact of two geotectonic units: the West Macedonian and Vardar zones, allowing us to classify it within the Vardar zone. The West Macedonian zone includes part of the Raduški peridotite massif, mostly covered by Upper Miocene sediments. In contrast, the Vardar zone consists of Cretaceous sediments, flysch, and reef limestone, mainly covered by Tertiary sediments. On the

surface of the investigated terrain, the oldest rocks are Jurassic peridotites from the Raduški massif, represented by three varieties: harzburgites, dunites, and a mixed series, which includes diabases and metagabbros. The rocks of the Raduški peridotite massif are tectonically damaged and cracked, and are largely serpentinized due to contact with surrounding rocks and fault structures.

Jurassic peridotites in the extreme NW part of the terrain are represented by two series: one of dunites and harzburgites, and a mixed series containing gabbros and metadiabases. The rocks of both series are tectonically damaged, with visible blocks exhibiting larger and smaller dislocations. Secondary cracking caused by the brittleness of the rocks is also present. Metamorphism phenomena such as serpentinization and shale formation have transformed these rocks under the influence of endogenous and exogenous factors, creating conditions conducive to the circulation and accumulation of groundwater (Fig. 1).



**Slika 1.** Geološka karta šire okoline lokaliteta Volkovo

**Figure 1.** Geological map of the extended area of Volkovo locality

Replenishment primarily occurs through precipitation, which infiltrates through permeable rocks and contact zones along the basin's rim. The groundwater level is located at a considerable depth from the ground surface, averaging 18 to 22 meters.

In the Volkovo region, mineral waters have been known for a very long time. The first reports about them were documented by B. Baić in 1929. Later, in 1975, exploratory drilling, detailed geological, hydrogeological, and geothermal research, as well as chemical analyses, provided new information about this locality. Specifically, during these investigations, the exploratory geothermal well GTD-1/86 was drilled to a depth of 186 meters, resulting in the discovery of thermomineral water with a temperature of 24.8°C, a flow rate of 63 l/s, and a pressure of 4.2 bar. Initially, the GTD-1/86 well was planned to be drilled to 300 meters, but due to the eruption of pressurized water, drilling was stopped at 186 meters. The well report indicates that between 184.3 and 186 meters, a fault coated with nickel-magnetite was encountered. Nickel-bearing magnetite is also present as fine inclusions in the core from this interval.

In the 1980s, this water was bottled under the name 'Skopjanka' and put on sale. The author G. Kotevski also performed a chemical analysis, and the results were presented at the VIII Yugoslav Symposium on Hydrogeology and Engineering Geology in Budva in 1984 (Kotevski & Gerasimova, 1984). The results showed that the water was hydrogencarbonate-calcium-magnesium-sodium with a mineralization of 2290 mg/l, although data on pH and temperature were missing. Later, during the construction of the aforementioned well, the water temperature was determined to be 24.8°C.

The hydrochemical results of the sample taken in August 2023 showed that the water type has changed and now it is hydrogencarbonate-sodium-magnesium, and also the concentrations of certain ions have changed significantly. While the water temperature in the 1986 report was 24.8°C, the latest measurement showed an increased value of 0.5°C, with the temperature now being 25.3°C. The latest analysis also indicates the presence of certain microcomponents, including Ba, Li, Mn, Ni, P, Se, and Sr. The results of the analysis are shown in Table 1, while Table 2 provides a comparative analysis of the basic components of these waters obtained in 1975 and 2023.

**Tabela 1.** Fizičko – hemijske karakteristike termomineralnih voda lokaliteta Volkovo**Table 1.** Physical and chemical characteristics of thermomineral waters from the Volkovo locality.

"In situ" measurements			Macrocomponents (Makrokomponente)								
T	pH	EC	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	B	Si
[°C]	[-]	[mS/cm]	[mg/L]								
25.3	7.5	2.53	168.9	1495.4	34.7	110.3	132.6	296.3	10.3	5.8	15.7
Microcomponents (Mikrokomponente) [µg/L]											
Ag	Al	As	Ba	Be	Cd	Co	Cr	Fe	Li	Mn	Mo
<5	<5	<5	158.08	<5	<5	<5	<5	<5	240.81	70.9	<5
Ni	P	Pb	Sb	Se	Sr	Ti	Tl	V	W	Zn	Zr
16.91	15.99	<5	<5	8.49	1099.3	<5	<5	<5	<5	<5	<5

