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Article

Cold and Thermal Waters Circulation Systems at the Makaresh Carbonate Karst Massif (Central Albania)

Romeo Eftimi ¹, Isabella Serena Liso ^{2,*} and Mario Parise ²

¹ Independent Researcher, 1001 Tirana, Albania; eftimiromeo@gmail.com

² Department of Earth and Environmental Sciences, University Aldo Moro, 70126 Bari, Italy; isabella.liso@uniba.it, mario.parise@uniba.it

* Correspondence: isabella.liso@uniba.it

Abstract: Carbonate rocks occupy about 6490 km² in Albania (23% of the country) and the total exploitable karst water resources are estimated in 2.84*10⁹ m³/year (about 65% of the total exploitable groundwater resources in the country, and about 70% of those used for water supply). In addition, karst massifs are very rich in thermal waters, related to the ascending fluids which are essential for the development of hypogenic karstification in the outer Albanides. This type of karst facilitates the circulation regime of deep fluids, which are revealed at the surface through both numerous phenomena of hypogene karst and hot springs. The relatively small Kruja Tectonic Zone is characterized by the presence of SE-NW oriented carbonate structures, rich in thermal sources, and contains more than the 80% of Albania thermal springs. One of its most interesting carbonate structures, for the presence of both cold and thermal waters, is the small karst structure of Makaresh, with a surface of 22 km². The purpose of this article is to describe the characteristics and factors that affect the quantitative and qualitative formation of cold and thermal groundwater in this massif. Based on the physico-chemical characteristics, groundwaters of the study area are classified in cold and thermal waters. The former are mainly of HCO₃-Ca or HCO₃-Ca-Mg type (Electrical Conductivity 580-650 μS/cm, Temperature 13.9-16.6° C). Thermal waters are mainly of the Cl-Na-Ca type (EC 7200-7800 μS/cm, T 18.5-22.5° C); further, they are characterized by high hydrogen sulphide concentration, up to about 350 mg/l. The presence of two groundwater types in the Makaresh massif is connected to the presence of two groundwater circulation systems. The main factors of the groundwater physico-chemical quality are the solution of rocks and minerals therein contained, the presence of hypogenic speleogenesis, and the mixing of the groundwater of the two systems. The hydrogeological studies proved that karst rocks contain considerable fresh water resources; the capacity of water wells used for the drinking water supply reaches up to about 50 l/s. Thermal waters are not currently exploited due to their temperature, but they are potentially suitable for thermal uses, by drilling boreholes at depth of about 1000 m.

Keywords: karst; hydrogeology; thermal waters; Albania

1. Introduction

Karst aquifers are among the richest in groundwater on Earth [1–5], and globally provide drinking water to almost a quarter of the world population [6–14]. They are used even more extensively in the Mediterranean area [15–20], and in south-eastern Europe where some large cities, including Tirana, are supplied with water from karst sources [21]. At the same time, carbonate aquifers are also large reservoirs often recharging important mineral and thermal springs in many countries of the world [22–24], including the Balkan countries [25].

Albania is characterised by wide presence of carbonate rocks [26,27]. They cover about 6490 km² and contain in total about 90 m³/s exploitable groundwater resources [28]. Likewise, Albania is rich also in thermal karst waters, which are mostly related to carbonate karst aquifers [28–32]. The Makaresh karst massif, object of this article, although relatively small is the only carbonate massif in Albania rich in both cold and thermal karst waters. The main purpose of this study is therefore to highlight the hydrogeological functioning of Makaresh massif, in close relation to its geological and structural features, and the role of hypogene speleogenesis [33–35] in the formation of its secondary

porosity. Eventually, given the existing threats in the massif, some considerations about degradation of the Makaresh karst environment are also presented.

2. Study area

The karst massif of Makaresh is located about 30 km north-west of the city of Tirana (Figure 1). Morphologically it represents a NW-SE oriented ridge where carbonate rocks crop out for about 22 km², while about 8 km², of the northern part are covered by Neogene formations. The highest peak of the massif (Picraga, 442 m above sea level), is in its central part, while the average altitude of the massif is about 300 m a.s.l. Climate of the area is a warm Mediterranean, characteristic for the coastal plain areas of the country [36]: the mean yearly temperature is about 14° C, with 6.2°C in January, and 23.0°C in August. Mean yearly precipitation is about 1300 mm, with about 70% falling during the period October-April. Main hydrological elements of the study area are the Droja River, which canyon crosses the northern part of the karst massif in E-W direction, and the small stream of Zheji, south of the former river.

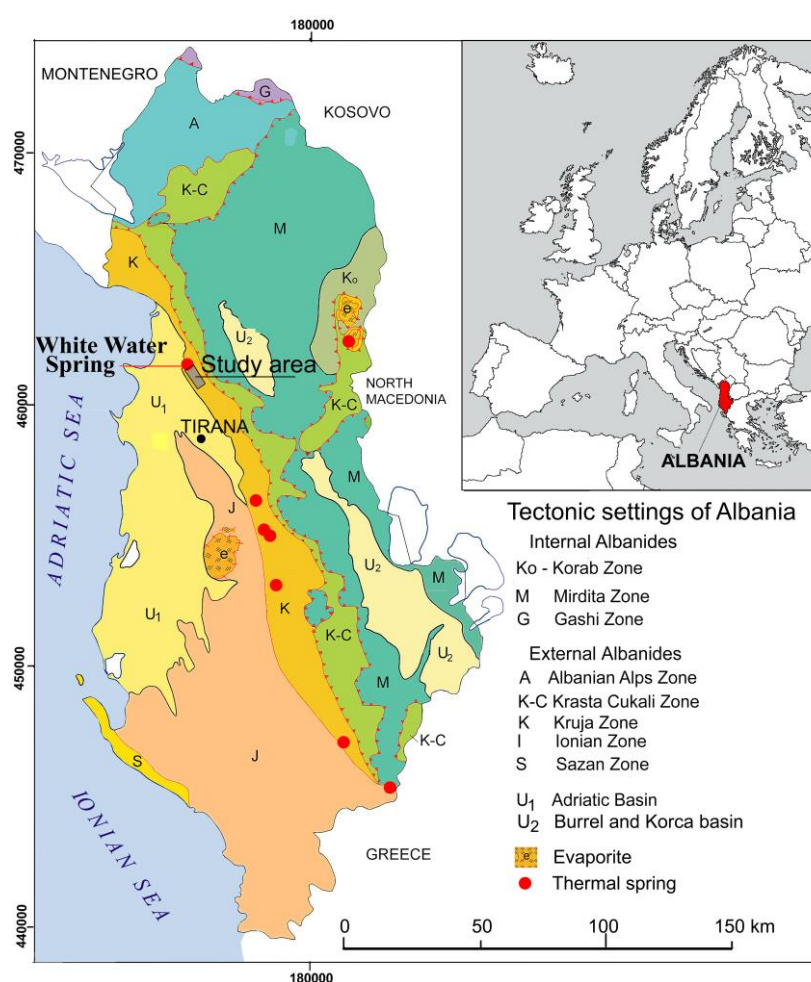


Figure 1. Map of the geological division of Albania (after [27]), showing location of the study area (Makaresh karst massif) and of the White Water thermal spring.

