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Hydrogeological Characteristics of the Makaresh Carbonate Karst Massif (Central Albania)

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Abstract: Carbonate rocks cover about 23% of Albania, with exploitable karst water resources estimated at 2.84×10^9 m^3/year (about 65% of the total exploitable groundwater resources in the country). The Kruja tectonic zone is characterized by the presence of SE–NW-oriented carbonate structures, rich in fresh and thermal groundwaters. More than 80% of the thermal springs in Albania are present in this tectonic zone. One of its most interesting carbonate structures, with the presence of both cold and thermal waters, is the small karst structure of Makaresh, with a surface of 22 km^2. The purpose of this article is to describe the hydrogeological characteristics of this massif; based on the physico-chemical characteristics, groundwaters of the study area are classified as cold waters (belonging to the local flow system) and thermal waters (originating in intermediate/deep flow systems). The former are mainly of HCO_3-Ca or HCO_3-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); they are further characterized by high hydrogen sulfide 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 dissolution of rocks and minerals contained therein, the presence of hypogenic speleogenesis, and the mixing of the groundwater of the two systems. The hydrogeological studies proved that karst rocks contain considerable freshwater resources, partly used for water supply. Thermal waters are not currently exploited due to their temperature, but they are potentially suitable for thermal uses by drilling boreholes to a depth of about 1000 m.

Keywords: karst; hydrogeology; thermal waters; Albania

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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 characterized by wide presence of carbonate rocks [26,27]. They cover about 6490 km^2 (23% of the country) and contain a total of about 7.15×10^9 m^3/year of natural groundwater resources, corresponding to about 80% of the total resources in the country [28]. Likewise, Albania is rich also in thermal karst waters, which are mostly related to carbonate karst aquifers [28–32]. Although relatively small, the Makaresh karst massif, the object of this article, 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 the Makaresh massif, in close relation to its geological and structural features, and the role of thermal groundwaters, including the related hypogene speleogenesis [33–35], in the formation of its secondary porosity. Eventually, given the existing threats in the massif, some considerations about the degradation of the Makaresh karst environment are also presented.

2. Study Area

The karst massif of Makaresh is located about 30 km north of the city of Tirana (Figures 1 and 2). Morphologically, it represents a NW–SE oriented ridge where carbonate rocks crop out for about 22 km^2, with about 8 km^2 of its northern part covered by Neogene formations (Figure 2). 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. The climate of the area is warm Mediterranean, characteristic of 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. The main hydrological elements of the study area are the Droja River, the canyon of which crosses the northern part of the karst massif in an E–W direction, and the small stream of the Zheji, to the south of the river.

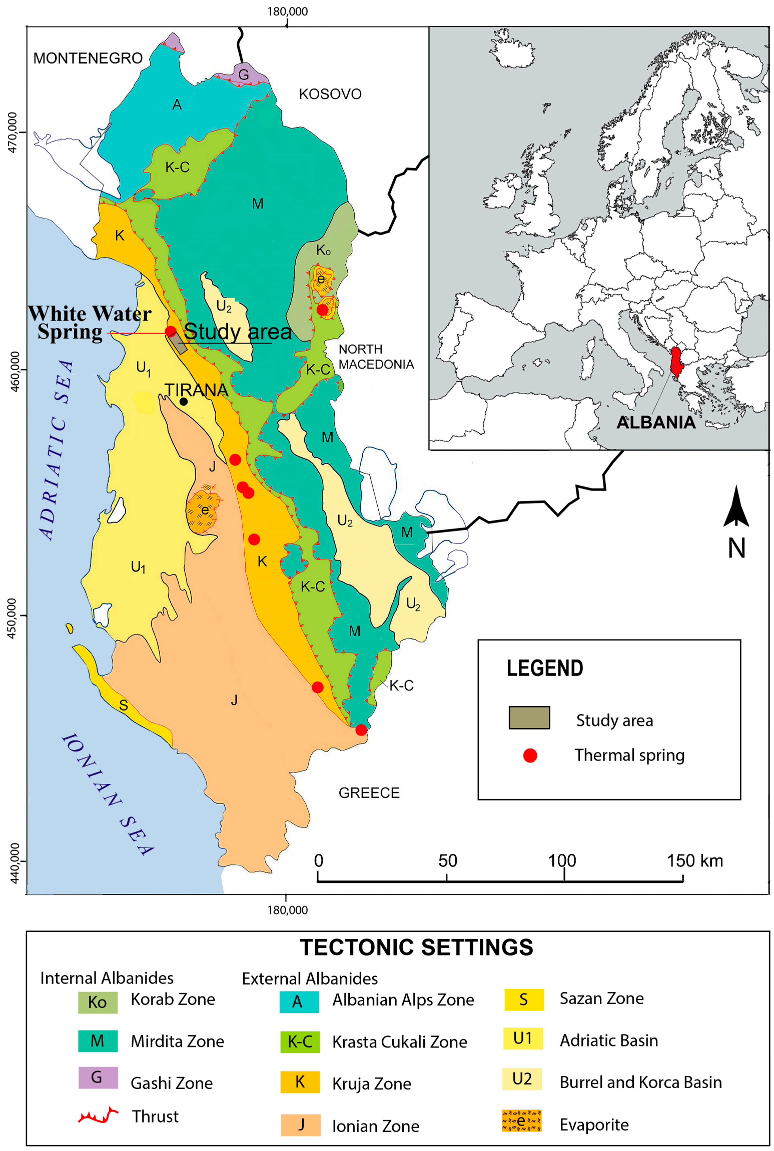

Figure 1. Map of the geological division of Albania (after [27]), showing location of the study area (Makaresh karst massif) and of the White Water thermal spring.

