Assessment of Groundwater Quality of Diyadin Springs, East Part of Turkey for Human Consumption

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Hydrogeological investigation were carried out to assess groundwater quality of Diyadin springs area for its suitability for human consumption, especially thermal activities. The research area consist of Paleozoic aged quartzschist, marble and diorite, Mesozoic aged ophiolitic melange, Cenozoic aged volcano-sedimentary series and alluvium, travertine and terrace conglomerate. Physical and chemical parameters of springs such as temperature, pH, electrical conductivity, total dissolved solids, Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_2^{2-}, HCO_3^-, SO_4^{2-} and Cl^- were determined. The concentrations of a large number of inorganic chemicals in groundwater for example Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, F^-, B^{3+} were also measured. Interpretation of analytical data shows that $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and $HCO_3^- > Cl^- > SO_4^{2-}$ are the dominant water types in the research area. Ni^{2+}, Cr^{3+}, Co^{2+} and Al^{2+} are absent and the other inorganic chemicals are within the permissible limits for human consumption and these spring waters are good for thermal activities.

Key Words: Thermal activity, Thermomineral spring, Ionic activity coefficient.

INTRODUCTION

Turkey is among the top countries in the world in terms of geothermal energy potential. Geothermal energy are mostly utilized for thermal activity (balneological usage and heating purposes). Groundwater quality is important to the suitability of water for thermal activity and so water quality analysis is an important issue in groundwater studies. Knowledge of an hydrogeochemistry is very important to assess the quality of thermal springs for understanding its suitability for various needs. In view of this, hydrogeochemical investigations were carried out in the east part of Turkey, Diyadin-Agri, to assess the quality of spring water and its suitability for thermal activity. As groundwater in Diyadin area is intensively exploited for thermal bath in basic condition, although there are no major industries in the region, it can be developed with health tourism. Hence, the present work had to objective of hydrogeochemistry constituents of thermal springs related to its suitability for health tourism and heating environment. Diyadin is a province of Agri city in the east part of Turkey and it is located in latitude 39º32' north and longitude 43º41' east.

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The area under investigation is in wet climate with cold and heavy rain in winter and dry-warm summers. The average maximum temperature recorded during July is about 36 ºC. The average minimum temperature is about -25 ºC recorded usually during the months of January-February. The average annual temperature is 5 ºC and the average annual rainfall is about 341 mm. The area has snow in winter almost 8 months and average snow thickness is 120 cm. Precipitation is the primary source of water in this area. Murat river is an important river in the region.

The geological formations in Diyadin district consists of quartzschiste, marble and diorite of Paleozoic age. The Paleozoic methamorphics outcrop extensively along northwest-southeast direction of the southwest of investigation area. These rocks have secondary porosity by fracturing and weathering and fractured zones especially in marble form potential host-rock of aquifers. These units are overlain by the rocks of ophiolite group of Mesozoic age. The Upper Cretaceous ophiolitic melange area composed of serpantinite, diabase and spillite. The bottom sequence rocks are transgressivelly overlain by the Neogene aged rocks.

There are angular unconformity between the basement rocks and Neogene rocks. Cenozoic age units were described as volcano-sedimentary series and they are consist of mica schist, tuff, conglomerate, limestone, basalt andesite, ignimbrite and pyroclastics. Alluvium and travertine and terrace conglomerate of Quaternary age occur around the all springs. The formation of geologic units have been affected by tectonism and Tendurek volcanism.

Diyadin geothermal area occur on some tectonic contours located northwest of Tendurek volcanic mountain. It can be said that the character of thermal waters in the investigation area were suspected to be related to regional geologic features which control the flowing of groundwater and influence the temperature and chemistry of the water discharging from springs. In the region, many thermal water springs are issuing, but some of them already are not suitable for human consumption and some of them are not safe area. Hence, four thermal springs (Köprü, Yilanli, Davut, Hidircayiri) are choosen for investigation. It was the purpose of this investigation to determine the hydrogeochemical properties of thermal springs and evaluation of these factors to identify establish the water quality and environmental protection due to Turkish Standard Institute[1]. As a result, the chemical database is used to describe spring chemistry and quality charateristics for human consumption.