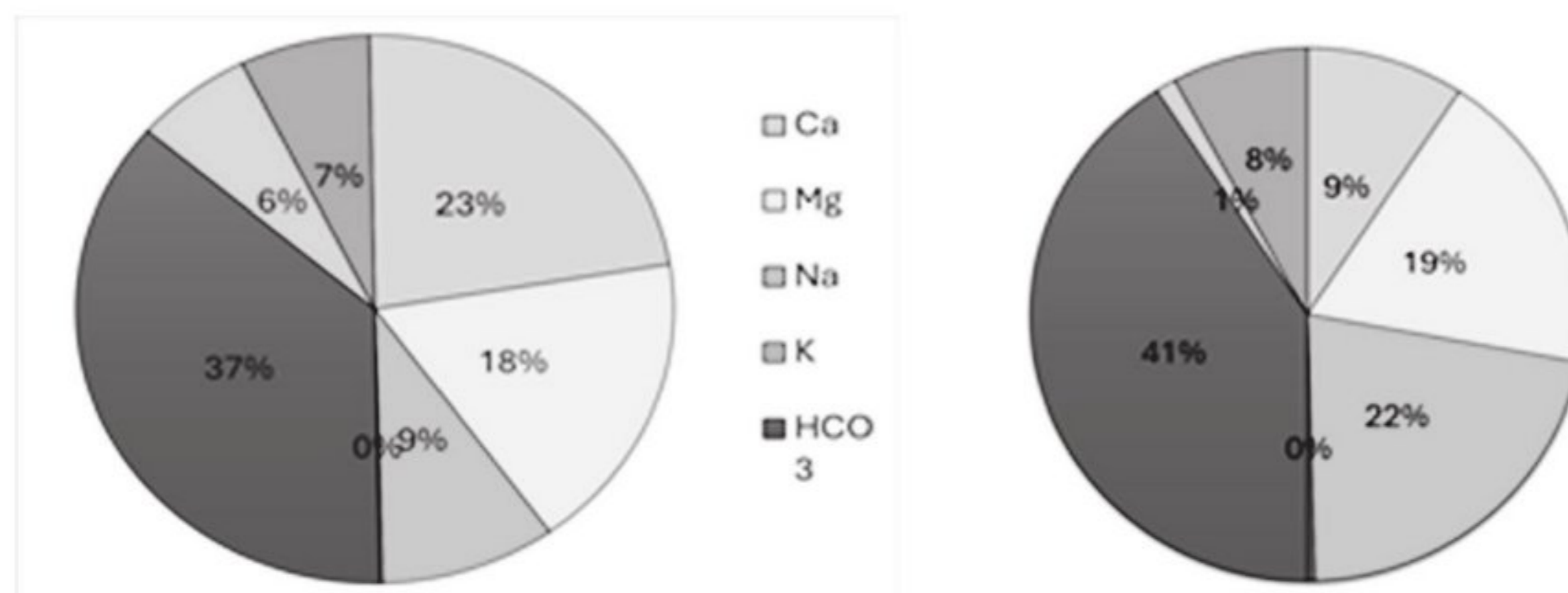
**Tabela 2.** Sadržaj osnovnih komponenti termomineralnih voda lokaliteta Volkovo iz 1975. i 2023. godine.**Table 2.** Content of basic components of thermomineral waters from the Volkovo locality in 1975 and 2023.

Year (Godina)	Cl <sup>-</sup> [mg/L]	HCO <sub>3</sub> <sup>-</sup> [mg/L]	SO <sub>4</sub> <sup>2-</sup> [mg/L]	Ca <sup>2+</sup> [mg/L]	Mg <sup>2+</sup> [mg/L]	Na <sup>+</sup> [mg/L]	K <sup>+</sup> [mg/L]
1975	283.9	2530	350.0	472.0	221.0	277.0	7.5
2023	168.9	1495	34.7	110.3	132.6	296.3	10.3

## DISCUSSION

From the comparative analysis, we can see that the concentration of chloride, hydrogencarbonate, sulfate, calcium, and magnesium decreased in percentage, while the concentration of sodium and potassium increased (Fig. 2). One of the factors contributing to these changes is undoubtedly anthropogenic activity. Urbanization in this part of the city, along with the presence of numerous shallow and deep wells, has led to the mixing of ground- and surface water, significantly affecting the water quality.

The hydrochemical type of this water has also changed from HCO<sub>3</sub>-Ca-Mg-Na to HCO<sub>3</sub>-Na-Mg. The dominant anion remains the hydrogencarbonate ion. Although the content of this ion expressed as % mval has increased (1975 – 73% mval, 2023 – 82% mval), the total concentration in mg/L has decreased by about 40%. The percentage of chloride ions in % mval is now similar to that in 1975 (14% and 16% mval, respectively), while sulfate ions now make up significantly less than they did 50 years ago (1975 – 12.8% mval, 2023 – 2.4% mval). Among the cations, sodium currently dominates (43% mval) followed by magnesium (37% mval), with calcium constituting about 18.5% mval. Analysis results from 1975 indicated that calcium then accounted for 43.5% mval, magnesium 34% mval, and sodium approximately 22% mval (Fig. 3).