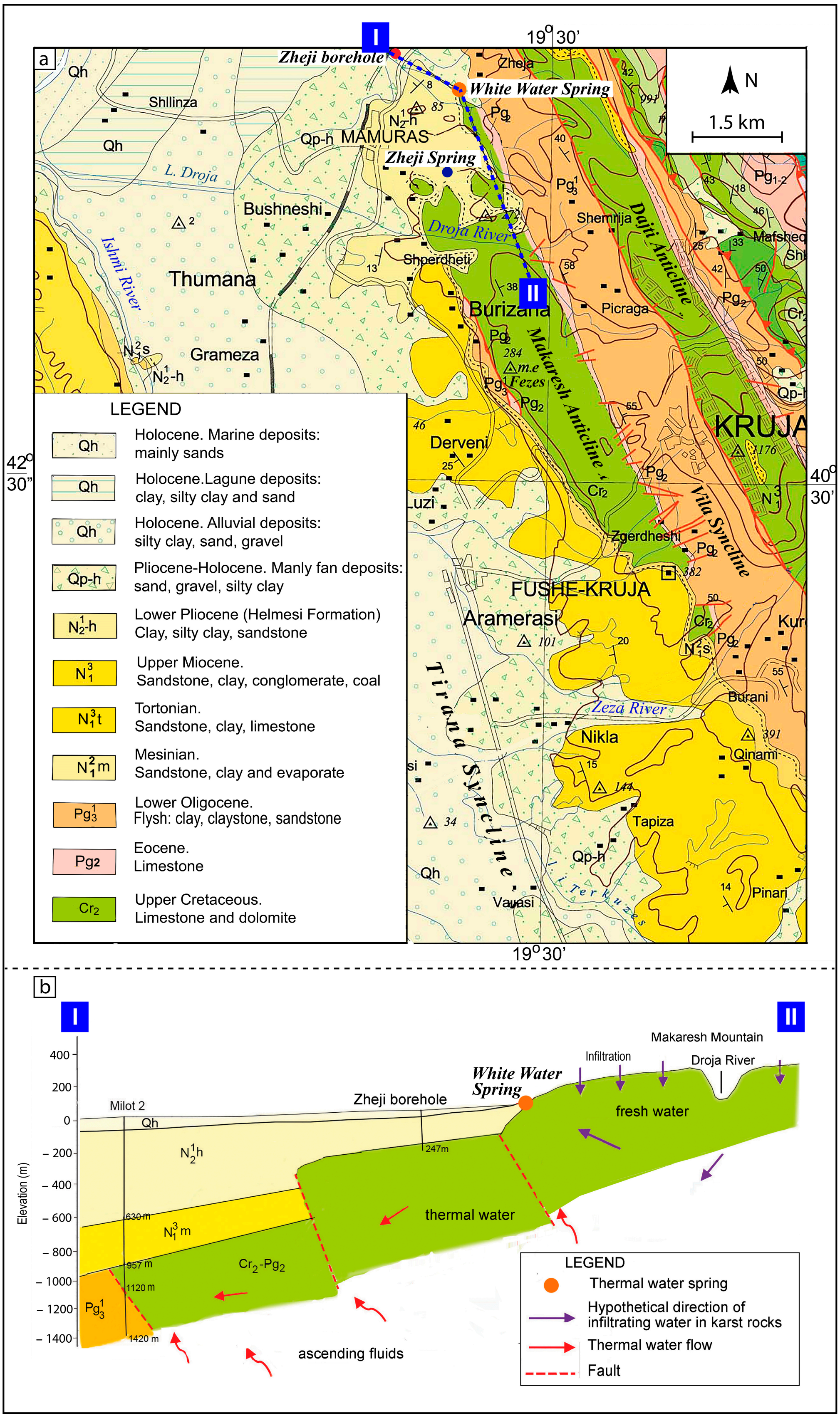

Figure 2. Makaresh karst structure and its surrounding areas: (**a**) geological map and (**b**) cross section along the transect I-II (after [27]).

3. Materials and Methods

To characterize the hydrogeology of the study area, a variety of sources and archives were scrutinized during this work, taking into consideration both the scientific literature and original studies carried out over several years by the authors. This integration of documents and reports from different sources was necessary due to the lack of a continuous series of monitoring data on the springs of the area.

The starting points were large-scale maps such as the geological map [27], the neotectonics map [37], and the hydrogeological map of Albania [26]. Then, we carefully analyzed the data from specific available studies. The first detailed hydrogeological study carried out at the *Uji Bardhe* (White Water) group of thermal springs, accompanied by detailed chemical analyses, was performed by Avgustinski and colleagues in 1957 [29]. During that study, eight springs were identified at the White Water thermal site, the most important being springs nos. 1, 5, and 6; these, as well as the Makaresh fresh spring, were analyzed for major and trace elements. Later, the thermal waters were again the object of studies in the 1970s, in the frame of the compilation of the hydrogeological map of Albania [26], and were further dealt with in a special edition dedicated to the thermal springs of Albania [32]. Detailed investigations aimed at finding fresh karst water resources for the water supply to the city of Mamurras were performed during the 1970s [38] and in 2002 [39]. The water samples were analyzed mainly for the major elements Mg^{2+}, Ca^{2+}, N^{+} + K^{+}, Cl^{-}, $SO_4{}^{2-}$, $HCO_3{}^{-}$, partially in the field, as well as in the laboratory of the Albanian Hydrogeological Service (AHS), using volumetric, spectro-photometric, and colorimetric methods. At the same time, the main parameters, such as pH, temperature, and electrical conductivity (EC), were measured in the field for 7 karst springs and 5 water wells.

Following all the above studies, in the period 2000–2023, numerous field measurements have been performed to monitor discharge, temperature, pH, and electrical conductivity of both the thermal and freshwater springs.

In this article, we present and analyze for the first time the hydrogeological characteristics of the entire Makaresh karst massif, by using all available materials at our disposal, integrating several original field investigations and measurements taken by the authors. Particular attention is paid to the comparative assessment of the physical and chemical characteristics of the thermal and fresh groundwaters. In detail, the Piper diagram, as well as other hydrochemical graphs like the correlation between different quality parameters created using the AquaChem program, were used for the hydrochemistry characterization of the groundwater. This enabled clarification of 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) consists of two major units: the Internal Albanides to the east and the External Albanides to the west [27,37,40]. The Makaresh karst structure is part of the Kruja zone, which is the easternmost sector of the External Albanides (Figure 1) and is distinguished by the presence of long NNW–SSE structures built up of sedimentary rocks. In greater detail, the Makaresh structure is an anticline consisting of Upper Cretaceous to Eocene carbonate rocks (limestone, dolomitic limestone, and dolomites) (Figure 2). These deposits dip eastward with angles of about 35° and are covered by Oligocene clay–claystone flysch that fills the Vila syncline (Figure 2a). In accordance with the tectonic style of the Kruja zone, the Makaresh structure was affected by westward longitudinal thrusts during Eocene and late Oligocene to Miocene times [27,40,41].

In addition to this, the Makaresh massif is broken by a series of deep transversal NE–SW faults that fragmentize the deep buried carbonate structures [42,43]. This is also testified by deep boreholes located in the northern part of the Makaresh structure (Figure 2a,b). West of it, the wide Tirana syncline is located, filled with Paleogene and Neogene molasses covering two buried parallel carbonate structures (Figure 2b). East of this structure, and parallel to it, the Dajti carbonate anticline is present (Figure 2a). The northern part of the

Makaresh carbonate structure 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, with at least three main discontinuity systems. The best developed is represented by bedding planes, dipping about 35° eastward, following the axis of the structure itself.

