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Hydrochemical Assessment of the Aquifer of Thermal Waters in Llixha, Elbasan, Using Stiff Diagrams †

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Abstract: The Elbasani region is characterized by its strong hydrodynamics regime, which comes from the powerful movements of underground water combined with many resources; therefore, the area has geothermal potential, and is one of the most popularly used in our country. This area has a number of sources, located in the form of a chain in the sector between Llixha and Hidrajt, and constitutes a thermomineral basin with a stable discharge and high temperature, at the upper limits of low enthalpy, reaching above 60 °C. The current average flow of thermal water is about 15–18 L/s and temperatures vary from 55 to 65 °C. It is estimated that these resources have specific reserves of 39.6 GJ/m^2 and the potential to install 2760 kW of power. To evaluate their basic physico-chemical parameters and nutrients, water samples were taken throughout 2022 at five monitoring stations, covering the entire aquifer. Stiff diagrams have been used to explain the similarities between the physico-chemical properties.

Keywords: Llixha; standard methods; physico-chemical parameters; Stiff diagram

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1. Introduction

Thermomineral waters are a natural asset for every country. They are deep waters that contain chemical elements and physical properties that can only be obtained from communication with the great depths of the underground. These waters meet on the surface in the form of surface springs, or in the mouths of deep wells drilled for oil and gas. The thermal waters in this area are spatially correlated with the low-velocity layers that give them their chemical elements and physical properties. Albania has significant geothermal energy potential. Sources of geothermal water that come to the surface extend over almost the entire territory of the country. Geothermal explorations have been carried out over the years, and in the second half of the last century, hot water gushed out of several deep wells drilled for oil and gas exploration. Until today, all mineral and geothermal resources have been used only for the purpose of curing various diseases. None of the old resources, including those discovered from the drilling of wells, have been used for the production of electricity or for direct-use purposes. Only low-enthalpy geothermal springs and wells are known in Albania. The maximum temperature of these waters reaches 65 °C. The region of Elbasan has the greatest geothermal energy potential in Albania [1–3].

2. Materials and Methods

The study was carried out in 2022 in the areas of Llixha and Hidraj, Elbasan, and 5 monitoring stations, representative of the area, were selected. The co-ordinates of the monitoring stations are shown in Table 1: Kozan (St 1), Tregan, Para Hotel Ylli (St 2), Tregan, Hotel Ylli (St 3), Tregan, Nosi (St 4), and Hidrajt Çekrezi (St 5). The sampling

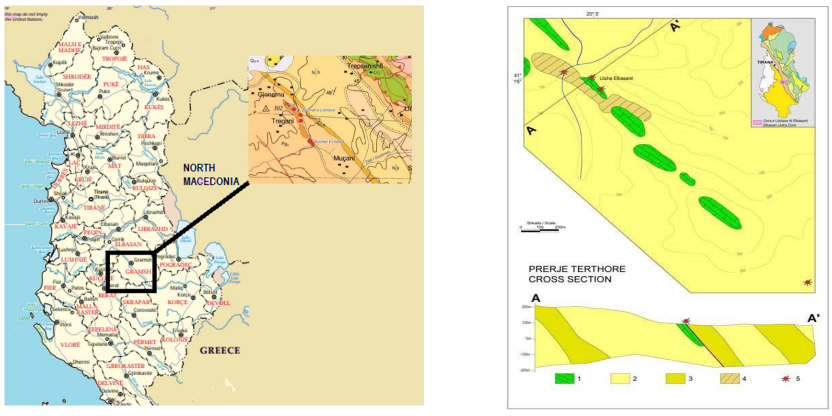
procedure was carried out according standard sampling methods described in "Standard Methods for the Examination of water and wastewater" (21st edition, 2005) APHA [4]. "The testing of water—Merck", 1998, [5] and the ISO standard 5667-2:1991, [6] were used for experimental procedures. The parameters of water temperature, pH, electrical conductivity, and TDS were measured directly in the field using a multiparametric probe. Heavy metals were detected using the method of Atomic Absorption Spectrometry (AAS), with graphite furnace atomization, SAA/AET [7].

