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Hydrogeological and Hydrogeochemical Features of the Heybeli Spa, Afyon, Turkey: Arsenic and the Other Contaminants in the Thermal Waters

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There are several geothermal fields in Turkey. Most of them are located in the western part of Turkey. These thermal waters are used for space heating, electricity generation, bathing, swimming and spa facilities. Heybeli Spa is one of them and thermal waters around Heybeli have been used for bathing and balneological purposes for many years. History of Heybeli Spa dates back to Roman times. Heybeli Spa was known as Red Church Spa in Byzantine and Ottoman times. The locations of some thermal waters in the study area were affected by an earthquake in 3 February 2002 (M=6.1). This earthquake affected the field characteristics of thermal springs in Heybeli Spa. Discharge rate of waters from wells and spring increased temporary and new low discharge springs appeared after the earthquake which is known as the Sultandağı-Çay earthquake. The chemical properties of the new springs are similar to the old ones but the discharge temperature is lower due to the mixing with cold ground waters. After the earthquake thermal waters flow from some drilled wells to the surface by artesian. Presently, residents from various places travel to Heybeli Spa to take baths with the aim of curing various ailments. Thermal waters are also used as mineral water and are drunk to cure such as stomach ailments. Thermal waters have various hydrogeochemical properties in Turkey. They are mostly suitable for bathing, swimming and balneological purposes. However, they may not be suitable to be used as mineral water due to the involving of pollutant chemicals such as hydrogen sulfide, arsenic, boron, mercury, lead, iron, zinc, manganese and lithium. Especially As concentrations in thermal waters may exceed the drinking water standards. The aim of this study is to evaluate the hydrogeochemical properties of the Heybeli spa and to determine the water quality of thermal waters by comparing with the various standards.

MATERIALS AND METHODS

Thermal waters issue from two localities in the study area (Figure 1). The first group (samples 1, 2, 3, 4 and 6) thermal waters are located around Heybeli Spa. Their temperature are between 42 and 48°C. Thermal waters are obtained from wells and springs are used to heat hotels and for spa facilities, bathing, swimming pools and balneological purposes in the Heybeli geothermal area. A well (sample 2) with 48°C and a spring (sample 4) now feeds the baths at Heybeli spa. Samples 7, 8, 9 and 10 are the second group of thermal waters which are located in south

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east of the Heybeli spa. This group of waters has lower discharge temperatures of 24 and 37°C. The cold ground water sample (sample 5) was taken from a shallow drilled well (Figure 1).

Two samples were collected from each sampling location. One of the bottles was acidified with HNO_3 to determine metal contents and the other was unacidified for anion analyses. Electrical conductivity, pH and temperature values were measured in the field. The major cations and trace elements in the water samples were analyzed in the Acme Analytical Laboratories (Vancouver-Canada) by ICP-ES. Cl and HCO_3 were determined volumetrically and SO_4 by gravimetry in Dokuz Eylül University laboratory (Table 1). Aquachem (Calmbach, 1997) computer code was used to evaluate their geochemical properties.

RESULTS AND DISCUSSION

Paleozoic to Mesozoic Metamorphic rocks that are mainly composed of schists and marbles and Neogene rocks of terrestrial sediments outcrop in and around the study area (Figure 1). Metamorphic rocks are the main reservoir of the thermal waters. The aquifer is developed by means of fractures, faults and karstified of marbles. Overlying Neogene terrestrial sediments (limestone, marl, tuff and sandstone) are the second reservoir for the thermal waters. Upper parts of this aquifer and Quaternary alluvium are the aquifer for the cold ground waters.

The chemical composition of water samples are reported in Table 1. Thermal and cold ground waters are near neutral (pH of 6.3 to 7). The chemistry of the thermal and cold waters in the study area is similar. Based on their chemical composition, the waters can be divided into two groups. 1) Na-Ca-HCO_3-SO_4 type waters (samples 1, 2, 3, 4 and 6) 2) Ca-Na-HCO_3 type waters (samples 7, 8, 9 and 10). This differentiation coincides with their geographic locations as well. The first group waters have electrical conductivity values of 3190-4410 µS/cm. Na and Ca concentrations of the thermal waters range from 356 to 633 mg/L and 320 to 368 mg/L, respectively. HCO_3 values are around 1227 and 1601 mg/L, and SO_4 concentrations are remarkably high about 865-1243 mg/L. The second group waters have lower temperatures and electrical conductivity values of 1000-2280 µS/cm. Ca and Na are the dominant cation similar to first group but their concentrations are lower. They vary between 127-170 mg/L and 87-317 mg/L, respectively.