The fissures of carbonate rocks are often filled with bitumen, related to weathering processes from the early pre-Neogene time when the Makaresh structure was an oil-bearing structure [40]. Freshly broken carbonate rock surfaces often smell of hydrogen sulfide (H_2S), as observed in the neighboring Dajti anticline structure [44]. On top of the Makaresh carbonate structure, a karst plateau hosting a great variety of karst landforms with many sinkholes [45–47] and vertical cave opening and fractures has developed. One of the most interesting karst phenomena is Sallas Cave *(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).

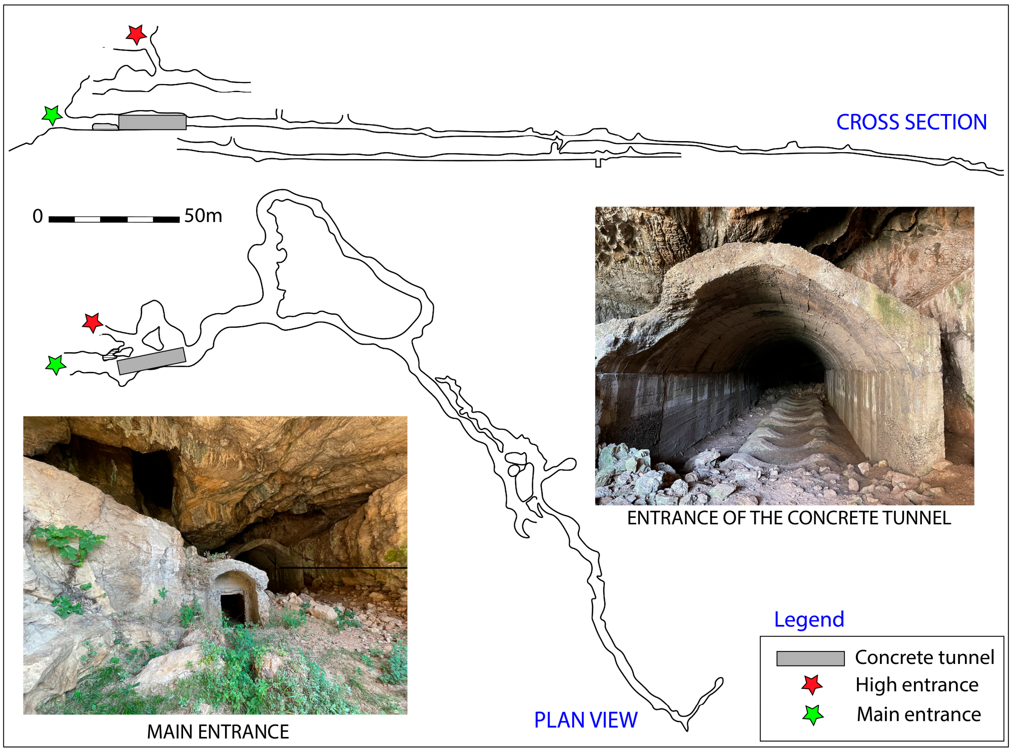

Figure 3. Shpella Sallas section and map with details of the main cave entrance and the concrete tunnel structure. This latter is a man-made tunnel built along the initial part of the natural cave; it was used during the Communist era for defensive purposes (redrawn after [48]).

The natural entrance of the cave is about 8–10 m wide and up to 6 m high. It continues with a 25 m long artificial tunnel, 4–4.5 m wide and about 3.0 m high (Figure 3). The cave walls are coated with calcite and sulfur pigments. It is likely that the sulfuric acid formed by the oxidation of pyrite pigments of the limestone plane fissures [44] mixes with the ascending thermal fluids, producing morphologies typical of sulfuric acid speleogenesis [19,33,35,49]. Sallas Cave has an overall length of over 700 m. About 6–7 m below, there is another small cavity where the largest karst spring of the massif, known as the Makaresh spring, issues (Figure 4).

