A contribution to the understanding of hydrochemical properties of thermomineral water on the L'dži locality (eastern part of North Macedonia)

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

10.52215/rev.bgs.2023.84.3.303

СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 84, кн. 3, 2023, с. 303–306

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 84, part 3, 2023, p. 303–306

Национална конференция с международно участие „ГЕОНАУКИ 2023“
National Conference with International Participation “GEOSCIENCES 2023”

A contribution to the understanding of hydrochemical properties of thermo-mineral water on the L’dži locality (eastern part of North Macedonia)

Hristina Petrova[1], Katarzyna Wątor[2], Piotr Rusiniak[2], Boris Vakanjac[3], Vesna Ristić Vakanjac[1], Ewa Kmiecik[2]

[1] University of Belgrade, Faculty of Mining and Geology; E-mails: g808-23@dok.rgf.bg.ac.rs; vesna.ristic@rgf.bg.ac.rs
[2] AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection;
E-mails: katarzyna.wator@agh.edu.pl; piotr.rusiniak@agh.edu.pl; ewa.kmiecik@agh.edu.pl
[3] Military Geographical Institute “General Stevan Bošković”; E-mail: boris.vakanjac@vs.rs

Принос към разбирането на хидрохимичните свойства на термоминералната вода в находището Лджи (източна част на Северна Македония)

Христина Петрова[1], Катажина Вонтор[2], Пьотр Русиняк[2], Борис Ваканяц[3], Весна Ристич Ваканяц[1], Ева Кмечик[2]

Abstract. Regarding the aspect of mineral, thermo-mineral, and thermal waters, on the territory of the Republic of North Macedonia, there are 65 registered locations, of which 8 are categorized as spas. This includes the Kežovica spa, also known as the Štipska spa. In the vicinity of Kežovica Spa is the thermo-mineral L’Dži spring with mineralization around 1.3 g/L and the water temperature at the time of sampling was 50.1 °C. Spring L’Dži is generated by a fault structure and is linked to a granite massif of Mesozoic age. These are alkaline waters (pH = 8.3) and the hydrochemical type is chloride-sodium. Regarding the trace elements, the water of the L’Dži spring contains a large amount of boron and silica. Water also contains an increased content of arsenic (200 µg/L) and tungsten (169 µg/L). Elevated concentrations of As and W are characteristic of alkaline thermal waters in reducing conditions. Often elevated concentrations of Mo are accompanied by elevated concentrations of As and W, which is also the case.

Keywords: thermo-mineral water, water chemistry, hydrochemical properties, L’dži locality, North Macedonia.

Introduction

According to Laurence and Stoyanov (1996), the use of thermal water began more than 1000 years ago. The Romans are believed to be the initial users, considering the archaeological sites where famous East European spa towns are found today (Puczkó, Smith, 2009). The Turks continued and developed the use of thermo-mineral waters during the reign of the Ottoman Empire.

There are numerous occurrences of thermal, thermo-mineral (hereafter TM), and mineral waters in North Macedonia. According to Metodijevski et al. (2012), there are 65 sites on record, of which only eight are used for balneotherapy. These are Banja Bansko, Debar Banja, Kočanska Banja, Katlanovska Banja, Kežovica, Kumanovska Banja, Negorska Banja, and a TM spring at Stranavac, where there is no accommodation or medical staff, only pools and showers. The water temperatures at these sites range from 30.4 °C (Kumanovska Banja) to 72 °C (Banja Bansko) (Metodijevski et al., 2012).

The hydrogeological feature studied, the TM spring at L’Dži, is located near the spa town of

https://doi.org/10.52215/rev.bgs.2023.84.3.303

Kežovica. The balneotherapy centre in Kežovica (also called Štipska Banja) is based on multiple springs on the right bank of the Bregalnica River, about 2 km southwest of downtown Štip, on the edge of the village of Novo Selo. The TM water originates from a fault structure. The TM water from Kežovica occurs at the contact of granites with upper Eocene flysch sediments, and the occurrence at L'Dži is within the granites (Fig. 1).