Previous investigations in the Diyadin area, Agri, were limited to volcanism[2] and geothermal potential of the thermal area[3-6].

EXPERIMENTAL

Water samples were collected from four springs issued in the thermal site. Techniques and methods were followed for collection, preservation, analyses of samples are given by American Public Health Association Standards[7]. Some of the chemical and physical parameters such as electrical conductivity (EC), the hydrogen ion concentration (pH) and temperature were measured in the field immediately after the collection of samples. The electric conductivity were measured by using the conductivity meter, pH measurements by pH meter with 0.01 precision and temperature measurements were done by means of thermometer. Water samples were taken into capped two 1500 mL polyethylene bottles, acid (suprapure HNO_3) was added to one of the bottles for cation analysis. The other bottle was stored unacidified for anion analysis. In the laboratory of Geological Engineering Department in Cukurova University (Adana, Turkey), samples were analyzed for cations; Na^+, K^+, Ca^{2+}, Mg^{2+} and anions; $Cl^–$, $HCO_3^–$, $CO_3^{2–}$, $SO_4^{2–}$. Concentrations of Ca^{2+}, Mg^{2+}, CO_3^{2-}, $HCO_3^–$, $Cl^–$ were analyzed by volumetric titrations. Sulphate content were estimated spectrophotometrically along with alkalinity standard titrimetry. Flame photometer was used to measure Na^+, K^+ ions and also heavy metal concentrations. The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally around 5 %. Total disssolved solids (TDS) and total hardness (TH) were also computed.

RESULTS AND DISCUSSION

To understand the quality of water is as important as its quality because it is the main factor determining its suitability for various purposes. The analytical results, computed values of the water samples are evaluated and they are given in Tables 1-4.

The pH values of springs range from 7.0 to 7.5 and the temperatures rank between 40 to 51 ºC. The EC values range from 2050 to 3150 µmho/cm. The abundance of the major ions of Diyadin springs is in the following order: $Ca^{2+} > Na^+ > Mg^{2+} > K^+ = HCO_3^– > Cl^– > SO_4^{2–}$. The total dissolved solids (TDS) range from 1933 to 2911mg/L and Ca^{2+} and $HCO_3^–$ are present in large amounts in the water samples. Ca^{2+} ion forms

TABLE-1
ANALYTICAL RESULTS OF KÖPRÜ (K1) SPRINGS

Ions	mg/L	% mg/L	meq/L	% meq/L	C (mol/L)	I	F	AC
K^+	51	6.7909	1.308	3.466	0.0013	0.0007	0.89	0.0012
Na^+	170	22.636	7.391	19.588	0.0074	0.0037	0.95	0.007
Mg^{2+}	80	10.652	6.579	17.436	0.0033	0.0066	0.82	0.0027
Ca^{2+}	450	59.92	22.455	59.51	0.0112	0.0225	0.82	0.0092
HCO_3^-	1860	86.111	30.492	80.502	0.0305	0.0153	0.95	0.029
SO_4^{2-}	145	6.713	3.019	7.97	0.0015	0.003	0.82	0.0012
Cl^-	155	7.1759	4.367	11.528	0.0044	0.0022	0.95	0.0041
Total cation	751	100	37.733	100	0.0232	0.0334		
Total anion	2160	100	37.877	100	0.0364	0.0205		
Total ions	2911		75.61			0.0538		

EC (µmho/cm)	2650	%Na	23.05
pH	7.5	rCa/rMg	3.413
TH (mg/L)	1453	$rCl/rSO_4 + rHCO_3$	0.13
TDS (mg/L)	2911	SIs (sulphate saturation index)	-0.348
SAR	1.94	SIs (calcite saturation index)	1.9237
% Error	-0.191	SId (dolomite saturation index)	1.7571