3. Materials and Methods

To characterize the hydrogeology of the study area, multiple geological and regional hydrogeological studies have been performed, and integrated data collected from different archives. Among the most important regional studies are geological maps [27] and neotectonics map [37], as well as the hydrogeological map of Albania [26]. The first detailed and important hydrogeological study carried out on *Uji Bardhe* (White Water) thermal spring, accompanied with detailed chemical analyses, was performed since 1957 [29]. Detailed hydrogeological observation on Makaresh karst

massif, including new chemical analyses of White Water have been carried out in the framework of the hydrogeological survey of the territory of Albania [26]. This spring was also treated in a special edition dedicated to the thermal springs of Albania [32]. Some archive materials of the Albanian Hydrogeological Service (AHS) reflect the results of detailed karst studies for the water supply of the city of Mamurras [38,39]. The water samples are analysed for the macro-components Mg^{2+} , Ca^{2+} , $N^{+}+K^{+}$, Cl^{-} , SO_4^{2-} , HCO_3^{-} , partially in the field, as well as in the AHS laboratory. The main physical parameters, such as pH, temperature and electrical conductivity (EC), have been measured in the field for 7 karst springs and 5 wells. Volumetric, spectro-photometric and colorimetric methods have been used for analysis. The Piper diagram, as well as other hydrochemical graphs created using the AquaChem program, have been used for the hydrochemistry characterization of the groundwater. The comparative assessment of the results of the chemical analyses of thermal springs performed at different times, as well as the comparison of the chemical composition between thermal and cold-water springs, represents an important element of this study. This enables to clarify the groundwater formation and circulation in the Makaresh massif, as a pre-condition for its rational use and protection.

4. Geology

The geological structure of Albania (Figure 1) comprises two major units, namely the Internal Albanides to the east and the External Albanides to the west [27,37,40]. The Makaresh karst structure belongs to the Kruja zone, which is the easternmost sector of the External Albanides (Figure 1), and is characterized by the presence of long NNW-SSE structures built up by sedimentary rocks. The Makaresh structure represents an anticline consisting of carbonate rocks (limestone, dolomitic limestone and dolomites) of Upper Cretaceous to Eocene age (Figure 2). These deposits dip eastward with angles of about 35° and are covered by Oligocene clay-claystone flysch filling the Vila Syncline. In accordance with the tectonic style of the Kruja zone, the Makaresh structure was affected by westward longitudinal thrusting during Eocene and late Oligocene to Miocene times [27,40,41].

Beside this, the Makaresh massif is broken by a series of deep transversal NE-SW faults, that fragmentize the buried carbonate structures [42,43]. This is testified also by deep boreholes located in the northern part of the Makaresh structure (Figure 2a and 2b). West of it, the wide Tirana syncline, filled with Paleogene and Neogene molasses, is located, to cover two buried parallel carbonate structures (Figure 3b) hosting thermal water tapped by deep oil wells [32]. East of this structure, and parallel to it, the Dajti carbonate anticline is present (Figure 2a). On the northern part of the Makaresh carbonate structure, it is covered by Lower Pliocene deposits of the Helmes suite, represented by intercalations of clays, claystones and sandstones.

5. Hydrogeology

The carbonate rocks forming the Makaresh structure are intensively fractured, at least with three main discontinuity systems, the most developed of which is represented by the bedding, dipping in the same direction of the axis of the structure itself. Fissured carbonate rocks often have bitumen content, related to weathering processes from the early pre-Neogene time when the Makaresh structure was an oil-bearing structure. Broken rock surfaces often smell of hydrogen sulphide (H_2S), as observed in the neighbouring Dajti anticline structure [44]. On top of this structure, a karst plateau hosting a great variety of karst landforms, with innumerable sinkholes [45–47] and vertical cave opening and fractures, is developed. One of the most interesting karst phenomena is Shpella Sallas, a cave located in the south-western part of the carbonate massif, in the immediate proximity of Makaresh spring - No. 3 (Figure 3).