**Slika 2.** Koncentracije glavnih jona u termomineralnoj vodi izražene u % mval  
**Figure 2.** The concentrations of major ions in the thermomineral water expressed in % mval

**Tabela 3.** Vrednosti izračunatih hidrohemijskih indikatora za uzorak vode uzet u 1975. i 2023. godini**Table 3.** Values of calculated hydrochemical indicators for the water sample collected in 1975 and 2023

Year	rNa <sup>+</sup>	rNa <sup>+</sup>	rSO <sub>4</sub> <sup>2-</sup> × 100	rHCO <sub>3</sub> <sup>-</sup>	rCa
Godina	rCl <sup>-</sup>	rNa <sup>+</sup> +rCl <sup>-</sup>	rCl <sup>-</sup>	rCl <sup>-</sup>	rMg
1975	1.51	0.60	91.18	5.19	1.28
2023	2.71	0.73	15.19	5.15	0.50

Changes in ion concentrations also affect the values of hydrogeochemical indicators (Tab. 3, Fig. 4). High sulfate index values may result from recharge by groundwater from karst formations, which often

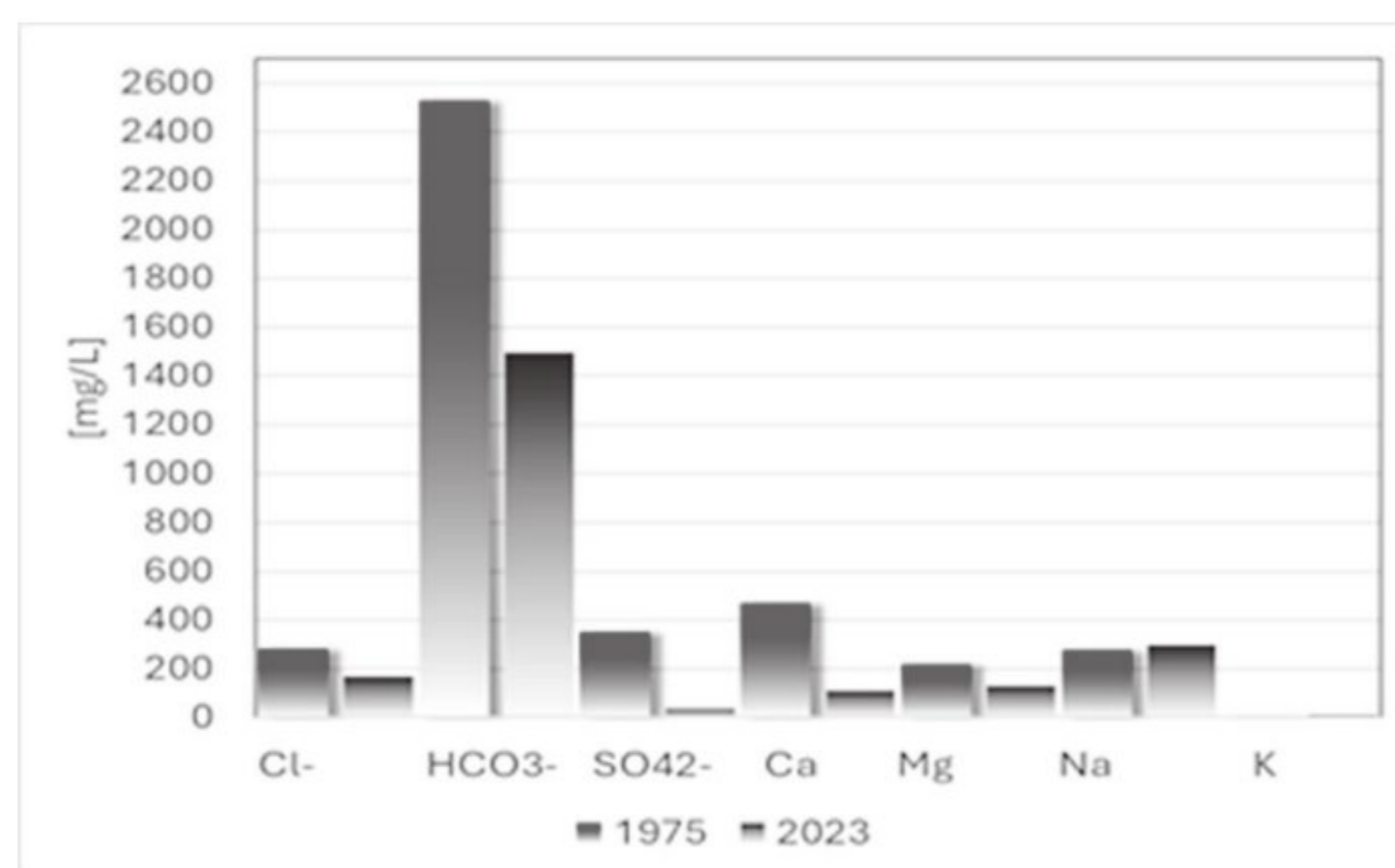
contain dissolved gypsum (Han et al. 2009). Currently, the value of this index, like  $rCa/rMg$ , has significantly decreased compared to 1975. On the other hand, the values of sodium indicators –  $rNa/rCl$  and  $rNa/(rNa+rCl)$  – have increased, suggesting inflow from an active water exchange zone. Equivalent ratio values of  $rNa+/(rNa+/rCl-)$  above 0.5 suggest that  $Na^+$  ions primarily originate from ion exchange processes between clay minerals present in marls or clays (Hounslow, 1995).