TABLE-2
ANALYTICAL RESULTS OF DAVUT (D1) SPRINGS

Ions	mg/L	% mg/L	meq/L	% meq/L	C (mol/L)	I	F	AC
K^+	57	10.071	1.462	5.16	0.0015	0.0007	0.9	0.0013
Na^+	130	22.968	5.652	19.957	0.0057	0.0028	0.95	0.0054
Mg^{2+}	71	12.544	5.839	20.616	0.0029	0.0058	0.82	0.0024
Ca^{2+}	308	54.417	15.369	54.267	0.0077	0.0154	0.82	0.0063
HCO_3^-	1095	71.104	17.951	63.226	0.018	0.009	0.95	0.0171
SO_4^{2-}	285	18.506	5.933	20.898	0.003	0.0059	0.82	0.0024
Cl^-	160	10.39	4.507	15.876	0.0045	0.0023	0.95	0.0043
Total cation	566	100	28.322	100	0.0177	0.0248		
Total anion	1540	100	28.392	100	0.0254	0.0172		
Total ions	2106		56.713			0.0419		

EC (μmho/cm)	2150	%Na	25.18
pH	7.4	rCa/rMg	2.632
TH (mg/L)	1061.5	$rCl/rSO_4 + rHCO_3$	0.190
TDS (mg/L)	2106	SIs (sulphate saturation index)	-0.2193
SAR	1.74	SIs (calcite saturation index)	1.729
% Error	-0.123	SId (dolomite saturation index)	1.6188

TABLE-3
ANALYTICAL RESULTS OF YILANLI (Y1) SPRINGS

Ions	mg/L	% mg/L	meq/L	% meq/L	C (mol/L)	I	F	AC
K^+	59	11.501	1.513	5.952	0.0015	0.0008	0.91	0.0014
Na^+	173	33.723	7.522	29.593	0.0075	0.0038	0.95	0.0071
Mg^{2+}	73	14.23	6.003	23.619	0.003	0.006	0.82	0.0024
Ca^{2+}	208	40.546	10.379	40.836	0.0052	0.0104	0.82	0.0042
HCO_3^-	1130	79.577	18.525	72.386	0.0185	0.0093	0.95	0.0176
SO_4^{2-}	150	10.563	3.123	12.203	0.0016	0.0031	0.82	0.0013
Cl^-	140	9.8592	3.944	15.411	0.0039	0.002	0.95	0.0037
Total cation	513	100	25.417	100	0.0172	0.0209		
Total anion	1420	100	25.591	100	0.024	0.0144		
Total ions	1933		51.009			0.0353		

EC (μmho/cm)	2250	%Na	34.86
pH	7.0	rCa/rMg	1.729
TH (mg/L)	820	$rCl/rSO_4 + rHCO_3$	0.182
TDS (mg/L)	1933	SIs (sulphate saturation index)	-0.6686
SAR	2.63	SIs (calcite saturation index)	0.8722
% Error	-0.342	SId (dolomite saturation index)	0.8533

40-60 % of cations, HCO_3^- ion constiute 63-88 % of anions in the total miliequivalent values. In addition to Ca^{2+} and HCO_3^-, high Na^+, Cl^- ions (comprising 7-30 and 12-16 %, respectively) indicated that some of the ions are derived from volcanic activity by the Tendurek volcanism.

TABLE-4
ANALYTICAL RESULTS OF HIDIRCAYIRI (H1) SPRINGS

Ions	mg/L	% mg/L	meq/L	% meq/L	C (mol/L)	I	F	AC
K^+	60	7.947	1.538	4.161	0.0015	0.0008	0.89	0.0014
Na^+	260	34.437	11.304	30.573	0.0113	0.0057	0.95	0.0107
Mg^{2+}	75	9.9338	6.168	16.681	0.0031	0.0062	0.82	0.0025
Ca^{2+}	360	47.682	17.964	48.585	0.0090	0.018	0.82	0.0073
HCO_3^-	1780	84.681	29.18	78.504	0.0292	0.0146	0.95	0.0277
SO_4^{2-}	147	6.9933	3.06	8.233	0.0015	0.0031	0.82	0.0012
Cl^-	175	8.3254	4.93	13.263	0.0049	0.0025	0.95	0.0047
Total Cation	755	100	36.975	100	0.0249	0.0306		
Total Anion	2102	100	37.171	100	0.0356	0.0201		
Total ions	2857		74.145			0.0507		

EC (µmho/cm)	3150	%Na	34.73
pH	7.3	rCa/rMg	2.670
TH (mg/L)	1207.8	$rCl/rSO_4 + rHCO_3$	0.153
TDS (mg/L)	2857	SIs (sulphate saturation index)	-0.439
SAR	3.26	SIs (calcite saturation index)	1.7077
% Error	-3.570	SId (dolomite saturation index)	1.5756

In the investigated area, it is observed that thermal waters contain dissolved CO_2 and H_2S gases but amounts of the gases cannot detected by volumetrically. Hydrogen sulphate occur from the reduction of SO_4^{2-} ions under suitable conditions and H^+ may also derive from the oxidation of pyrite and the anaerobic alteration of organic matter[8].