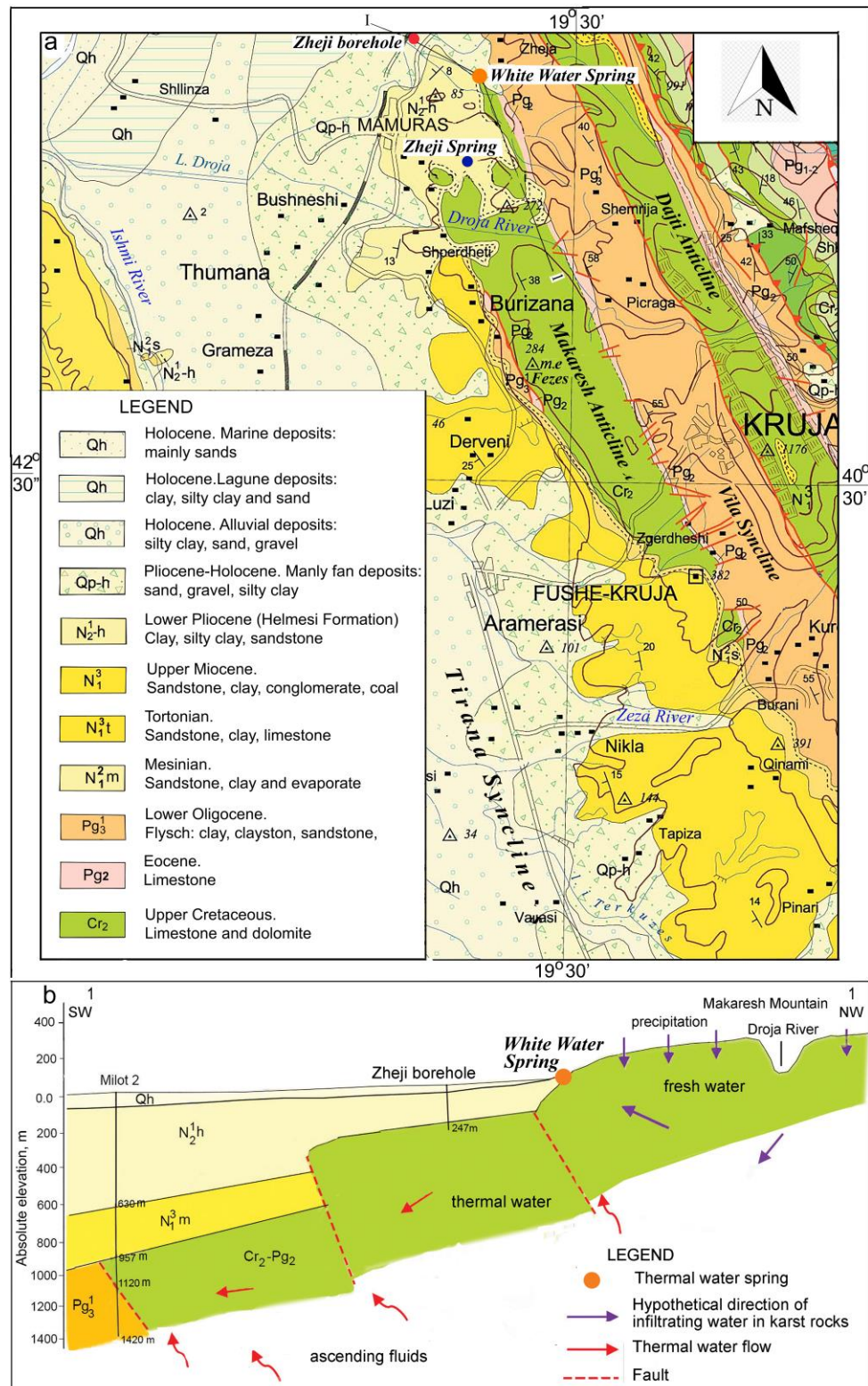


Figure 2. Geological map of the Makaresh karst structure and its surrounding areas (after [27]).

The entrance of the cave, after the initial part with a concrete tunnel built during the Communist time, is about 8-10 m wide, with maximum height of about 6 m. It then continues like a tunnel for about 25 m, 4-4.5 m wide and about 3.0 m high (Figure 3). The cave walls are coated with calcite and sulphur pigments. It is not excluded that in a such environment the sulfuric acid formed by the oxidation of pyrite pigments of the limestone plane fissures [44], as many authors describe [19,33,35,48] mixes with the ascending thermal fluids and produces morphologies typical of speleogenesis by sulphuric acid. Shpella Sallas has an overall length of over 700 meters. About 6-7

below the described cave there is another small cavity where the largest karst spring of the massif, known as the Makaresh spring, issues (Figure 3).

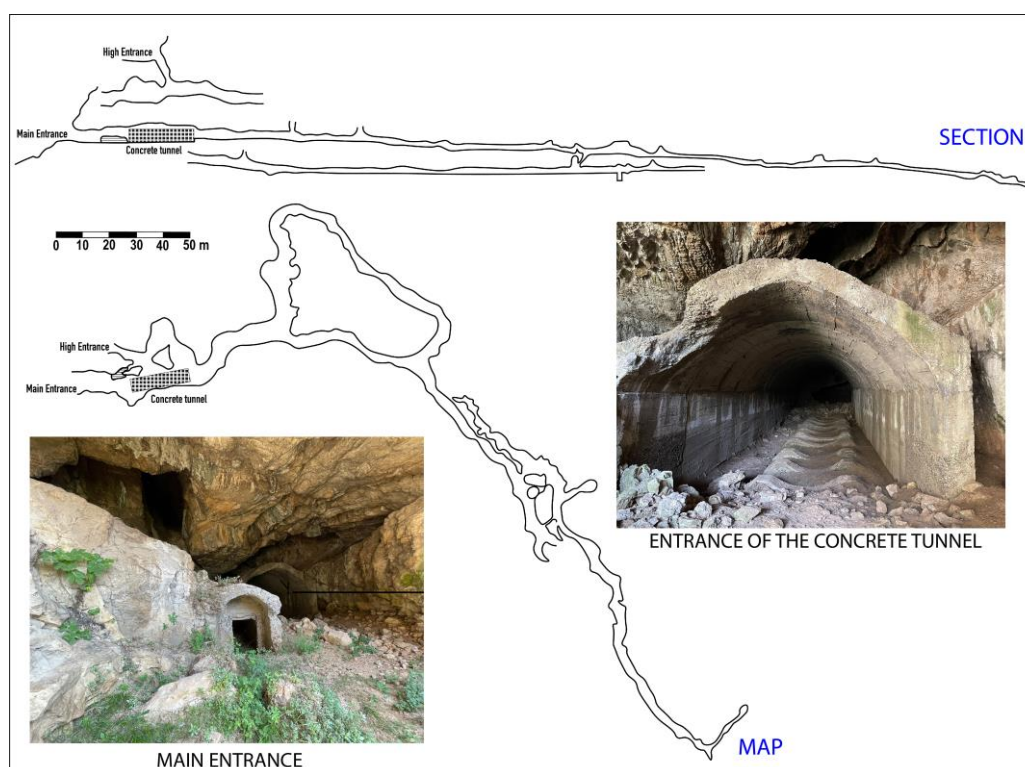


Figure 3. Shpella Sallas section and map with details of the main cave entrance and the concrete tunnel structure. This latter is a man-made tunnel built along the initial part of the natural cave; it has been used during communist time for defending purposes (redrawn after [49]).

The intensive karstification of the Makaresh massif facilitates infiltration of the abundant rainfall. Based on climatic data [36], the extrapolated annual rainfall for the average elevation of this structure is about 1300 mm, while the average annual temperature is 14.0°C. The evapotranspiration calculated with the formula by Turc [50] is 600 mm and the infiltration results 700 mm/year. The fast discharge during short periods following the heavy rains is estimated at about 10%, or 130 mm/year, while the efficient infiltration of the precipitation is equal to 570 mm/year. For the entire outcrop area of carbonate rocks at the Makaresh massif (22 km²), the renewable groundwater resources consist approximately in 12.54*10⁶ m³/year, or 400 l/s corresponding to an underground flow module of the massif of about 18 l/s/km². The calculated values match with the estimated values for low-elevation karst massifs in Central Albania [51].

The springs emerging from the Makaresh massif essentially differ regarding their physical and hydro-chemical characteristics, and consist of two well different groups; cold and thermal (Figure 4). Temperature of the cold springs is about the yearly average temperature of the area (15°C), while the thermal springs show temperature higher than 5°C [22,52].