Figure 2 show the relative concentrations of Na+K, Ca and Mg (a), Cl, HCO_3 and SO_4 concentrations of the waters (b) and the distribution of water samples in Schoeller diagram (c). Both group plots on the bicarbonate area of the diagram (Fig 2b) but first group waters are also close to the sulfate area. In Schoeller diagram thermal waters give similar peaks. However, second group thermal waters are located in lower parts of the diagram due to the more ground water mixing. This coincides with the relatively lower discharge temperatures. Ca is one of the dominant cation in first and second type waters indicating that carbonate rocks are

Table 1. Chemical properties of the water samples.

		1 (well)	2 (well)	3 (spring)	4 (spring)	5 (well)	6(well)	7 (spring)	8(spring)	9 (well)	10(spring)	TS 1997
t°C		46	48	42	43.2	19	44.1	37	24	28	30.4	
pH		6.86	6.68	6.42	6.34	6.93	7	6.72	6.9	6.88	6.67	6.8-9.2
EC	µS/cm	4410	3970	3420	3190	1070	3370	2280	1006	1480	1077	2000
Ca	mg/L	356.8	368.1	322	321.9	166.3	320.8	170.4	127.5	141.9	145.3	200
Mg	mg/L	74.5	79.9	64.8	64	24.8	65	36.2	16.8	36.1	36.6	50
Na	mg/L	633.2	526.9	356.4	360.4	58	370.4	317.7	87.7	155.8	159.9	175
K	mg/L	58.8	51.5	33.2	33.5	1.2	32.5	37.2	10.8	20.3	22.2	
Cl	mg/L	205	175	131	121	40	127	70	37	41	48	600
SO_4	mg/L	1241.9	1139.4	864.2	876.1	160.4	865.2	220.6	70.4	174.9	131.7	250
HCO_3	mg/L	1601.2	1525	1227.4	1259.1	591.4	1257.4	1298.1	622.2	875	916.5	
Al	mg/L	< .1	< .1	< .1	0.1	0.1	0.1	< .1	< .1	< .1	0.2	0.2
As	µg/L	1417	1249	1123	1248	< 30	1122	152	30	57	88	50
B	µg/L	5739	2670	1565	1567	281	1486	863	323	519	531	
Ba	µg/L	40	45	38	39	107	39	66	83	73	75	
Pb	µg/L	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	50
Cu	µg/L	< 2	< 2	6	7	5	3	2	< 2	< 2	2	3000
Fe	mg/L	0.05	5.11	0.27	0.52	0.02	1.13	0.34	< .01	0.25	0.33	0.2
Li	mg/L	0.93	0.81	0.49	0.49	< .05	0.49	0.34	0.08	0.16	0.17	
Mn	mg/L	0.01	0.04	0.01	0.02	0.06	0.17	0.02	< .01	0.01	0.01	0.5
Si	mg/L	12.03	11.31	9.38	9.66	4.59	8.81	9.86	7.09	6.21	6.78	
Zn	µg/L	24	34	22	20	23	5	< 5	< 5	< 5	6	5000