Table 1. Co-ordinates of the main sources in Llixha and Hidrajt, Elbasan.

Stations	Coordinates X	Coordinates Y
St 1	N 41°07′35″	E 20°00′59.7″
St 2	N 41°01′59.3″	E 20°04′18.7″
St 3	N 41°01′58.9″	E 20°04′13.6″
St 4	N 41°01′22.7″	E 20°05′7.77″
St 5	N 41°01′13.7″	E 20°05′15.8″

3. The Thermomineral Springs of Llixha and Hidrajt, Elbasan

The area of the Elbasan springs is bounded by flychoidal formations of the Oligocene as well as mollasic formations of the Miocene. The border between these formations runs parallel to the source line, and, in some places, is less than 100 m to the east. The thermomineral springs of the Elbasan Spa are located about 12 km south of the city of Elbasan (Figure 1a). They consist of two groups of sources: the sources of Llixha and the sources of Hidrajt. The sources of Llixha emerge in a line with a length of about 500 m and an azimuth of 320° [2,8,9].



(**a**) (**b**)

Figure 1. Map of Llixha and Hidrajt, Elbasan, Albania. (**a**) monitoring stations, (**b**) hydrogeological scheme of thermomineral springs.

These sources of thermomineral water come to the surface in two main sectors: Llixha and Hidrajt. They are of the hydrochemical type chloride—sulfate of Na-Ca, with a high content of free H_2S. The springs of Llixha emerge about 12 km south of the city of Elbasan (Figure 1b), on the left side of the Prifti stream valley, at about 500 m long and around 3 km away from the Elbasan–Cërrik–Gramsh highway. The Hidrajt springs come out about 1.5 km south-east of the sources of Llixha, on both sides of the valley of the Banja River, and around 2 km east of the new Elbasan–Llixha–Gramsh highway [10,11]. The formation scheme of the Llixha, Elbasan, resources, as well as the main data of the resources that make them up, are presented in Figure 1b.

3.1. Hydrogeochemical Characteristics

The results of the general physico-chemical analyses of the springs and the contents of the microcomponents and gases are given in Table 2. The temperature of the main

thermomineral springs fluctuates from 50 to 65 °C, which classifies them as "very hot". The water has a "slightly acidic" or "neutral" reaction; the pH fluctuates at around 6.6 to 6.8 [12]. The sources of the springs of Elbasan are classified as having "medium salinity", which remains dry in most of the springs and fluctuates at around 6800–7300 mg/L. Based on the predominant ions with a content above 25% mg/eq, the water is named "chloride-sulfate-sodium-calcium". The predominant value of the total hydrogen sulfide gas (H_2S) content fluctuates at around 350 to 420 mg/L. According to the content of this indicator, the thermomineral springs of the spas are classified as "strong sulfides".

Table 2. Physico-chemical parameters of the Llixha and Hidrajt springs, Elbasan.

	t	pH	Cond	TDS	COD	S^{2-}	F^-	Cr	Cu	Ni	Pb
	°C		mS/cm	g/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
St 1	64.5	6.75	11.44	6.15	363	92.8	2.64	1.98	0.10	4.15	6.12
St 2	53.5	6.54	13.0	7.90	589	150.4	4.25	3.95	0.22	2.95	3.85
St 3	51.0	6.53	13.8	6.94	494	158.4	3.20	3.90	0.55	4.23	5.12
St 4	53.4	6.34	14.7	4.90	696	176.8	4.62	4.21	0.55	5.13	5.80
St 5	56.0	6.60	15.6	7.64	530	187.2	4.79	4.12	1.23	1.93	4.15

3.2. Climate of Area

The climate of the area is Mediterranean. It is characterized by a variety of relief forms, which influence the regime of the meteorological elements. The average annual temperature ranges from 11 to 13 °C, and in the lower parts, up to 15 °C. The average temperature in January fluctuates between 4 and 6 °C [13]. Rainfall has a uniform distribution of 1100–1300 mm per year. The number of days with precipitation during the year fluctuates between 95 and 105.