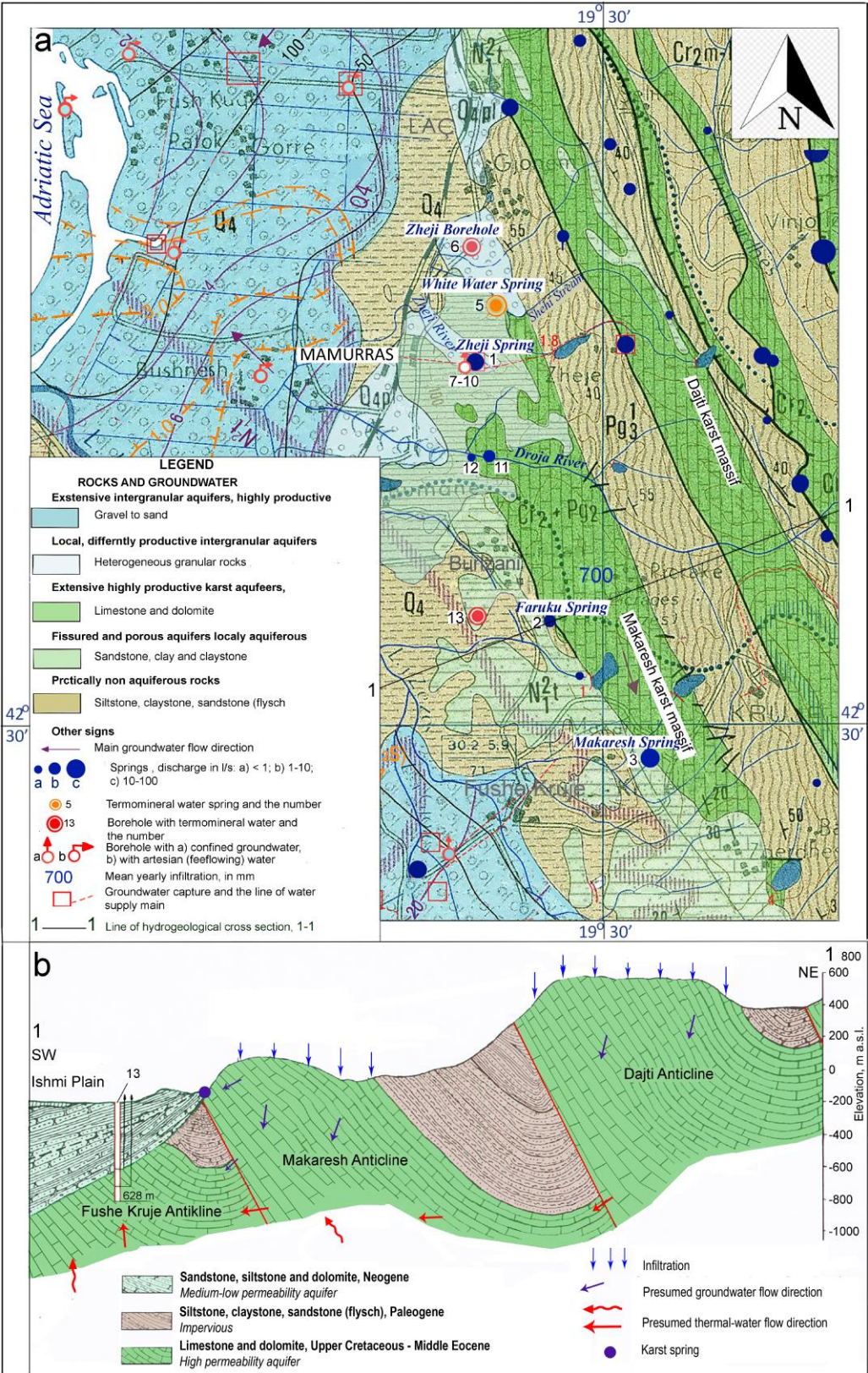


Figure 4. a) Hydrogeological map of the Makaresh carbonate structure and surrounding areas (after [26]), b) Hydrogeological cross section 1-1 (SW-NE).

5.1. Cold springs

The few cold springs are located in the western periphery of the Makaresh karst structure, where the limestone formations crop out at lower elevation, or at the base level of the structure (Figure 4a). Among them there is Zheji spring (no. 1) discharging about 5 to over 50 l/s. Several small sources

emerge in the village Burizan, the largest of which is the Farruku spring (no. 2), flowing about 2 l/s. In the narrow gorge of river Droja, crossing the karst massif, there are several minor springs with total flow of about 20 l/s; among them, springs nos. 11 and 12 discharge about 6.5 and 0.5 l/s, respectively. It is believed that the groundwater seepage from the limestone massive to the Droja River along the canyon could be in average some tenths of litres per second.

One of the most interesting springs in the study area is the Makaresh Spring (no. 3 in Figure 6), emerging inside the homonymous cave. The spring has ascending character, and according to non-systematic observation its discharge varies from about 100 l/s to more than 500 l/s, while the water temperature is 16.2° C. The spring water has a weak smell of sulphurous gas and a light white colour (Figure 5).

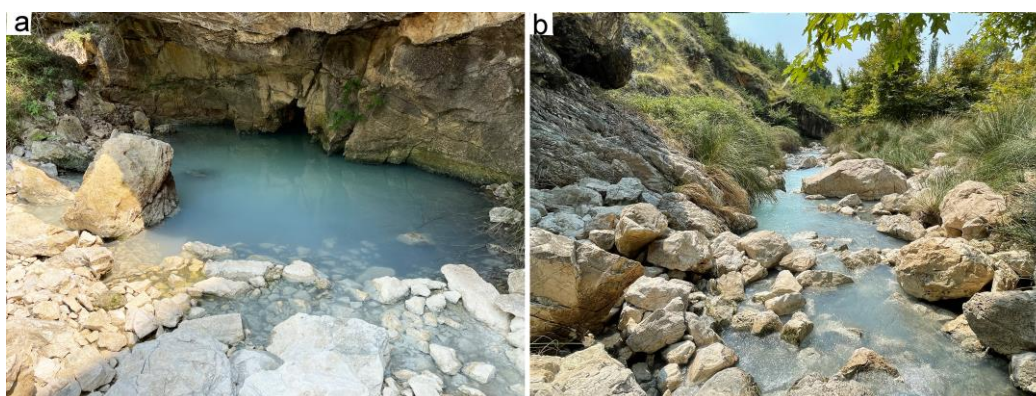


Figure 5. Makaresh spring: **a)** The spring flows from a cave-like karst cavity. **b)** On 5 October 2023, the discharge of the spring was about 110 l/s (photo, Eftimi R.).

5.2. Thermal springs

These springs are represented by a group called White Water springs, as well as by the Zheji borehole free-flowing thermal water (Figure 4). The spring emerges at the contact between Pleistocene deposits (local name “Helmasi Series”) consisting of sandstone, conglomerates and clay, and the underlying Cretaceous-Eocene carbonate rocks. White Water is a group of springs issuing closely within an area of about 120x70 m (Figure 6). Discharge of the different springs varies from about 1 to more than 20 l/s, the largest one being no. 5, located near some travertine deposits (Figure 6). According to non-systematic measurements, the total discharge of White Water Spring varies from 20 to about 100 l/s, with average discharge of about 40-50 l/s, and water temperature ranging from 20 to 22.8°C.