The average discharge of the main spring at Kežovica is about 7 L/s and the temperature 66 °C. This occurrence is known for its radioactivity and is believed to be the most radioactive balneotherapy site not only in North Macedonia, but in the entire Balkans. Water is largely used for medicinal and recreational purposes, but could also be exploited to heat buildings and generate electric power (Gorgieva, Popovski, 2003).

General features of the extended area of L'dži

The TM water occurrence at L'dži is located in the eastern part of North Macedonia. In tectonic terms, it belongs to the Serbian-Macedonian massif and the Vardar zone. The coordinates of the site are E597901 and N4620956, and the elevation is 285 m. The terrain is mostly hilly, and the location itself is between the hills of *Isarot* and *Kumlako* on the left and *Merite* on the right side of the Bregalnica River. The climate is temperate continental, with a modified Mediterranean influence and mountain climate conditions in the highlands (Mt. Plačkovica). The average annual air temperature in the valleys of streams is 12–13 °C. However, it decreases with altitude and amounts to 7.5 °C at the highest elevations. The warmest months are July and August, with a mean monthly temperature of 23.5 °C. The coldest month is January, with a mean monthly temperature of 1.2 °C. On average, the study area receives 423.8 mm of precipitation per year. The wettest month is November, and the driest August.

The geologic framework of the extended area of the L'Dži locality comprises Precambrian gneisses and mica schists and Mesozoic igneous (granites) and sedimentary rocks. The Tertiary period is represented by a basal series of upper Eocene conglomerates, marls and sandstones, and Eocene flysch sediments. There are also Quaternary sedimentary rocks, including conglomerates, clays, marls, and sandstones (Rakićević et al., 1974).

The central part of the area is an uplifted block of Jurassic–Cretaceous biotitic granite. Alluvial sediments of small thickness follow the course of the Otinja (which meanders through granite along neotectonic faults) (Rakićević et al., 1974).

The most distinguished hydrogeological feature is a fractured aquifer in the Mesozoic granites. It is largely associated with parts of the terrain that are weathered and cracked the surface. There are considerable groundwater reserves related to fault structures. Recharge is based on precipitation and infiltration of water from other aquifers with which it is in contact. Specifically, these are intergranular aquifers formed in alluvial sediments of the Bregalnica and Otinja. The groundwater level largely follows the topography. The aquifer is drained by low-discharge