4. Discussion

The temperature of the main thermomineral springs fluctuates from 50 to 65 °C, which classifies them as "very hot". The water has a "slightly acidic" or "neutral" reaction; the pH fluctuates at around 6.4 to 7.1. The sources of the springs of Elbasan are classified as having "medium salinity", which remains dry in most of the springs and fluctuates at about 6800 mg/L [7]. Based on the predominant ions with a content above 25% mg/eq, the water is named "chloride-sulfate-sodium-calcium". The predominant value of the total hydrogen sulfide gas (H_2S) content fluctuates at around 350 to 420 mg/L. Feeding, moving, and draining the thermomineral waters of Llixha remains a difficult problem. On the surface of the springs lie the silty clay formations of the Oligocene and the sandy-conglomeratic ones of the Aquitanian. These formations are characterized by generally low and very low permeability; even the clay varieties are practically impermeable. This fact determines in depth the difficulties, or, more precisely, the impossibility, of feeding thermomineral waters from infiltrations of atmospheric precipitation or of surface waters, towards a water-bearing structure.

4.1. Stiff Diagrams Comparison

Comparisons using Stiff diagrams show the differences in groundwater movements between the five sources. The study of the hydraulic connection between the sources was carried out to observe if there was any change in the underground waterways connecting these stations [14–16]. Several samples were taken for analysis in Llixha and Hidrajt, during all four seasons, to observe changes from a hydrogeological point of view. In this case, there are no changes or differences between the diagrams built on the basis of the average of the springs and the other diagrams that present the springs in Figure 2. Observing those diagrams, you can see the similarities between the diagram of st 1 with st 2, st 3, st 4 and st 5.