Zheji borehole (no. 6) is located about 1.4 km northwest of White Water springs, at the northern periclinal of the submerged Makaresh anticline (Figure 4a) and was drilled during 1958 for bauxite investigations [53]. After passing Holocene and Pliocene deposits, the borehole at depth 178.0 m tapped Upper Cretaceous dolomite limestones and limestones, down until depth of 241.6 m. The borehole tapped artesian free-flowing groundwater, which initial discharge in 1959 was 4 l/s, but today it has a constant discharge of about 1.8 l/s (Figure 6b). The water is warm with a temperature ranging during the year from 22.0 to 22.8°C and has a strong sulphur gas smell.



Figure 6. White Water (Uji Bardhe) thermal springs at the Makaresh karst massif. **a)** Main spring issue; **b)** Measuring the water conductivity at the free-flow Zheji borehole (photo Eftimi R.).

6. Hydrogeochemical characteristics

Groundwater circulation can be understood in the framework of hierarchical flow systems, consisting of local, intermediate, and regional flow system [54–56], or shallow groundwater, and deep groundwater reservoirs [57]. Water circulation in thermal karst systems is generally gravity-driven, caused by topographic gradients [56], however temperature-induced density gradients and reduced viscosities facilitate the upward flow of hot water toward the springs [22]. The simplest approach to delineate flow components in a karst aquifer is to use thermal data [57].

The results of the physico-chemical analysis of the springs at the Makaresh carbonate structure (Table 1) and the following Piper diagram, as well as other hydrochemical graphs created using the AquaChem program, have been used for the hydrochemistry characterization of the groundwater of the studied area (Figures 7 and 8). The hydrochemical assessment includes the springs, as well as the groundwater of wells no. 1, 2, 3 and 4, located near the Zheji spring (no. 1). The chemical parameters like TDS, Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , as well as the groundwater temperature (Figures 7 and 8) evidence the differences between the two groundwater groups of cold and thermal waters, likely related to presence of two groundwater circulation systems, one shallow and one deep.

Cold water springs derive from the shallow circulating system, characterized by temperatures around 14–16.4°C and by a weakly alkaline pH (7.05–7.45). These waters present low mineralization (TDS 240–370 mg/l; TDS 580–650 $\mu S/cm$) and low hardness $Th=10-20$ °G. Major ion concentrations fall within the following ranges (in mg/l): Ca^{2+} 57–100; Mg^{2+} 10–25; Na^+ 3–18; HCO_3^- 270–415; SO_4^{2-} 7–30; Cl^- 9–16. Taking into consideration the ions with concentration > 25 % mg/eqv/l, the hydrochemical type of cold waters is mainly of the HCO_3^- -Ca-Mg type. To this typology springs such as Faruku (no. 2), and Zheji (no. 1) belong, as well as four shallow water supply wells located near the latter (Table 1).

In the cold waters group, the Makaresh spring is slightly different, being characterized by temperature of 16.2°C, pH 6.95, TDS 616 mg/l, and a total hardness $Th = 26.7$ °G. The other chemical parameters generally show increased concentrations (mg/l): Ca^{2+} 102.4; Mg^{2+} 53.7, Na^+ 29; HCO_3^{2-} 341; SO_4^{2-} 83; Cl^- 115.6. The hydrochemical type is in this case HCO_3^- -Cl-Ca-Mg (Table 1), due to the significant increase in the concentration of Cl^- and Mg^{2+} ions. However, the main characteristics of the Makaresh spring is the presence of H_2S gas (about 14.8 mg/l) classifying it as weak sulphide mineral spring [58].

Thermal springs are represented by White Water Spring and the Zheji borehole. The eight issues of White Water have very similar physical and chemical characteristics, excluding the issue no. 1, where the water temperature and the concentration of the chemical parameters is lower than at the other springs (Table 1). The groundwater temperature varies from about 19 °C in issue no. 1 to 21.5–22.3°C in issues nos. 5 and 6, and have weakly acidic reaction, with pH 6.6–6.9.

Table 1 Chemical analyses of groundwaters at the Makaresh karst massif.

Number spring-Sp water well-WW	Date [d/m/y]	Q l/s	T °C	pH	EC µS/cm	TDS mg/l	Th °C	H2S mg/l	Ca mg/l	Mg mg/l	Na+K mg/l	NH4 mg/l	Cl mg/l	SO4 mg/l	HS mg/l	HCO3 mg/l	Hydrochemical type	rHCO3rCa/ rMg / rCl	rNa/ rMg rCl
1 Zheji Sp	07/02/1990 ³⁾	6.0	14.1	7.14	-	340	18	no	87.4	25.0	16.1	no	14.2	30.4	-	370.9	HCO3-Ca-Mg	15.2	2.13
2 Faruku Sp	3/17/1993....		14.5	7.05	-	243	10.2	no	56.7	9.7	17.2	-	8.9	13.1	no	234.8	HCO3-Ca	15.4	3.53
3 Upper-Zheji Sp	3/17/1993....	?	13.9	7.10	-	256	14.0	no	71.9	16.8	3.0	no	10.6	7.4	no	271.4	HCO3-Ca-Mg	17.8	2.6
4 Makaresh Sp	27/12/1955 ¹⁾	500	16.2	6.95	-	616.3	33.0	14.8	102.4	53.7	29.4	-	115.6	83.1	-	341.0	HCO3-Cl-Ca-Mg	1.71	1.51
5 White water Sp-1	1/12/1955 ¹⁾	20.0	18.5	6.9	-	1254	33.0	69.7	150.3	51.1	242.4	2.4	432.6	131.7	21.5	413.6	Cl-HCO3-Na	0.56	1.79
	-/10/1970 ²⁾	7.0	19.7	6.6	-	1005	37.3	70.0	144.1	74.3	145.1	10.0	294.3	97.1		420.9	Cl-HCO3-Na	0.83	2.35
5 White water Sp-5	1/12/1955 ¹⁾	20.0	22.5	6.75	-	5332	93.0	357.8	388.8	167.8	1264.5	16.6	2382.0	615.6	114.2	531.9	Cl-Na-Ca	0.13	1.41
	-/10/1970 ³⁾	6.0	22.3	6.65	-	6130	120.0	-	583.0	168.0	1011.6	-	2220	788.0		480.6	Cl-Na-Ca	0.13	2.11?
5 White water Sp-6	1/12/1955 ¹⁾	7.0	21.5	6.85	-	5190	93.0	326.5	388.8	166.4	1300.9	6.1	2340.5	599.0	94.7	526.4	Cl-Na-Ca	0.13	1.42
6 Water well no 10	10/10/1970 ²⁾	3.8	22.0	6.90	-	5282	82	-	434.4	91.66	1044.3	125.0	2109.9	579.4	-	579.3	Cl-Na-Ca	0.16	2.77
7 Water supply well	25/11/2002	40	16.4	7.4	645	350	19	no	98.2	22.5	16.1	no	16.0	12.8	no	409.9	HCO3-Ca-Mg	15.0	2.65
8 Water supply well	7/2/1990	??	16.4	7.5	613	369	19	no	100.2	21.45	17.25	trace	14.2	15.2	no	414.8	HCO3-Ca-Mg	21.2	2.8
9 Water well	7/2/1990	??	16.4	7.45	612	365	336	no	99.2	21.45	18.4	-	16.0	14.4	no	413.6	HCO3-Ca-Mg	15.0	2.8
10 Water well	7/2/1990	???	16.4	7.05	577	327	194	no	93.3	21.45	16.1	trace	12.4	11.1	no	398.9	HCO3-Ca-Mg	18.7	2.6
11 Droja Sp-1	29/3/1999	6.5	13.8	7.5	459	275											HCO3-Ca-Mg		
12 Droja Sp-2	29/3/1999	0.5	14.1	7.7	565	339											HCO3-Ca-Mg		