These chemical result demonstrate that the springs are relatively stable in chemical composition over this time research. The chemical analysis gave high concentration of Ca^{2+} and HCO_3^- and these data is mainly related to the high CO_3^{2-} contents in the marbles, whereas the high Na^+, concentration arises from the existing volcano-sedimanter series.

For evaluation of the hydrogeochemical properties of water, ion concentrations as mg/L are utilized to calculate the ion activity coefficient (F), ionic activity (AC), ionic strength (I), saturation indice (SI). These parameters for all spring water are calculated (under 25 ºC temperature and 1 atm. pressure conditions) by using the following equations and the results are presented in Tables 1-4.

Ionic strength (I) = $0.5\ \Sigma C_i (Z_i)^2$ where C: molarite, Z: the charge number of the ion.

Ionic activity number (F) = $\log F = -A (Z_i)^2 I^{0.5}$ (Debye-Huckel equation)[9] where A is a constant with related to temperature and pressure and it is accepted as 0.51 for 25 ºC and 1 atm. pressure.

Ionic activity (AC) is one of the factor control chemical reaction rate between ions and dissolution of salts in water. It describes real concentration of ions in water and is calculated by AC = F × C. These AC values used for calculation of calcite, dolomite and sulphate saturation index (SI). It should be noted that if saturation index for calcite, dolomite and sulphate are lower than 0.1, minerals can dissolve or not, the minerals can accumulate. So that, the chemical precipitation of minerals cause the crusting problems in the pipes and production wells. In the study area the waters have positive and high saturation indices with respect to calcite and dolomite and so, they are oversaturated.

The results of major ion concentration (meq/L) were plotted in a hydro-chemical facies diagram originally presented by Piper (Fig. 1). From the Piper diagram, it is clear that samples are scattered in zones 5. Zone-5 is characterized by a composition where the carbonate hardness 50 %. It means that chemical properties of water are dominated by alkaline earth elements (Ca^{2+} + Mg^{2+}) with weak acids (CO_3^{2-}+ HCO_3^{-}).

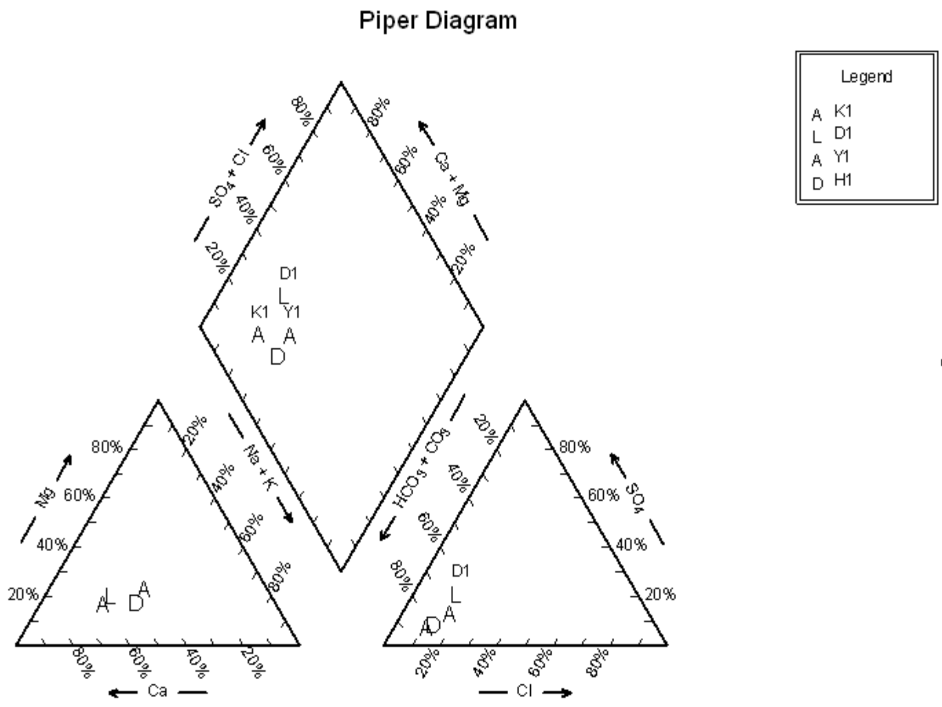

Fig. 1. Chemical classification of water (Piper diagram)