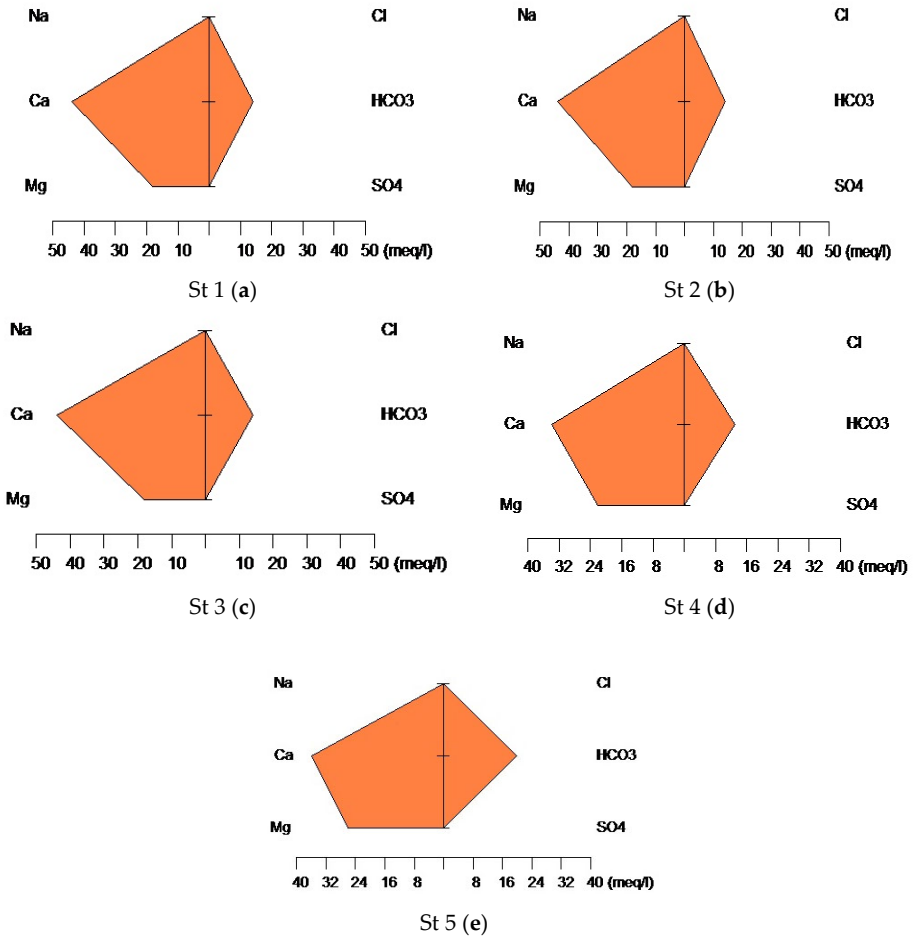


Figure 2. Stiff diagrams of Llixha and Hidrajt springs: (**a**) Station 1, (**b**) Station 2, (**c**) Station 3, (**d**) Station 4, (**e**) Station 5.

4.2. Hydrochemistry

The abundance of the major cations and anions in the water are in the order of $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$ and $Cl^{-} > SO_4{}^{2-} > HCO_3{}^{-}$. The hydrochemical water types of the water samples from the studied area are represented in Piper diagrams (Figures 3 and 4) [15,16]. The pH values range between 6.8 and 7.1. According to the chemical content, the springs are of the calcium sulphate class and the main ions are placed in the order of anions at $Cl^{-} > SO_4{}^{2-} > HCO_3{}^{-}$, and cations at $Ca^{+2} > Mg^{+2} > K^{+} > Na^{+}$. These types of analyses helped in understanding the water movements in the area, which appear to be very complex and unpredictable. The Stiff diagram method helped to draw a general conclusion regarding all the samples collected in the study area over one hydrologic year. The same can be said for the springs in the area, in that they share water chemical similarities. The Piper diagram (Figure 3) shows the direction of the changes in the thermal water chemical composition from well-washed zones (st 2–st 4 sampling points) to less-washed zones (st 1–st 5 sampling points). Along with the direction of the thermal water flow, their hydrogeochemical types changed from bicarbonate-magnesium-calcium ($HCO_3{}^{-}$;Mg^{2+};Ca^{2+}) to chloride-sulphate-calcium-sodium (Cl^{-};$SO_4{}^{2}$;Ca^{2+};Na^{+}) and sulphate-magnesium-calcium ($SO_4{}^{2-}$;Mg^{2+};Ca^{2+}).