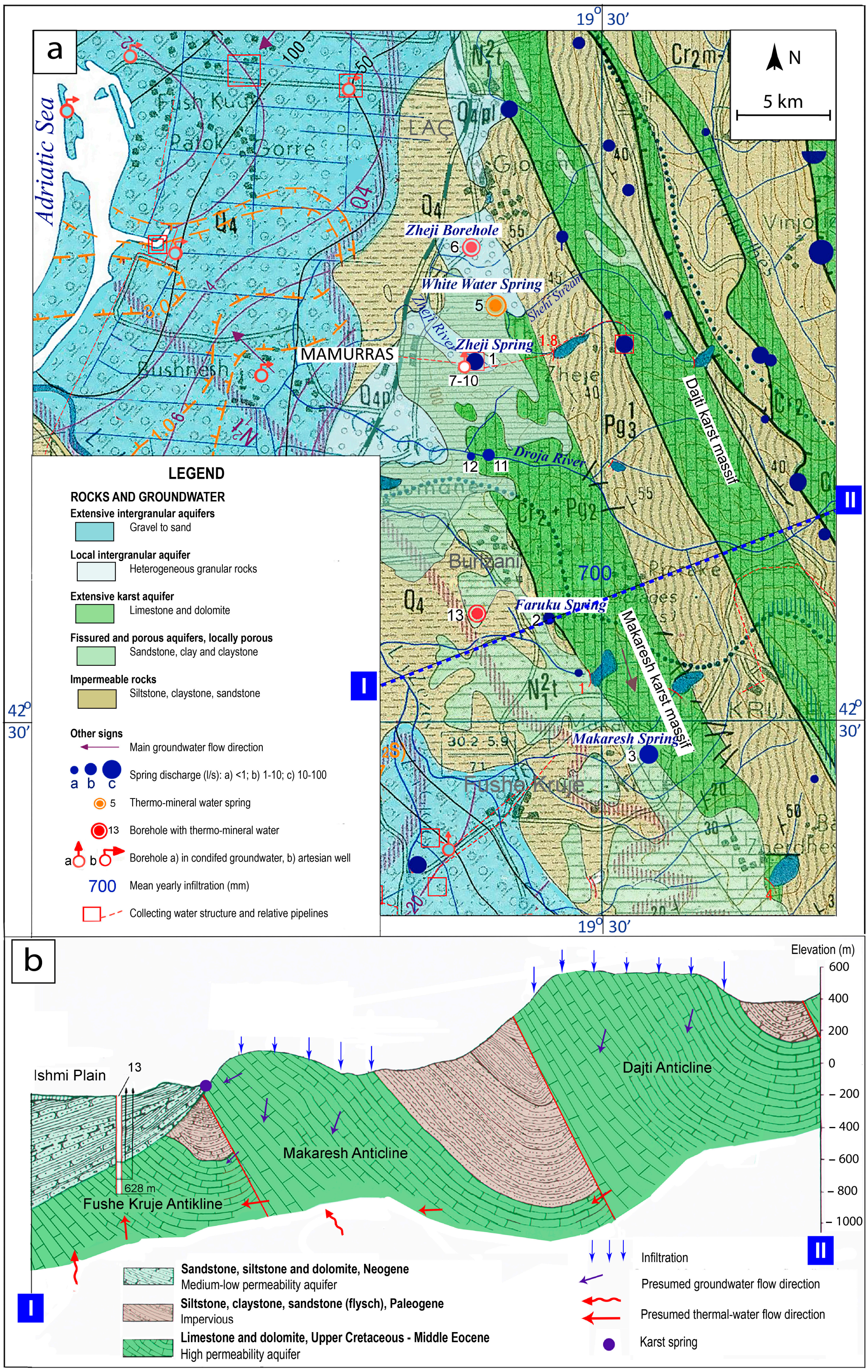

Figure 4. (**a**) Hydrogeological map of the Makaresh carbonate structure and surrounding areas (after [26]), (**b**) hydrogeological cross section AI-AII (SW–NE).

The intensive karstification of the Makaresh carbonate massif facilitates infiltration by the abundant rainfall. Based on climatic data [36], the annual rainfall 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 700 mm/year. Fast discharge during short periods following the heavy rains is estimated at about 10%, or 130 mm/year, while the efficient infiltration by the precipitation equals 570 mm/year. For the entire outcrop area of carbonate rocks in the Makaresh massif (22 km^2), the renewable groundwater resources consist of approximately 12.54×10^6 m^3/year, or 400 l/s, corresponding to an underground flow module of the massif of about 18 l/s/km^2. These values match with the estimated values for low-elevation karst massifs in central Albania [51].

The springs emerging from the Makaresh massif essentially differ in terms of their physical and hydro-chemical characteristics and consist of two well defined groups: a cold and a thermal one (Figure 4). The temperature of the cold springs is about the yearly average temperature of the area (15 °C), while the thermal springs show a temperature value about 5 °C higher than the mean annual air temperature [22,52].

5.1. Cold Springs

The few cold springs are mainly located in the western periphery of the Makaresh karst structure, near its base level (Figure 4a). Among them is the Zheji spring (no. 1 in Figure 4a) discharging about 5 to over 50 L/s. Several small sources emerge in Burizan village, the largest of which is the Farruku spring (no. 2), flowing at about 2 L/s. In the narrow gorge of the Droja River, in the northern sector of the karst massif, there are several minor springs with a total average flow of about 20 L/s; among them, springs nos. 11 and 12 (Figure 4a) discharge about 6.5 and 0.5 L/s, respectively. It is believed that the groundwater seepage from the carbonate massif to the gorge of the Droja River could be on average some tens of litres per second.

One of the most interesting springs in the study area is the Makaresh spring (no. 3 in Figures 4a and 5). The spring has an 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 sulfurous gas and a light white color (Figure 5).

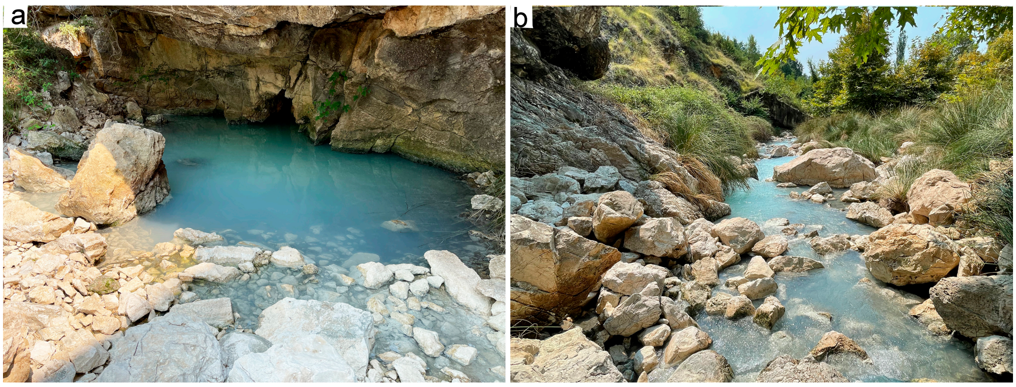

Figure 5. Makaresh spring: (**a**) The spring flows from a small karst cave. (**b**) On 5 October 2023, the discharge of the spring was about 110 L/s (photo, Eftimi R.).

5.2. Thermal Springs

These springs are represented by the White Water group (no. 5), as well as by the Zheji borehole free-flowing thermal water (no. 6, Figure 4). The springs emerge at the contact between Pleistocene deposits (local name "Helmasi Series") consisting of sandstone, conglomerates, and clay, and the underlying Cretaceous–Eocene carbonate rocks (Figure 4). The White Water group consists of eight springs distributed close to each other within an area of about 120 × 70 m. The 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 an average discharge of about 40–50 L/s and water temperature ranging from 20 to 22.8 °C.

Figure 6. White Water (Uji Bardhe) thermal springs at the Makaresh karst massif. (**a**) The main spring; (**b**) measuring the water conductivity at the free-flowing Zheji borehole (photo Eftimi R.).

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

6. Hydrogeochemical Characteristics

Groundwater circulation can be understood in the framework of hierarchical flow systems, consisting of local, intermediate, and regional flow systems [54–56], or as shallow 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 (Figures 2b and 4b) [22]. The simplest approach to delineate flow components in a karst aquifer is to use thermal data [57].

Results of the physico-chemical analysis of the springs at the Makaresh carbonate structure are presented in Table 1, while some non-systematic field measurements from the period 1999–2023 are shown in Table 2. The Piper diagram (Figure 7) and other hydrochemical correlation graphs were used for characterizing the groundwater quality in the studied area (Figures 7 and 8). The hydrochemical assessment included the springs as well as wells nos. 1, 2, 3, and 4, located near the Zheji spring (no. 1). All these charts (Figures 7 and 8) testify the presence of two well-defined groups of groundwater: a cold one and a thermal one.