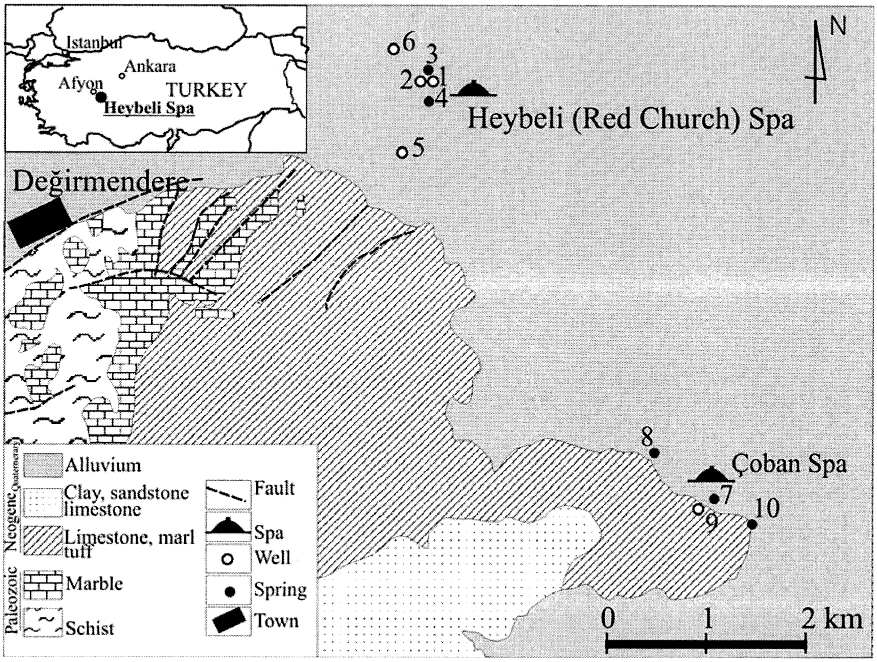

Figure 1. Simplified geological map of the study area (after Erişen et al., 1996) and the locations of the water samples.

the main reservoir rocks for these waters. The main process that controls the chemical properties of water is the dissolution of carbonated, silicated rocks. Dissolution of host rock and ion-exchange reactions in the reservoir of the geothermal system shift the Ca-HCO_3 type cold ground waters to the Na-Ca-HCO_3 and SO_4 type thermal waters. Mg concentrations of high temperature thermal waters are expected to be low (around 0.1 mg/L) (Nicholson 1993). Mg contents of the thermal waters from the study area range from 16 to 79.9 mg/L indicating that water rock interactions at low temperatures and mixing with cold ground waters.

Sulfate concentrations were high in the thermal waters especially for the first group. Relative concentrations of Ca, SO_4 and HCO_3 of waters are shown in Fig. 3 (after Kavouridis et al 1999). The graph indicates the dissolution and deposition of calcite and gypsum. Water samples show a trend suggesting that dissolution of $CaSO_4$ is one of the important processes in water-rock interaction for Heybeli thermal waters. Waters dissolve $CaSO_4$ in various amounts during the circulation in the aquifer. Along the trend line Ca/SO_4 ratio decreases due to the increasing $CaSO_4$ dissolution (Gemici et al 2004). As $CaSO_4$ dissolves, SO_4/HCO_3 values increase, changing the water from HCO_3–dominant to HCO_3 and SO_4–dominant (Fig. 3). The relations of some major ions and trace elements in water samples were presented in Figure 4. Sulfate with Ca and Mg show positively good relations of 0.98 and 0.97, respectively.

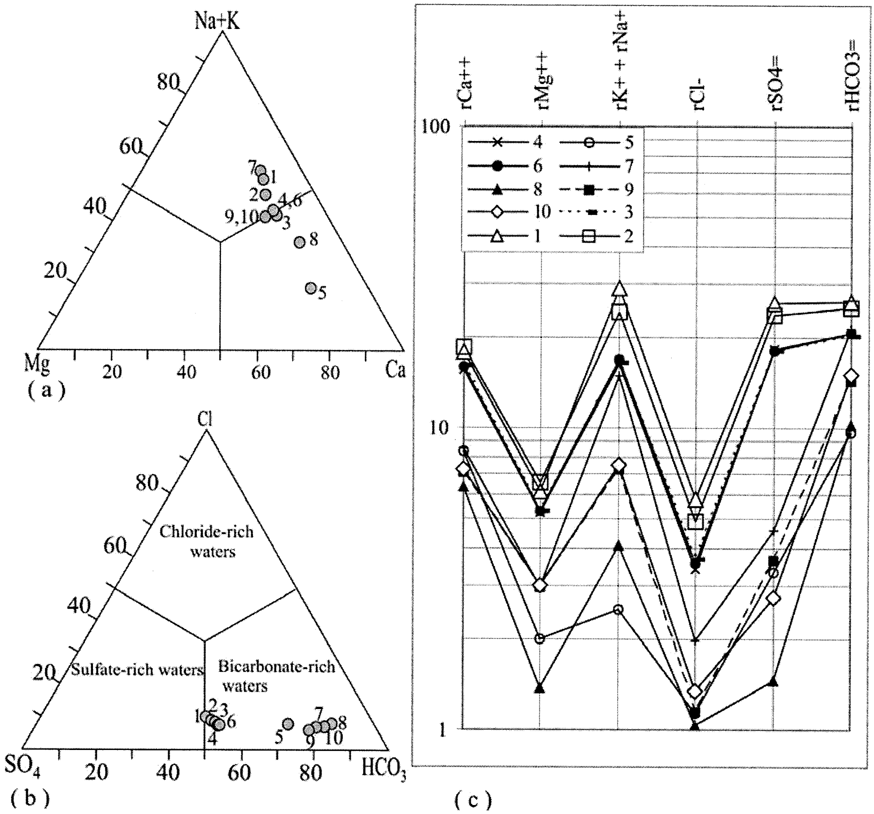

Figure 2. Relative Na+K, Ca and Mg (a), Cl, HCO_3 and SO_4 concentrations of waters (b) and their distribution in Schoeller diagram (c).