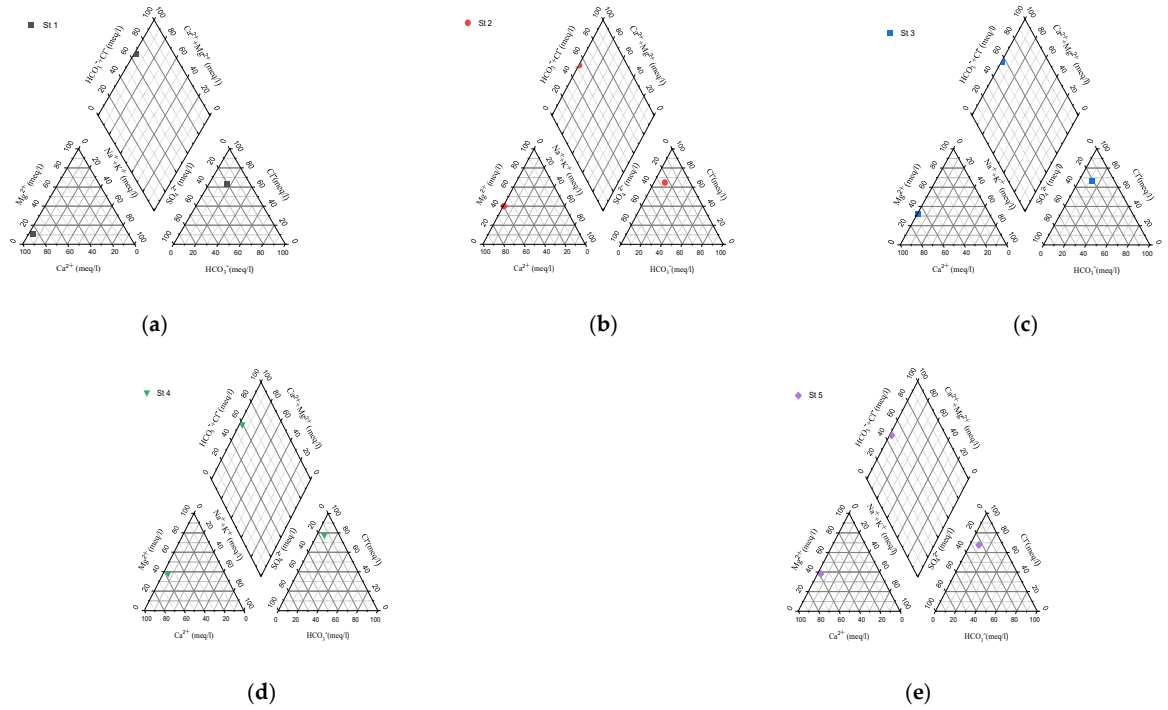


Figure 3. Piper diagrams of springs in Llixha and Hidrajt, Elbasan, Albania: (**a**) Station 1, (**b**) Station 2, (**c**) Station 3, (**d**) Station 4, (**e**) Station 5.

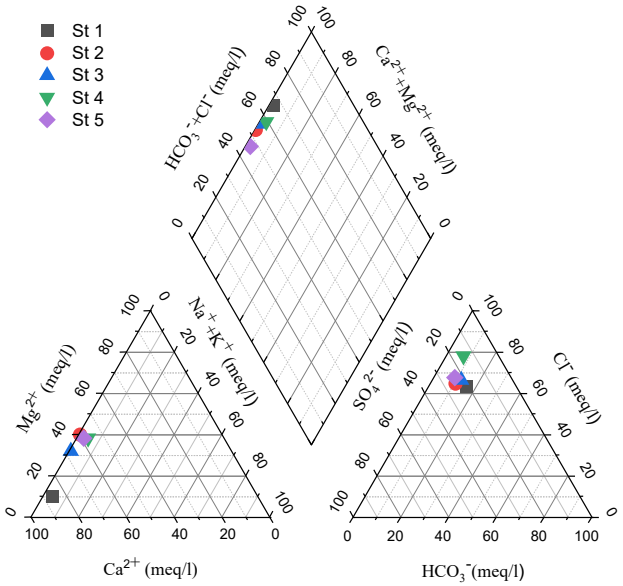


Figure 4. Hydrogeological scheme of thermomineral springs of Llixha and Hidrajt, Elbasan, Albania.

5. Conclusions

From the Stiff diagram comparisons, we can conclude that the results are the same. Expressing the classification in a more concise way, the springs of Llixha, Elbasan, can be identified as hyper-thermal sulfhydryl springs of the chloride–sulfate–sodium–calcium type. The almost-identical composition of all the springs of Llixha, Elbasan, as well as the identical geological conditions, prove that they have the same origin. Undoubtedly, all the springs of Llixha are different exits from a horizon of mineral waters. A rare quality of the thermal springs of Elbasan is their ability to cure, relax, and regenerate the human organism, making them valuable. Distributed in two beautiful and green valleys, in the

vicinity of touristic places such as the highlands of Gjinari and the lakes of Belshi, these sources are pearls of ecotourism. The same can be said for the springs in the area; they have chemical similarities which appear to be very complex and unpredictable. The Stiff and Piper diagram methods help to draw a general conclusion regarding all the samples collected in the study area over one hydrologic year. The same can be said for the springs in the area; they have chemical similarities.