Cold water springs are characterized by temperatures around 14–16.4 °C and are weakly alkaline (pH 7.05–7.45). These waters have low mineralization (TDS 240–370 mg/L; EC 580–650 μS/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 hydrochemistry of the cold waters is mainly of the HCO_3-Ca-Mg type. Faruku (no. 2), and Zheji (no. 1) springs belong to this group, as well as four shallow water supply wells located near the latter (Table 1, Figure 7).

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 °G	H_2S mg/L	C mg/L	Mg mg/L	Na + K mg/L	NH_4 mg/L	Cl mg/L	SO_4 mg/L	HS mg/L	HCO_3 mg/L	Hydrochemical Type	$rHCO_3$/ rCl	rCa/ rMg	rNa/ rCl
1 Zheji Sp	7 February 1990 (3)	6.0	14.1	7.14	-	340	18	no	87.4	25.0	16.1	no	14.2	30.4	-	370.9	HCO_3-Ca-Mg	15.2	2.13	1.75
2 Faruku Sp	17 March 1993	-	14.5	7.05	-	243	10.2	no	56.7	9.7	17.2	-	8.9	13.1	no	234.8	HCO_3-Ca	15.4	3.53	3.0
3 Upper-Zheji Sp	17 March 1993	-	13.9	7.10	-	256	14.0	no	71.9	16.8	3.0	no	10.6	7.4	no	271.4	HCO_3-Ca-Mg	17.8	2.6	0.43
4 Makaresh Sp	27 December 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	HCO_3-Cl-Ca-Mg	1.71	1.51	0.39
5 White water Sp-1	1 December 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-HCO_3-Na	0.56	1.79	0.86
	October 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-HCO_3-Na	0.83	2.35	0.76
5 White water Sp-5	1 December 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	0.82
	October 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	0.70
5 White water Sp-6	1 December 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	0.86
6 Water well no 10	10 October 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	0.82
7 Water supply well	25 November 2002	40	16.4	7.4	645	350	19	no	98.2	22.5	16.1	no	16.0	12.8	no	409.9	HCO_3-Ca-Mg	15.0	2.65	1.56
8 Water supply well	7 February 1990	-	16.4	7.5	613	369	19	no	100.2	21.45	17.25	trace	14.2	15.2	no	414.8	HCO_3-Ca-Mg	21.2	2.8	1.5
9 Water well	7 February 1990	-	16.4	7.45	612	365	336	no	99.2	21.45	18.4	-	16.0	14.4	no	413.6	HCO_3-Ca-Mg	15.0	2.8	1.8
10 Water well	7 February 1990	-	16.4	7.05	577	327	194	no	93.3	21.45	16.1	trace	12.4	11.1	no	398.9	HCO_3-Ca-Mg	18.7	2.6	2.0
11 Droja Sp-1	29 March 1999	6.5	13.8	7.5	459	275	-	-	-	-	-	-	-	-	-	-	HCO_3-Ca-Mg	-	-	-
12 Droja Sp-2	29 March 1999	0.5	14.1	7.7	565	339	-	-	-	-	-	-	-	-	-	-	HCO_3-Ca-Mg	-	-	-

Notes: Q—discharge; T—temperature; EC—electrical conductivity; TDS—total dissolved solids; Th—total hardness, H_2S—total; ions in "r" are in mg/eqv/L (1) Analyzed by Avgustinski et al. [29]. (2) Analyzed by the Institute of Hygiene and Epidemiology. (3) Analyzed by the Hydrogeological Service.

Table 2. Measurements of some physico-chemical parameters.

Location	Date d/m/v	Q l/s	T °C	pH	EC µS/cm	Water Group
White Water, no. 1	17 November 1999	3.0	21.1	-	5530	Thermal
	10 February 2002	-	20.9	-	5720	
	13 April 2000	-	21.2	-	5730	
	2 August 2000	-	21.2	-	5340	
	15 December 2000	-	21.0	-	6350	
	15 August 2010	3.5	21.2	6.8	6080	
	23 August 2023	2.8	21.5	6.47	4980	
White Water, no. 2	17 November 1999	0.7	21.3	-	6970	Thermal
	15 August 2010	3.0	22.3	6.6	6890	
White Water, no. 3	17 November 1999	0.8	20.9	-	7430	Thermal
	15 August 2010	1.0	22.6	6.6	5990	
White Water, no. 4	17 November 1999	3.0	21.2	-	7210	Thermal
	15 August 2010	1.5	22.8	6.6	7840	
White Water, no. 5	17 November 1999	8.0	21.7	-	6880	Thermal
	15 August 2010	4.7	22.5	6.63	7260	
	23 August 2023	7.8	22.5	6.54	5960	
White Water, no. 7	15 August 2010	1.5	21.7	6.65	7390	
White Water, no. 8	17 November 1999	20.0	20.1	-	4430	Thermal
	10 February 2000	-	19.9	-	4190	
	13 April 2000	-	20.0	-	4120	
	2 August 2000	-	20.2	-	4700	
	15 December 2000	-	20.2	-	4900	
	15 August 2010	11.0	19.8	6.7	4300	
Zhjeji borehole, no. 6	16 November 1999	2.2	22.0	-	6380	Thermal
	10 February 2000	-	22.0	-	6417	
	13 April 2000	-	22.1	-	6880	
	2 August 2000	-	22.8	-	7400	
	15 December 2000	-	22.0	-	7470	
	15 August 2010	1.8	22.0	6.75	8200	
Makareshi spring	27 June 2007	85	16.2	-	970	Fresh
Zheji fresh-water spring	7 February 1990	6.0	14.1	7.14	577	Fresh
Water supply well, no. 48	25 November 2002	40	16.6	7.4	645	Fresh

Among the cold water springs, the Makaresh spring is slightly different, being characterized by a 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 higher 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 of the fresh waters is HCO_3-Cl-Ca-Mg (Table 1), due to the significant increase in the concentrations of Cl^{-} and Mg^{2+} ions. A further important characteristic of the Makaresh spring is the presence of H_2S gas (about 14.8 mg/L), classifying it as a weak sulfide mineral spring [58].

Thermal springs are represented by the White Water group and by the Zheji borehole. Among the eight springs of White Water, seven have very similar physical and chemical characteristics, whilst only spring no. 8 (Figure 8) is different. In this latter, the water temperature and concentration of ions are lower than at the other springs (Table 1).