The average heavy metal concentrations which are presented in Table-5 evaluated according to the Turkish Standards[1] and World Health Organization[10,11] limit values. It is determined that Ni^{2+}, Cr^{3+}, Co^{2+}, Al^{2+} are absent in the samples and the average value of B^{3+} concentration rank between 34-37mg/L. As seen in Table-5, all springs water belongs to the Quality Class 1 based on Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, SO_4^{2-}, the Quality Class II based on Cl^{-} and Mg^{2+}. The water classified in Quality Class I and II can be used for household purposes after a treatment like disinfection and purification. On the other hand, most of the samples are located in Quality Class III and IV based on Pb^{2+}, F^{-}, Na^{+}, Cd^{2+}, B^{3+}, Ca^{2+} and TDS. Quality Class III can be made fit for

TABLE-5
WATER QUALITY CLASSES OF THE SAMPLES

Ions	Drinking water		Mineral water	Swimming water	Water samples			
	WHO (mg/L)	TS (mg/L)	TS (mg/L)	TS (mg/L)	K1	D1	Y1	H1
Fe^{2+}	0.1-1	0.1-1	-	-	0.055 (I)	0.05 (I)	0.1 (I)	0.05 (I)
Mn^{2+}	0.05-0.5	0.5	0.5		0 (I)	0.16 (I)	0.08 (I)	0 (I)
Zn^{2+}	5-15	15	(3)		0.005 (I)	0.005 (I)	0.010 (I)	0.015 (I)
Cu^{2+}	0.05-1.5	1.5	1		0.013 (I)	0.013 (I)	0.013 (I)	0.013 (I)
Pb^{2+}	0-0.05	0.05	0.05	0.01	0.024 (III)	0.024 (III)	0.030 (III)	0.024 (III)
Cd^{2+}	0-0.01	0.005	0.005	-	0.008 (IV)	0.010 (IV)	0.010 (IV)	0.008 (IV)
F^-	1.5				1.50 (III)	1.95 (III)	1.6 (III)	1.85 (III)
B^{3+}	10	10			35^6 (IV)	28^6 (IV)	37^6 (IV)	-
Na^+	25-250	25-250	-		170 (III)	130 (III)	173 (III)	260 (III)
Ca^{2+}	75-200	75-200			450 (IV)	308 (IV)	208 (IV)	360 (IV)
Mg^{2+}	50-150	150	-		80 (II)	71 (II)	73 (II)	75 (II)
$SO4^{2-}$	200-400	200-400	-		145 (I)	285 (III)	150 (I)	147 (I)
Cl^-	200-600	250-750	-		155 (II)	160 (II)	140 (II)	175 (II)

Note: I, II, III, IV show the water quality classes.

industrial usage but Quality Class IV waters are not suitable for human consumption. If F^- exceeds the maximum allowable limit, it can cause fluorosis disesase.

The calculated total dissolved solids (TDS) and total hardness (TH) values are exceed the maximum allowable limits (the most desirable limits for TDS: 1500 mg/L and for TH: 500 mg/L) (Table-6 and 7). In that case, all spring waters fall in the moderately hard-hard and brackish water category and these waters can cause gastrointestinal irritation. The exceeding the permissible limits cause the undesirable effect on human system.