Notes: Q – discharge; T – temperature; EC – electrical conductivity; TDN – total dissolved solids; Th – total hardness, H2S - total; ions in “r” are in mg.eqv/l
1) Analysed by Avgustinski et al. [29]
2) Analysed by Institute of Hygiene and Epidemiology
3) Analysed by Hydrogeological Service

The concentration of hydrochemical parameters of thermal water (issues nos. 5 and 6) are distinctly higher than for the cold waters, with increased mineralization (TDS 4100-7800 mg/l) and hardness (Th = 33-93 °G). The major ion concentrations fall within the following ranges (mg/l): Ca²⁺ 388-583; Mg²⁺ about 168; Na⁺ 1100-1300; HCO₃⁻ 480-530; SO₄²⁻ 600-788; Cl⁻ 2200-2380. Taking into consideration the ions with concentration > 25 % mg/eqv/l, the hydrochemical typology of the thermal springs is mainly of the Cl-Na-Ca type.

The most important hydrochemical characteristics of the White-Water Spring is the high concentration of H₂S, about 325-360 mg/l. Comparing with other thermal springs of Albania, only in that of Llixha Elbasan, the concentration of this gas is higher, about 410 mg/l [32]. In Table 2 the concentrations of some micro-components and gases in White Water Spring, are provided: among the gases it could be noticed the increased presence of hydrogens sulphide HS (114.2 mg/l) and free carbonic gas CO₂ (141.7 mg/l).

Among the gases freely released from water, nitrogen (N) dominates with 71.5% of the volume, followed by carbon dioxide (CO₂ 15.41%), and further methane and sulphur gas representing the sum of S₂O₃²⁺ and SO₃²⁺. As for dissolved gases, H₂S (155 mg/l) and CO₂ (71.7 mg/l) prevail. The only analysed micro-components bromide and iodide have low concentrations, respectively 1.2 and 0.4 mg/l. Based on the classification of thermal waters [58], White Water Spring can be classified as: *"Very strong hydrogen sulphide (H₂S) gas warm water with medium salinity"*.

Table 2. Concentration of micro-components and gases in White Water thermal spring (after [29]).

Components	Unit	Issue 5.5	Issue 5.1	Issue 5.6	Makaresh spring
Brom, Br	mg/l	1.2			
Jodi, J	mg/l	0.4			
Hydrosulphite, HS	mg/l	114.2	21.5	94.7	6.9
Thiosulphate, S ₂ O ₃	mg/l	1.1			1.1
Sulphite, SO ₃	mg/l	0.2			0.2
Acid salicylic, H ₂ SiO ₃	mg/l	28.0	13.0	27.6	32.4
Acid boric, HBO ₂	mg/l	17.8			
Total sulfidic gas, H ₂ S	mg/l	357.8	69.7	326.5	14.8
Free sulfidic gas, H ₂ S	mg/l	239.0	47.3	228.7	7.2
Free carbonic gas, CO ₂	mg/l	141.7	74.4		138.6
Free nitrogen gas, N ₂	% volume	71.5			
Free carbonic gas, CO ₂	% volume	15.41			
Free methane gas, CH ₄	% volume	8.66			
Free sulfidic gas, H ₂ S	% volume	4.43			
Dissolved sulfidic gas, H ₂ S	ml/l	155.1			
Dissolved carbonic gas, CO ₂	ml/l	71.7			
Dissolved nitrogen gas, N ₂	ml/l	14.7			
Dissolved methane gas, CH ₄	ml/l	8.45			

7. Groundwater circulation

Cold water springs are fed by the shallow circulation system and moves into a predominantly dolomite-limestone environment. The main process conditioning the formation of the chemical composition of shallow-circulating groundwater is solution of the carbonate rocks by infiltrating waters, enriched in carbon dioxide in the vegetal cover of the karst massif, a process strongly dependent by the contact time between water and rock [59,60]. Although the groundwater moves into the dolomite environment the concentration of Ca²⁺ in water is higher than that of Mg²⁺ due to higher solubility of the limestones [44,61,62]. According to many researchers the rCa²⁺/rMg²⁺ ratio (r indicating the concentration in mg/eqv/l) is a sensitive indicator of the composition of carbonate rocks. The ratio rCa²⁺/rMg²⁺ in dolomite groundwater fluctuates in the range 1.5 to 2.2, while in limestone waters it is usually over 2.5, but can reach values up to 10 [63–65]. This ratio varies from 1.6 to 2.1 in the groundwater of the dolomite massif of Dajti Mountain [44], while in the pure limestone massif of Mali me Gropa it varies from 7.2 to 13.8 [66]. Data of the cold waters of Makaresh

karst massif support the above-mentioned conclusions, since the rCa^{2+}/rMg^{2+} value generally varies between 2.1 and 2.8, with the lower value (1.5) at the Makaresh spring.

Thermal waters are recharged by the deep circulation system, characterised by high water temperature, high concentration of chemical parameters and the presence of gases dissolved in water. Based on the hydrogeological regionalization of the thermal waters of Albania, the Makaresh carbonate aquifer is part of the Kruja tectonic zone [32] and has a great potential for hypogenic karstification in the Upper Cretaceous to Eocene carbonate formations [67].

Karst reservoirs are characterized by very low matrix porosity and by high porosity related to fissures and karst, developed more intensively at the crests of anticlinal structures [42,67]. Transverse trend (NW-SE) breakdowns in the external tectonic areas of Albania are predominant as fluid movement routes, as well as these are favoured by presence of open gaps, calcium fillings and bitumen [41]. In conditions of difficult groundwater circulation in deep structures, their enrichment with different chemical components is mainly related to two processes.

The first relates to the presence of evaporitic rocks below the Mesozoic carbonate structures [68,69], which facilitates the formation and movement of sulphatic fluids rich in salts and gases such as H_2S and CO_2 and micro-components, that transfer warm water to sources [22,23,70]. Fluids may also be rich in Na and Cl ions, as related to the halite deficiency usually found in evaporite deposits [32,71]. The second process is the enrichment of thermal waters with sulphate by oxidation of pyrite, a phenomenon occurring in oxidation environment [72], and that is likely to be present in the Makaresh massif, as well as in the neighbouring Dajti [44]. This could explain the mainly Cl-Na-Ca composition with high concentration of H_2S and CO_2 gases at the White Water thermal spring.