The groundwater temperatures of this group vary from about 20 °C at spring no. 8 to 21.5–22.3 °C at springs nos. 5 and 6, and the water is weakly acidic, with pH 6.6–6.9. The ion concentration of thermal water (springs nos. 5 and 6) is distinctly higher than the cold waters, with increased mineralization (TDS 4100–7800 mg/L) and hardness (Th = 33–93 °G). Concentrations of the major elements fall within the following ranges (mg/L): Ca^{2+} 388–583; Mg^{2+} about 168; Na^{+} 1010–1300; $HCO_3{}^{-}$ 480–530; $SO_4{}^{2-}$ 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 characteristic of the White Water spring is the high concentration of H_2S, with maximum measured values of 325–360 mg/L. Compared with other thermal springs in Albania, only in that of Llixha Elbasan is the concentration of this gas higher, about 410 mg/L [32]. Table 2 reports the outcomes of non-systematic field measurements of temperature, pH, and EC. These data confirm the seasonal stability of the parameters, with temperature variations lower than 5%, while EC varies about 10%.

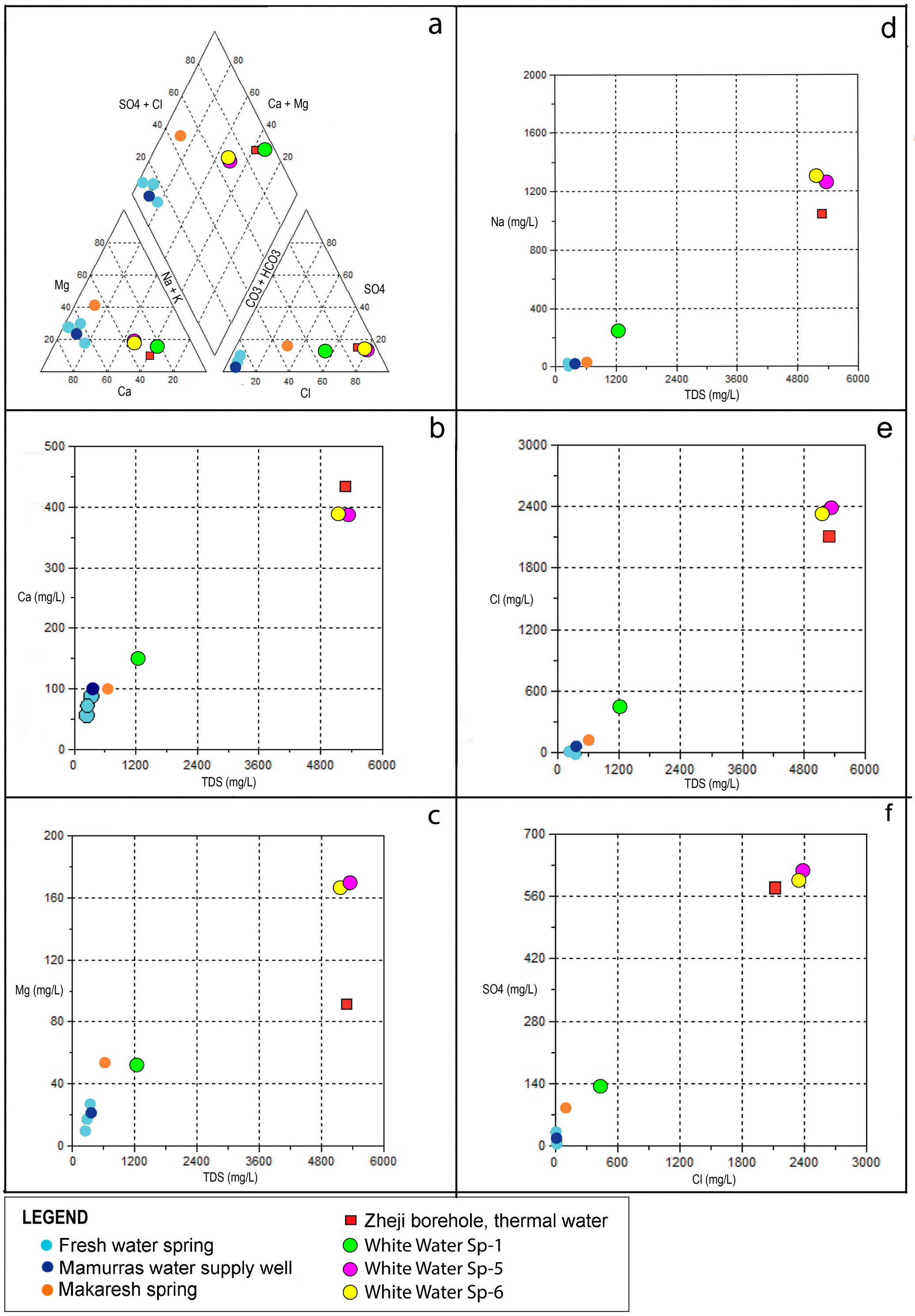

Figure 7. (**a**) Piper diagram showing hydro-chemical signatures of the sampled points of the groundwater of the Makaresh karst massif and hydro-chemical correlations: (**b**) Ca-TDN; (**c**) Mg-TDN; (**d**) Na-TDN; (**e**) Cl-TDN; (**f**) SO_4-Cl.

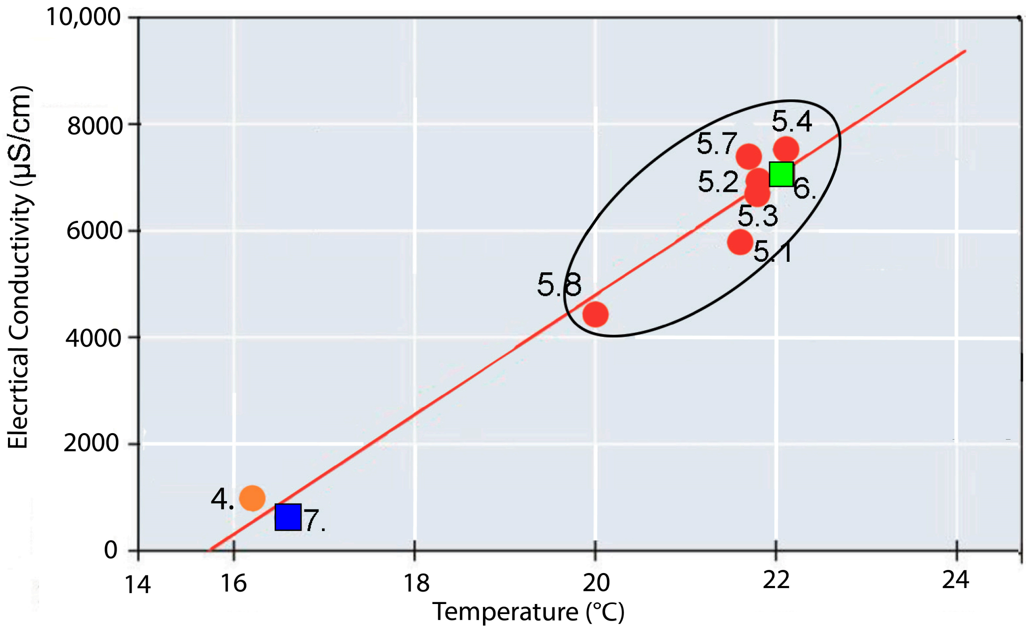

Figure 8. Correlation of EC vs. water temperature. Numbers represent: 4. Makaresh Spring (orange circle); from 5.1 to 5.8 different springs of the White Water thermal group (red circles); 6. Zheji boreholes (green square); 7. Mammuras water supply borehole no 48 (blue square). The equation thethe best fit line is y = 1121.8 x (−17,650); R^2 = 0.9722.