TABLE-6
GROUNDWATER CLASSIFICATION BASED ON TDS VALUES

TDS (mg/L)	Nature of water
< 1000	Fresh water
1000-10000	Brackish water
10000-100000	Saline water
> 100000	Brine water

TABLE-7
GROUNDWATER CLASSIFICATION BASED ON TOTAL HARDNESS (TH) VALUES

TH (mg/L)	Water class
< 75	Soft
75-150	Moderately hard
150-300	Hard
> 300	Very hard

The waters are also used for irrigation purposes. The parameters determining irrigation potential of water alongwith samples are listed in Table-8. According to the salinity criteria, only waters with less than 0.5 salinity are suitable for irrigation. A moderately saline water has a salinity of 0.5 to 1.5. All water samples have less than 0.5 salinity value. Sodium adsorption ratio (SAR) values used to evaluate the sodium hazard in combination with EC shown in Fig. 2 indicated that these samples are scattered in C_3S_1 and C_4S_1 class. According to this graph, these spring waters can also be used for irrigation. C_3S_1 indicates high salinity and low sodium water and it can be used for irrigation with little danger of exchangeable sodium. C_4S_1 class shows very high salinity and low alkalinity hazard. In this case, the water can be used for plants having good salt tolerance and need adequate drainage to overcome salinity problems.

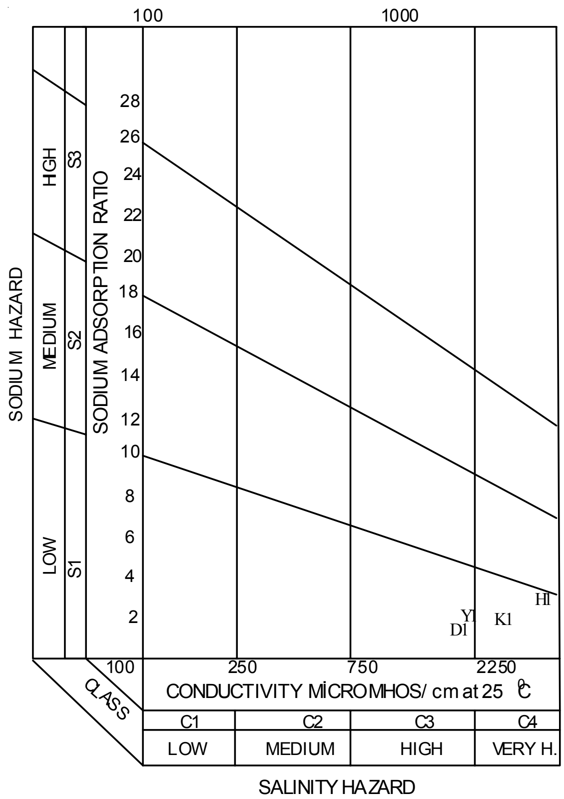

Fig. 2. Plotting of water samples in relation to salinity and sodium hazard (USA salinity diagram)

Conclusion

The hydrochemical interpretation of analytical data shows that $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-}$ are the dominant ions water present in the research area. The Paleozoic aged marble is the potential host-rock of waters which

TABLE-8
SUITABILITY OF WATER FOR IRRIGATION

	EC (μS/cm)	SAR	Na %
Excellent	< 250	< 10 (S1)	< 20
Good	250-750	10-18 (S2)	20-40
Permissible	750-2000		40-60
Doubtful	2000-3000	18-26 (S3)	60-80
Unsuitable	> 3000	> 26 (S4)	> 80
K1	Doubtful	Excellent (S1)	Good
D1	Doubtful	Excellent (S1)	Good
Y1	Doubtful	Excellent (S1)	Good
H1	Unsuitable	Excellent (S1)	Good

have the high concentraions of Ca^{2+} and HCO_3^-. On the basis of IAH classification waters are Ca^{2+}-Mg^{2+}-HCO_3^- bearing thermal and mineral waters. Graphical representation shows that, the study area has calcium, magnesium bicarbonate waters and alkaline earth elements exceed alkalis and weak acids slightly exceed strong acids. The analytical results of physical and chemical parameters also reveals that these waters are within the permissible limits of some major ions and they can be drinkable after a treatment. Total hardness values are generally high in the water (greater than 80 mg/L) and are categorized as hard water. The hard water is not suitable for domestic purposes, because it coagulates soap lather. Interpretation of analysis with respect to the irrigation suitability of the water was made and the study area falls into the category of the high salinity-low sodium and very high salinity-low alkalinity. The thermal waters, on the other hand, it can be used for health purposes as taking bath and also for heating the environment.

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