Correlating electrical conductivity and water temperature for the different issues of White Water spring (Figure 8), it appears that issue no. 8, and to a lesser extent issue no. 1, have the highest contribution of cold water. Accepting as the mixing end-members the well no. 48 and the issue no. 4, we can calculate the rate of mixing of water points located between them: issue no. 8 consists of a mixing of approximately the same amount of cold and thermal waters, while issue no. 1 derives from a mixing of about 75% thermal water with 25% cold water. In the remaining springs (nos. 2, 3, 4, 6 and 7) the mixing of thermal and cold water is not significant.

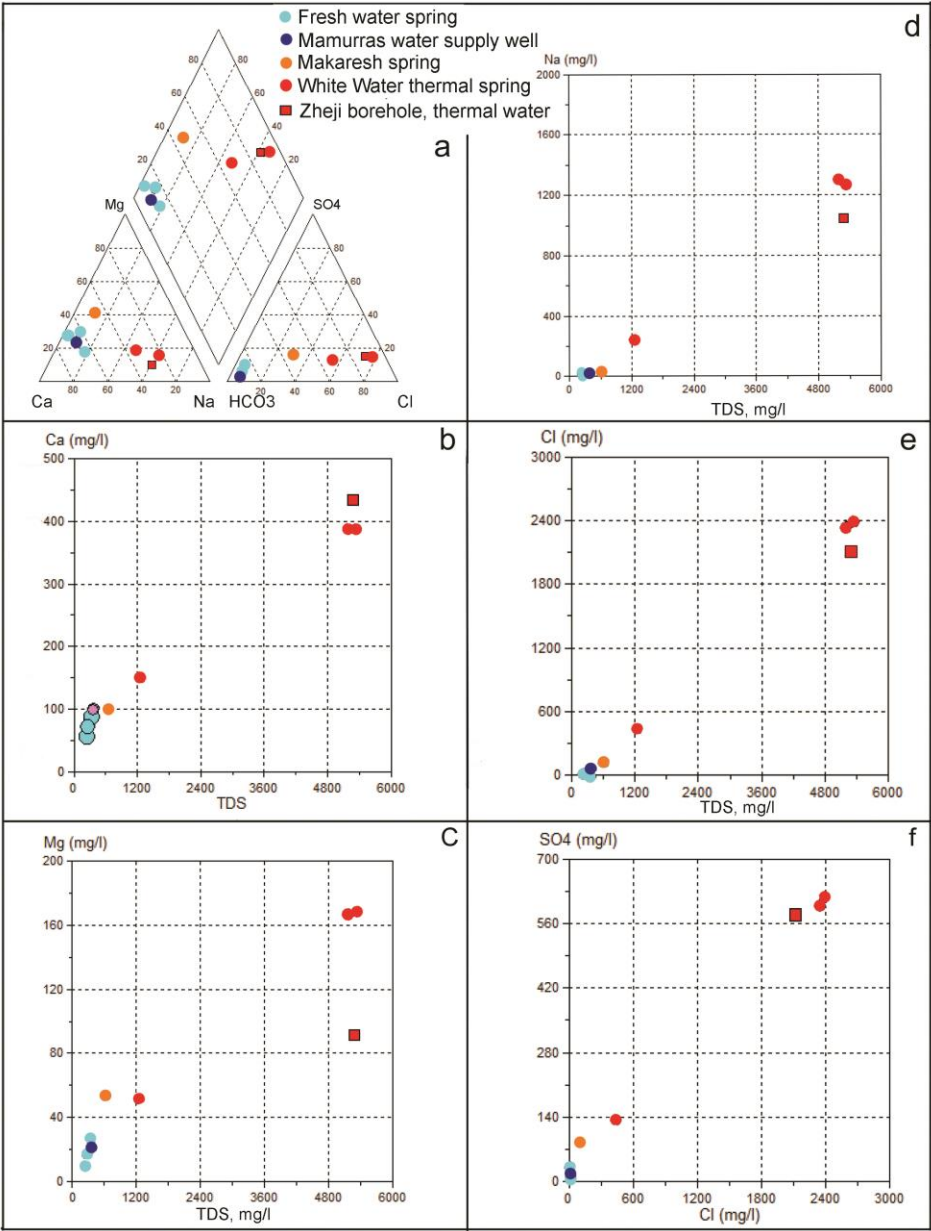


Figure 7. a Piper diagram showing hydro-chemical signatures of the sampled points of the groundwater of the Makareh karst massif, and hydro-chemical correlations: b Ca-TDN; c Mg-TDN; d Na-TDN; e Cl-TDN; f SO₄-Cl.

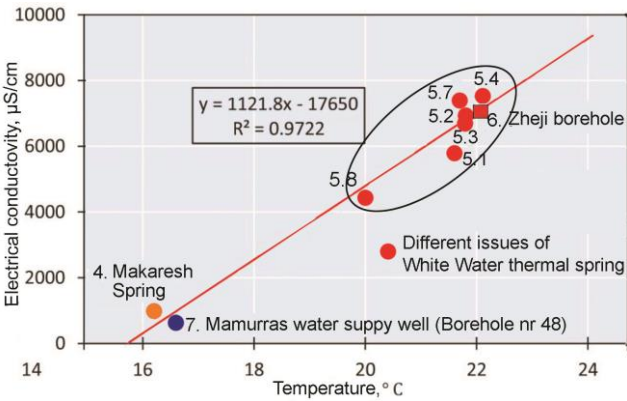


Figure 8. Correlation of EC vs water temperature (measures carried out on August 15, 2010).

8. Groundwater exploitation

8.1. Cold waters

Groundwater of the Makaresh karst massif is used for water supply of some important urban, rural and industrial centres such as the city of Mamurras, the villages of Burizan and Zgërdhesh, and the Titan Cement Factory. The study of the water supply of the city of Mamurras through drilling pointed out to some important features of the karstification, and highlighted the abundance of groundwater in the karst massif [39]. To meet the water requirements of the growing city, in 2002 a water supply capacity of 60 l/s was required. Taking into account the capacity of natural springs in the Makaresh massif, drilling water wells remains the only possibility to solve the problem. In the area around the existing water tapping there are two aquifers: (a) one in intergranular rocks, and (b) a carbonate rock aquifer. Analysing the hydrogeological conditions of the Zheji stream area it was concluded that the gravelly aquifer has no capacity to provide the required amount of 60 l/s.