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References

1. Avgustinski, V.L.; Astashkina, A.A.; Shukevich, L.I. *Mineral Waters of Albania–Report*; Ministria e Shëndetësisë: Tirana, Albania, 1957. (In Russian)
2. Atlas of Geothemal Resources in Albania. 2004. Available online: http://itc.upt.al/nfra/projects/geothermal/AlbanianGeothermalAtlas.pdf (accessed on 30 August 2023).
3. Bujakowski, W.; Tomaszewska, B.; Miecznik, M. The Podhale geothermal reservoir simulation for long-term sustainable production. Renew. *Energy* **2016**, *99*, 420–430.
4. *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; American Public Health Association/American Water Works Association/Water Environment Federation: Washington DC, USA, 2005; Volume 3, pp. 154–196.
5. Merck "The Testing of Water". 1998. Available online: https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/scientific/technical-documents/white-papers/apha-water-testing-standard-methods-introduction-white-paper.pdf (accessed on 30 August 2023).
6. *ISO 5667-2:1991*; Water Quality—Sampling—Part 2: Guidance on Sampling Techniques. International Organization for Standardization: Geneva, Switzerland, 1991.
7. Çomo, E.; Tako, E.; Hasimi, A.; Ormeni, R.; Gjuzi, O.; Ndrita, M. Physico-Chemical Characteristics and Possibilities of Utilization of Elbasan Thermal Waters. In Proceedings of the ICGTEGS 2023: 17. International Conference on Geothermal Technologies and Enhanced Geothermal Systems, Athens, Greece, 3–4 April 2023; 23GR040081.
8. Eftimi, R.; Tafilaj, I.; Bisha, G.; Sheganaku, X. Hydrogeological Map of Albania, Scale 1:200.000, Tirana, Albania. 1985. Available online: https://shop.geospatial.com/publication/XCAMKH2E3DZDM4PRWH8H3WG294/Albania-1-to-200000-Scale-Geological-Map (accessed on 30 August 2023).
9. Kodhelaj, N. Albanian possibilities on geothermal direct utilization. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2534–2544. [CrossRef]
10. Frashëri, A.; Kodheli, N. *Geothermal Energy Resources in Albania and Platform for Their Use*; Faculty of Geology and Mining, Polytechnic University of Tirana, Typography KLEAN: Tirana, Albania, 2010.
11. Geotermal Resources in the Balcan; Idaho Operations Office, Idaho National Engineering & Environmental Laboratory: 2001. Available online: https://www.cdc.gov/niosh/oerp/ineel.html (accessed on 30 August 2023).
12. Mehl, V.; Johannsen, K. Calculating chemical speciation; pH; saturation index and calcium carbonate precipitation potential (CCPP) based on alkalinity and acidity using Open Modelica. *J. Water Supply Res. Technol.* **2018**, *67*, 1–11. [CrossRef]
13. *Climate of Albania*; Institute of Hydrometeorology Academy of Sciences: Tirana, Albania, 1976. (In Albanian)
14. AquaChem v.5.1. User's Manual—Water Quality Data Analysis, Plotting, and Modeling, Schlumberger Water Services; Canada. 2007. Available online: https://www.waterloohydrogeologic.com/wp-content/uploads/PDFs/aquachem/AquaChem_DemoGuide.pdf (accessed on 30 August 2023).

15. Kiri, E.; Voudouris, K.; Reci, H.; Panagopoulos, A.; Como, E.; Venetsanou, P. "Hydrodynamics" study of the Ohrid-Prespa lakes using Stiff diagrams. In Proceedings of the 11th International Hydrogeological Congress of Greece, Athens, Greece, 4–6 October 2017.
16. Kiri, E. Hydrodynamic and Hydrochemical Investigation of the Transboundary Aquifer System in Prespa–Ohrid Watershed. Ph.D. Thesis, Aristotel University, Thessaloniki, Greece, 2021.