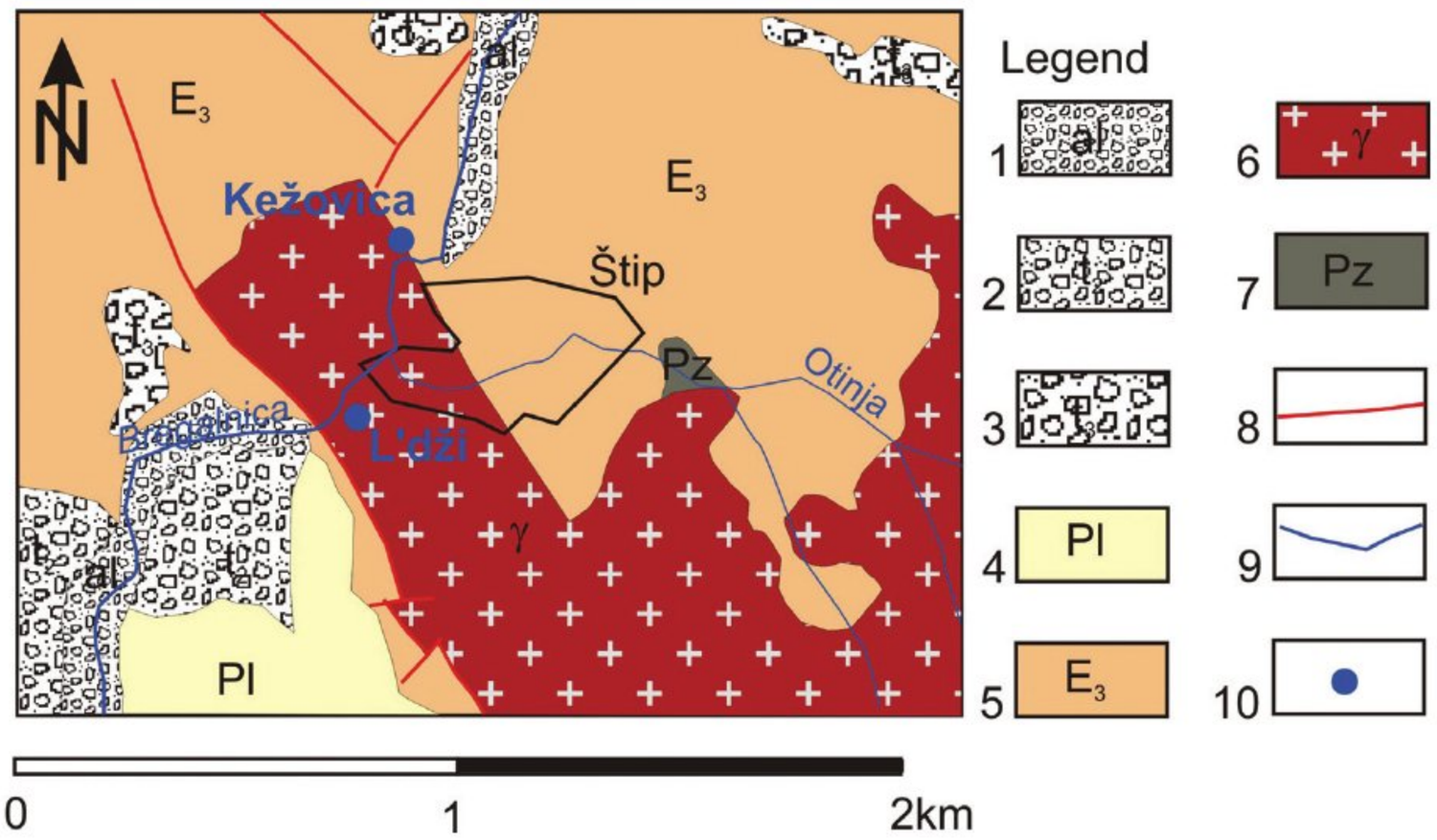

Fig. 1. Geological map of the extended area of the spa town of Kežovica and the L'dži locality. Legend: *1*, alluvium (gravel, sand and clay); *2*, lower terrace (conglomerate, clay, marl and sandstone); *3*, upper terrace (conglomerate, clay, marl and sandstone); *4*, Pliocene sediments; *5*, upper Eocene conglomerate, marl, sandstone, and flysch; *6*, granite massif; *7*, gneiss and mica shist of Pre-Mesozoic age; *8*, fault; *9*, river; *10*, thermomineral spring.

Table 1. Results of physicochemical measurements

Field measurements			Major ions									
T	pH	EC	Cl^-	HCO_3^-	CO_3^{2-}	SO_4	Ca	Mg	Na	K	B	Si
°[C]	[–]	[mS/cm]	[mg/L]									
50.1	8.3	2.22	490.3	94.04	47.38	145.2	12.90	0.487	417.0	12.20	20.29	39.30

Trace elements											
Ag	Al	As	Ba	Be	Cd	Co	Cr	Fe	Li	Mn	Mo
[µg/L]											
<5	9.5	200	5.9	<5	<5	<5	<5	4.7	179	6	8.9
Ni	P	Pb	Sb	Se	Sr	Ti	Tl	V	W	Zn	Zr
[µg/L]											
<5	<5	<5	<5	<5	275	<5	<5	<5	169	<5	<5

springs. Groundwater level fluctuations are seasonal and closely related to hydrology (river stage and discharge). The groundwater flow directions follow slopes and are virtually identical to the streams' directions. Thermal and thermo-mineral waters occurence, such as at the L'Dži locality, are associated with deep fault structures (Kotevski, 1987).