As concerns groundwater flow in the karst rocks, it is usually concentrated in conduits, which location is difficult to determine, since in short distances they alternate with impervious rocks [3,8,11,48,73]. After the detailed observations of the hydrogeological situation in the Zheji stream area, it was thus decided to drill two water wells, 50m-deep, in the immediate vicinity of Mamurras spring (no. 1, Figure 4), and to isolate the gravel aquifer. During the implementation of the wells, the EC and groundwater temperature were continuously measured in order to record any possible change of groundwater quality with depth. Well no. 7 flowed 40 l/s, while the pumped capacity was recommended to be 60 l/s. According to the chemical analyses the water quality respects the Albanian Drinking Water Standard (Table 2); TDS was measured in 350 mg/l, the temperature is 16.4°C and the water chemical type is $\text{HCO}_3\text{-Ca}$.

8.2. Thermal waters

White Water thermal spring is not used for balneological purposes, due to its temperature, not sufficiently high, although the content of hydrogen sulphide (H_2S) in water shows significant values, even though not reaching that at the well-known Peshkopi thermal springs [32]. A restricted number of the inhabitants of local villages use them for curative baths using primitively-made ponds. However, if special pools were built, they would be sufficiently useable in the winter season when the spring water temperature of 22° is perceived as warm, while during the summer the water temperature in the ponds would increase because the summer air temperature in this area usually exceeds 30 °C. Since the White Water thermal spring water is not used, it is not protected, too.

Boreholes with depth about 1000 m could provide thermal waters with temperatures of about 30° C with high balneological qualities (high salinity of about 5 gr/l and significantly higher content of H_2S gas of about 400 mg/l) in the area of White Water spring. The geological-hydrogeological data here presented support such an assumption. Further, it must be stressed the significant environmental value of this thermal area, due to its privileged geographical location, at a distance of only 35 km from the capital city of Tirana.

8.3. Groundwater protection

Two cement factories have been built in the Makaresh massif, respectively at its southern suburbs and in the central part of the massif (Figure 9). To provide the factories with limestones, as well as for construction purposes in general, several quarries exercise their activity in the massif, too. Location of such factories and quarries on the Makaresh karst plateau (Figure 9) represents a typical negative example of human activities degrading the beautiful mountain karst landscape that borders the eastern side of the Tirana depression. It is well known and documented that quarrying activity has many negative impacts on the karst environment: first, it destroys the epikarst [74], the most surficial part of the karst that acts as the main recharge zone for karst aquifer; then, it impacts through clearing of the vegetation cover, in turn causing an increase in surface runoff, and in erosion as well, even on low-gradient slopes [75].

Advancement of the quarrying face results in destruction of karst caves, and of the natural resources therein, often without any possibility to ascertain whether these might be scientifically important or not [76–80]. Further, these activities eventually result in pollution of karst waters, as already documented in several sites of the Albanian karst [81–83]. An example worth to be mentioned is the pollution of Bogovo spring used for water supply of the cities of Berat, Kuçova and Urra Vajgurore, by the quarrying activity at Mount Tomori [84]. The high vulnerability of the karst environment by activity of the cement factories, the likely produced damage, or the possibility of future environmental problems, should represent issues of further analysis, as a pressing task for the future, also by using some of the dedicated indices defined for karst environment [85–89], aimed at ascertaining and qualitatively assess the damage produced by such anthropogenic activities.

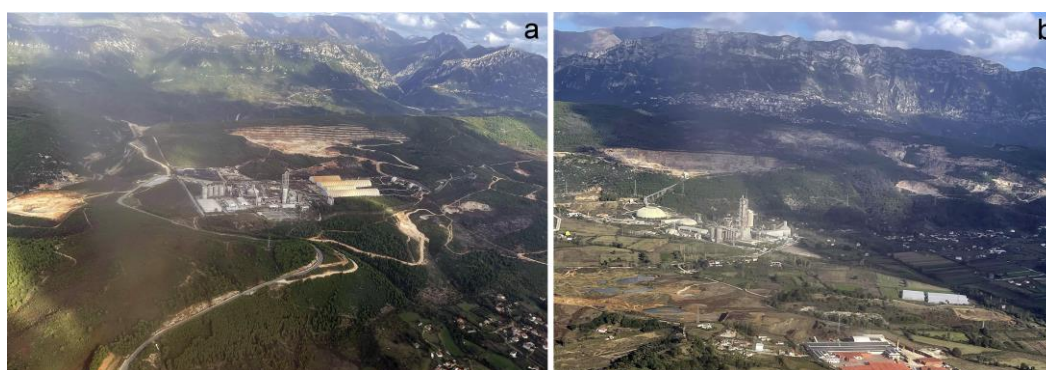


Figure 9. Bird-eye-views of the cement factory, showing **a** its location at the top of the karst plateau, and **b** the many quarries in its surroundings.

9. Conclusions

The Kruja tectonic zone is characterized by presence of SE-NW oriented structures of Upper Cretaceous to Eocene carbonate formations, locally exposed below the overlying Oligocene flysch deposits. In this zone there are over 80% of the thermal springs of Albania. The Makaresh karst massif, with an area of 22 km², is one of the most interesting karst structures hosting, within relatively short distances, both fresh and thermal waters. Geological and hydrogeological investigations, combined with physico-chemical analyses, allowed to identify the presence of two groundwater circulation systems in the Makaresh karst massif.

The shallow circulating waters are cold, fresh and belong to a HCO₃-Ca or HCO₃-Ca-Mg hydrochemical facies, with EC varying around 580-650 µS/cm, and water temperature ranging from about 13.9 to 16.6°C. The deeper circulating waters are mineralized, with lower acidic pH and higher total hardness; they are mainly of the Cl-Na-Ca type, whilst EC varies in the range 7200-7800 µS/cm, and the water temperature is about 18.5-22.5° C. Thermal waters can be also distinguished for the high content of the total sulphide gas H₂S (about 350 mg/l), a concentration higher than for most of the thermal waters in Albania.

The main factors responsible for the qualitative formation of shallow circulating groundwater is the solution of the carbonate rocks and of the metallic elements they contain, like pyrite and marcasite. Deep ascending fluids moving upward along transversal faults are the main recharge source for the thermal springs. Their mixing in different proportion with cold water is not very significant.

The renewable groundwater resources of Makaresh massif are estimated at about 400 l/s. Cold water is used for the water supply of the city of Mamurras for about 60 l/s. The White Water thermal spring is not used for curative purposes, due to its insufficient temperature, notwithstanding the high content of hydrogen sulphide (H₂S). In the area of White Water (Uji Bardhe) thermal spring, through deep boreholes about 1000 m deep, it could be possible to provide thermal waters with temperatures of about 30°C, with high balneological qualities.

In the Makaresh massif, presence of anthropic activities (namely, a cement factory situated on the karst plateau in its central part, and several quarries providing limestones for cement production

and for construction purposes) is definitely a negative aspect for the preservation of the pristine landscape, at the origin of degradation of the natural karst in this area bordering the eastern side of the Tirana depression.

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