The analysis results were also compared with the requirements of EU and Macedonian legislation concerning mineral, spring, and table waters (Directive, 2003; Služben vesnik na RM, 2018) (Tab. 4).

**Tabela 4.** Usporedni prikaz dobijenih rezultata sa EU i Makedonskom regulativom

**Table 4.** Comparison of results of analysis with EU and Macedonian regulations

Parameter	Directive, 2003; Regulation, 2018 [mg/L]	DWD, 2020 [mg/L]	Concentration [mg/L]
Sb	0.005	0.010	<0.005
As	0.010	0.010	<0.005
Ba	1.0	Not established	0.158
B	Not established	1.5	5.80
Cd	0.003	0.005	<0.005
Cr	0.050	0.025	<0.005
Cu	1.0	2.0	<0.005
Pb	0.010	0.005	<0.005
Mn	0.50	0.050	0.071
Ni	0.020	0.020	0.017
Se	0.010	0.020	0.009
Al	Not established	0.200	<0.005
Cl	Not established	250	168.9
Fe	Not established	0.200	<0.005
SO <sub>4</sub>	Not established	250	34.7
Na	Not established	200	132.6



**Slika 4.** Promene u koncentracijama glavnih jona u ispitivanoj vodi tokom godina  
**Figure 4.** Changes in the concentrations of major ions in the studied water over the years

No exceedances were found for any of the tested parameters with respect to the requirements for mineral waters. However, attention should be paid to the concentrations of selenium and nickel, which are very close to the maximum allowable concentrations specified in the Directive (2003) and Regulation (2018). The tested waters do not meet the requirements for water intended for human consumption. Exceedances of the standards set by the DWD (2020) were found for boron and manganese.

From the perspective of trace elements present in the studied water, strontium and lithium stand out. Strontium concentrations are above 1 mg/L, while lithium concentration is 0.24 mg/L. Strontium, due to its chemical similarity to calcium, positively influences bone health by integrating into their structure, particularly when present as Sr(II). Supplementation of this element positively affects bone density, volume, and microarchitecture (Shahnazari et al., 2006). Strontium, in the form of strontium ranelate, is used as a treatment for osteoporosis (Reginster et al., 2003; Fogelman & Blake, 2005; Blake & Fogelman, 2006). On the other hand, lithium is observed to have a positive effect on psychiatric therapy, particularly in reducing mortality due to suicide attempts among patients with affective disorders (Barjasteh-Askari et al., 2020). It is used in therapy as a mood stabilizer. Research on lithium exposure and its effects on health is ongoing

and debated, often due to difficulties in translating findings to populations and lack of information on variables that may significantly impact the behavior of individuals with affective disorders (Knudsen et al., 2017).

## CONCLUSION

Taking into account all the aspects mentioned above, we can summarize that the Volkovo locality is located in the western part of the Skopje valley and is part of the capital of the Republic of North Macedonia, Skopje. During 1975, chemical analysis was carried out by G. Kotevski, while in 2023 a sample was taken again for analysis. The comparative analysis of these results showed that, as a result of urbanization and anthropogenic factors, the hydrochemical type of the water in this area has changed significantly. Comparing the results of the analysis with the rulebook on the special requirements for the safety of natural mineral, spring water and other packaged water, the concentrations of selenium and nickel are close to the limit of maximum permissible concentrations specified in the above rulebook. The water does not meet the criteria for drinking, but an increased concentration of certain microcomponents, specifically boron, manganese, strontium and lithium, whose medicinal effect can be used in the treatment of various diseases, has been registered.

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