The discharge of the spring at L'dži varies from 1 to 1.5 L/s. The water temperature range is 50–62 °C. It should be noted that as the water level of the Bregalnica River increases, so does both the discharge and the water temperature of the spring (Delipetrev, 2020f[1]).

Hydrochemical properties of thermo-mineral water on the L'dži locality

The sample was collected in the polyethylene bottle after prior rinsing on 20 August 2023. The samples portion for the determination of trace elements were filtered through membrane filters with a pore size of 0.45 µm and acidified with concentrated nitric acid to a final pH of approximately 1–2. In the field measurements of temperature (T), electric conductivity (EC), and pH were made. After collection, the sample was protected against the effects of the external environment, cooled to a temperature of approximately 4 °C and transported in a refrigerator to the Hydrogeochemical Laboratory, Department of Hydrogeology and Engineering Geology, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Krakow. Laboratory analyses included measurements of the major ions (Cl^-, HCO_3^-, SO_4, Ca, Mg, Na, K) and several microelements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Si, Sr, Ti, Tl, V, W, Zn, Zr). For chlorides and bicarbonates determination, the classical titration method was used (Mohr method (ISO, 1989) and acid-base titration (ISO, 1994), respectively). Quantification of the rest of the above mentioned elements was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) with the Thermo Scientific iCAP PRO XP spectrometer according to the ISO 11885 standard (ISO, 2007). The Burgener MiraMist nebulizer was used, and the measurements were performed with axial or radial plasma view, dependent on element, to ensure optimal operating conditions of the instrument and avoiding detector saturation especially at high concentrations.

The results of the analysis are summarized in Table 1.

The water of the spring at L'dži is characterized by a TDS value of 1324 mg/L, a temperature above 50 °C and an alkaline pH (8.3). The hydrochemical type of water is chloride-sodium. The water contains a high amount of boron, above 20 mg/L (which corresponds to 82.3 mg/L of HBO_2) and silica – 84.2 mg/L which is corresponds to 109.5 mg/L of metasilicic acid (H_2SiO_3). The first classification of medicinal waters was established during the First International Balneological Congress in Nauheim in 1911. As silica water, waters with H_2SiO_3 above 50 mg/L was considered. Water containing at least 5 mg/L of HBO_2 was classified as boric water. Silica-rich waters are used in balneotherapy, for example, in the treatment of tuberculosis, some types of cancer or stomach ulcers, as well as in dermatological problems or bone diseases (Dobrzyński, Exley, 2010; Skrzypczak, 2012; Mika, Korzec, 2015; Gittler et al., 2017; Huang et al., 2018). Boric waters were used in balneotherapy mostly due to their antiseptic properties (Chruszcz-Lipska et al., 2020). Particular attention should also be paid to the high concentrations of arsenic and tungsten in the tested water. Although in the past arsenic was

[1] Delipetrev, M. 2020. *Project for Detailed Geological Research of Mineral Raw Material-Thermo-Mineral Water at the Locality "Merite" Municipality Shtip at the Site of Pecom-Engineering Import-Export Dooel Shtip*, 19 p. (in Macedonian).

considered as a specific component of medicinal waters (in concentration greater than 200 μg/L) and its compounds were used in the treatment of many diseases (Paul et al., 2023). Currently it is treated as an undesirable element and the difference between the therapeutic dose (0.7 mg/L) and the toxic dose (1 mg/L) is quite narrow. Tungsten which is present in tested water is also a harmful element to humans. Elevated concentrations of tungsten and arsenic can be observed in thermal waters with alkaline pH and under reducing conditions. Sometimes high concentrations of these elements coincide with an elevated amount of molybdenum (Cidu et al., 2021), which can be observed actually in the tested water from the location of L'dži, where Mo in a concentration of 9 μg/L cooccurs with a high amount of As and W which is about 200 μg/L.