In Table 3, the concentrations of some minor and trace elements and gases at White Water are provided. Among the gases, the increased presence of hydrogen sulfide HS (114.2 mg/L) and free carbonic gas CO_2 (141.7 mg/L) can be noted.

Table 3. Concentration of minor and trace elements and gases in individual springs at White Water and Makaresh springs (after [29]).

Components	Unit	Spring 5.5	Spring 5.1	Spring 5.6	Makaresh Spring
Brom, Br	mg/L	1.2			
Jodi, J	mg/L	0.4			
Hydrosulfite, HS	mg/L	114.2	21.5	94.7	6.9
Thiosulfate, S_2O_3	mg/L	1.1			1.1
Sulfite, SO3	mg/L	0.2			0.2
Acid salicylic, H_2SiO_3	mg/L	28.0	13.0	27.6	32.4
Acid boric, HBO_2	mg/L	17.8			
Total sulfidic gas, H_2S	mg/L	357.8	69.7	326.5	14.8
Free sulfidic gas, H_2S	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_2S	% volume	4.43			
Dissolved sulfidic gas, H_2S	ml	155.1			
Dissolved carbonic gas, CO_2	ml	71.7			
Dissolved nitrogen gas, N_2	ml	14.7			
Dissolved methane gas, CH_4	ml	8.45			

Among the gases freely released from water, nitrogen (N) dominates with 71.5% of the volume, followed by carbon dioxide (CO_2 15.41%), and further methane and sulfur gas representing the sum of $S_2O_3{}^{2+}$ and $SO_3{}^{2+}$. As for dissolved gases, H_2S (155 mg/L) and CO_2 (71.7 mg/L) prevail. The only analyzed trace elements, bromide and iodide, have low concentrations of 1.2 and 0.4 mg/L, respectively. Based on the classification of thermal waters [58], White Water spring can be classified as "*Very strong hydrogen sulfide (H_2S) gas warm water with medium salinity*".

7. Groundwater Circulation

Cold water springs are fed by the shallow local flow system that predominantly runs in a dolomite–limestone environment. The main process defining the formation of the chemical composition of shallow-circulating groundwater is the dissolution of the carbonate rocks by infiltrating waters further enriched in carbon dioxide from the soil and the vegetal cover of the karst massif, a process strongly dependent on the contact time between water and rock [59,60]. The rCa^{2+}/rMg^{2+} ratio (r indicating the concentration in mg/eqv/L) is a sensitive indicator of the composition of carbonate rocks [44,61,62]. In dolomite groundwater, it 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 in the Makaresh karst massif, mainly dolomitic, support the above-mentioned conclusions, since the rCa^{2+}/rMg^{2+} value generally varies between 2.1 and 2.8, with a lower value (1.5) at the Makaresh spring.

Deep fluids circulating in carbonate rocks, in addition to positive thermal anomalies, are often characterized by increased concentration of ions and by the presence of H_2S and CO_2 [22]. High sulfate concentrations frequently occur in thermal springs discharging from carbonate aquifers, together with a direct relationship between sulfate and temperature [22]. The artesian water flowing from the deep wells tapping the carbonate structures in the Kruja tectonic zone at depths from about 1300 to more than 2800 m, is classified as deep circulating groundwater [32].

Karst reservoirs are typically characterized by high porosity related to fissures and karst conduits that have 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 routes for the movement of fluid, and these are favored by the 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 process relates to the presence of evaporitic rocks below the Mesozoic carbonate structures [68,69], which facilitates the formation and movement of sulfatic fluids rich in salts and gases such as H_2S and CO_2 and micro-components; such fluids transfer warm water to sources [22,23,70]. Fluids may also be rich in Na and Cl ions, related to the halite deficiency usually found in evaporite deposits [32,71]. The second process is the enrichment of thermal waters with sulfate by oxidation of pyrite, a phenomenon occurring in an oxidation environment [72], such as is likely to be present in the Makaresh massif as well as in the neighboring Dajti massif [44]. This could explain the mainly Cl-Na-Ca composition with high concentrations of H_2S and CO_2 gases at the White Water thermal spring.

Correlation of electrical conductivity and water temperature for the different individual springs at White Water (Figure 8) shows that the investigated water points are positioned into two well-defined groups, potentially belonging to different water circulation systems: namely, a local flow and an intermediate flow system. Cold water springs belong to the local flow, characterized as HCO_3-Ca-Mg type groundwater, with temperatures in the range 13.9–16.6 °C and EC about 580–650 µS/cm. Thermal waters, on the other hand, belong to the intermediate flow system and are artesian waters of the CL-Na-Ca type, with increased temperature (18.5–22.5 °C), EC ranging from 7200 to 7800 µS/cm, and increased SO_4 concentration (about 400 to 600 mg/L).

8. Groundwater Exploitation

8.1. Cold Waters

Groundwater of the Makaresh karst massif is used for water supply for some important urban, rural, and industrial centers such as the city of Mamurras, the villages of Burizan and Zgërdhesh, and the Titan Cement Factory. The water supply study for the city of Mamurras pointed to some important features of the karstification and highlighted the abundance of fresh groundwater in the karst massif [39].

Groundwater flow in karst rocks is usually concentrated in conduits; since carbonate rocks alternate with impervious rocks, the locations of conduits are difficult to determine [3,8,11,49,73]. To solve this problem in the Zheji stream area, two 50 m deep water wells were drilled in the immediate vicinity of Mamurras spring (no. 1, Figure 4). Both wells testified the very high transmissivity of the carbonate rocks, with artesian flow of 40 L/s. The water quality meets the Albanian drinking water standard (Table 2); TDS was measured at 350 mg/L, the temperature was 16.4 °C, and the water chemical type is HCO_3-Ca.

8.2. Thermal Waters

The White Water thermal group is not used for balneological purposes, due to its temperature, which is not sufficiently high, although the content of hydrogen sulfide (H_2S) in the water shows significant value. A restricted number of the inhabitants of local villages use them for curative baths, using primitively made ponds. Since the White Water thermal site is not used, it is not protected, either.

Since the temperature gradients in the Kruja tectonic zone range from 7 to 11 °C/km [31], it would have been expected that boreholes drilled near White Water to a depth of about 1000 m could provide thermal waters. Based on the geological–hydrogeological data presented in this article, the tapped water would have temperatures of about 30 °C with high salinity (about 5 gr/L) and significantly high content of H_2S gas (about 400 mg/L).

8.3. Groundwater Protection

Two cement factories have been built in the Makaresh massif, at its southern suburbs and in the central part of the massif, respectively (Figure 9). To supply the factories with limestone, as well as for construction purposes in general, several quarries were established in the massif, too. The location of such factories and quarries on the Makaresh karst plateau (Figure 9) represents a typical negative example of human activity 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 the karst aquifer, then, it impacts through the clearing of the vegetation cover, in turn causing an increase in surface runoff and also in erosion, even on low-gradient slopes [75].

Advancement of quarrying activity results in the destruction of karst caves, and of the natural resources therein, often without any possibility to assess whether these might be of scientific importance or contain high-quality water, biodiversity, etc. [76–80]. Furthermore, these activities eventually result in pollution of the karst waters, as already documented in several sites on the Albanian karst [81–83]. An example worth mentioning is the pollution of Bogovo karst spring in central Albania, used for the 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 to the activity of the cement factories, the probable damage produced, and the possibility of future environmental problems should represent issues of further analysis as a priority for the future, also using some of the dedicated indices defined for the karst environment [85–89], aimed at ascertaining and qualitatively assessing the damage produced by such anthropogenic activities.

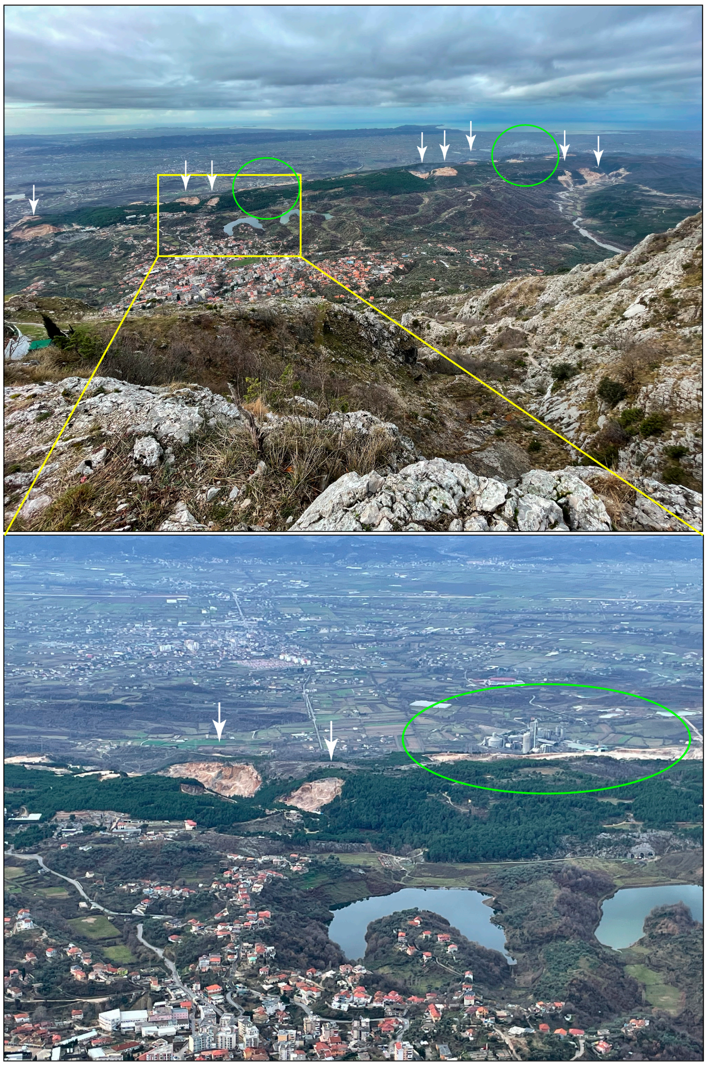

Figure 9. Panoramic views of the Makaresh area: the picture above shows the many quarries (white arrows) and the location of the two cement factories (green circles) located at the top of the karst plateau; below, magnification of the area delimited by the yellow rectangle.

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. Over 80% of the thermal springs in Albania are located in this zone. The Makaresh karst massif, with an area of 22 km^2, is one of the most interesting karst structures, hosting both fresh and thermal waters within relatively short distances. Geological and hydrogeological investigations, combined with physico-chemical analyses, allowed the presence of two groundwater circulation systems to be identified in the Makaresh karst massif.

Groundwaters of the local (shallow) circulating system are cold, fresh, and belong to HCO_3-Ca or HCO_3-Ca-Mg hydrochemical facies, with EC varying around 580–650 µS/cm, and water temperature ranging from about 13.9 to 16.6 °C. Groundwaters of the intermediate circulating system 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 are also distinguished by the high content of total sulfide gas H_2S (about 350 mg/L), a concentration higher than in most of the thermal waters in Albania.

The main factors responsible for the qualitative formation of local circulating groundwater are the solution of the carbonate rocks and oxidation of the metallic elements they contain, like pyrite and marcasite. On the other hand, the ascending fluids from the intermediate flow system, moving upward along transversal faults, are the main recharge source for the thermal springs.

The renewable groundwater resources of the Makaresh massif are estimated at about 400 l/s during low flow. Cold water is used for the water supply to the city of Mamurras at a constant rate of 60 L/s. The White Water thermal group of springs is not used for curative purposes, due to its insufficient temperature, notwithstanding the high content of hydrogen sulphide (H_2S). In the White Water area, through deep boreholes about 1000 m deep, it could be possible to provide thermal waters with temperatures of about 30 °C and high balneological qualities.

Notwithstanding the relevance of its groundwater resources, the Makaresh massif hosts a cement factory in the central part of its karst plateau, together with several quarries providing limestone for cement production and for construction purposes. All these activities definitely represent negative aspects for the preservation of the pristine landscape and the degradation of the natural karst in this area bordering the eastern side of the Tirana depression.

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