References

Chruszcz-Lipska, K., B. Winid, G. A. Madalska, J. Macuda, Ł. Łukańko. 2020. High content of boron in curative water: from the spa to industrial recovery of borates? (Poland as a case study). – *Minerals*, *11*, 1, 8; https://doi.org/10.3390/min11010008.

Cidu, R., R. Biddau, F. Frau, R. B. Wanty, S. Naitza. 2021. Regional occurrence of aqueous tungsten and relations with antimony, arsenic and molybdenum concentrations (Sardinia, Italy). – *J. Geochemical Exploration*, *229*, 106846, 16 p.; https://doi.org/10.1016/j.gexplo.2021.106846.

Dobrzyński, D., C. Exley. 2010. Solubility control and therapeutic potential of silicon in curative mineral waters of the Sudetes Mountains, Poland. – *Acta Balneologica*, *52*, 4, 296–304.

Gittler, J. K., J. F. Wang, S. J. Orlow. 2017. Bathing and associated treatments in atopic dermatitis. – *Am. J. Clinical Dermatology*, *18*, 45–57.

Gorgieva, M., K. Popovski. 2003. Thermal spas in Macedonia. – In: *Intern. Workshop on Balneology and "Water Tourist Centers", Chapter 1.5*, 37–48.

Huang, A., S. Seité, T. Adar. 2018. The use of balneotherapy in dermatology. – *Clinics in Dermatology*, *36*, 3, 363–368.

ISO. (1989). ISO 9297:1989 – Water quality – Determination of chloride – Silver nitrate titration with chromate indicator (Mohr's method). International Organization for Standardization, 4 p.

ISO. (1994). ISO 9963-1:1994 – Water quality – Determination of alkalinity – Part 1: Determination of total and composite alkalinity. International Organization for Standardization, 6 p.

ISO. (2007). ISO 11885 – Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization, 28 p.

Kotevski, G. 1987. Hydrogeology of mineral, thermal and thermomineral water on the territory of R. Macedonia. – In: *Selfmanagement Practices Skopje*. 89–97 (in Macedonian).

Lawrence, L. R., B. Stoyanov. 1996. *Geothermal Opportunities in Eastern Europe, a Survey*. Bob Lawrence & Associates.

Metodijeski, D., N. Taskov, T. Džaleva, O. Filipovski, Z. Temelkov. 2012. Opportunities for development of thermal tourism in the Republic of Macedonia. – In: *IV Spa Congres Banja with International Participation*, 1–4 (in Serbian).

Mika, A., K. Korzec. 2015. Assessment of the stability of metasilicic acid concentrations in thermal waters drawn from the Bańska PGP-1 well in Bańska Niżna. – *Geological Exploration Technology*, *54*, 2, 89–96 (in Polish).

Puczkó, L., M. Smith. 2009. *Health and Wellness Tourism*. Oxford, Butterworth-Heinemann/Elsevier.

Paul, N. P., A. E. Galván, K. Yoshinaga-Sakurai, B. P. Rosen, M. Yoshinaga. 2023. Arsenic in medicine: Past, present and future. – *Biometals*, *36*, 2, 283–301.

Rakićević, T., N. Dumurdžanov, P. Petkovski. 1974. *Guid of Basic Geological Map 1:100 000 on Sheet K 34-81 Shtip.*

Skrzypczak, R. 2012. Waters of Krzeszowic: sulfur, sulphate and silicon – a contemporary asset of the most fashionable resort in Poland in the mid-19th century. – *Geological Exploration Technology*, *51* (in Polish).