Similarly, Ca and Mg show a close positive correlation (r= 0.97). The close positive linear correlation between Ca, Mg, SO_4 and some of the other ions corroborates the dissolution of carbonated and sulphated rocks. There is an inverse relation for pH and and positive good correlation for temperature between element concentrations of water samples. Arsenic has high positive correlations with B (r=0.6), Zn (r=0.63), Cu (r=0.82) and Li (r=0.89) and major ions with correlation coefficients of higher than 0.8. Positive correlations are seen between As and SO_4 (r = 0.98). The relations between As and the other elements suggest a possible rock leaching.

Chemical analyses indicate that surface and ground waters are more or less enriched in a number of elements. The first groups of thermal waters (samples 1, 2, 3, 4 and 6) have relatively high total dissolved solids due to the higher reservoir temperature and low mixing ratios with cold ground waters. Electrical conductivity, Ca, Mg, Na and SO_4 values exceed the Turkish drinking water

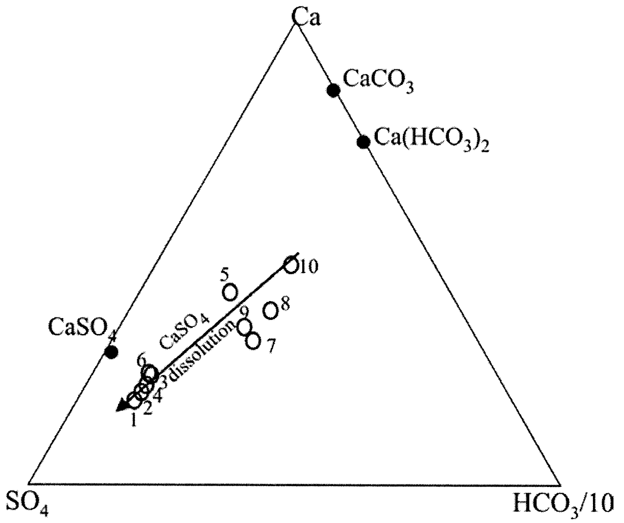

Figure 3. Relative Ca, HCO_3 and SO_4 concentrations (mg/L) of thermal waters from the study area.

standards (TS 1997) (Table 1) for these samples. Especially, SO_4 concentrations are remarkably high (865-1142 mg/L). Al, Ba, Cu, Li, Mn, Zn and Pb concentrations are below the potable water standards which were presented in Table 1. Fe concentrations are between 0.05 and 5.11 mg/L and samples 2, 3, 4 and 6 have higher values that the drinking water standards, 0.2 mg/L (TS 1997; WHO 1993). Boron concentrations of thermal waters are relatively low compared to the geothermal fields of western Turkey (with boron values of reaching to 60 mg/L) (Gemici and Tarcan, 2001). Elevated boron concentrations do not pose the same health risk as As. However the contribution thermal waters with high boron contents to cold ground waters and surface waters can be detrimental to crops. Boron concentrations of first group thermal water that are between 1456 and 5739 µg/L exceed irrigation water the standards, 1 mg/L (USEPA 1972). Second group of thermal waters (samples 7, 8, 9 and 10) have relatively lower dissolved solids. All major ion concentrations and electrical conductivity values are below the potable water standards with the exception of Na and Ca for sample 7. Fe contents are between 0.01 and 0.34 mg/L and slightly exceed the drinking standards. The all constituents of the cold groundwater (sample 5) are below the standard limits and are suitable for drinking and irrigation.

Modern geothermal fluids may contain as much as 50 mg/L As, although concentrations between 1 and 10 mg/L are more typical (Ballantyne and Moore, 1988). In deep geothermal fluids As is predominantly in a +3 state (arsenite, mainly as arsenic acid H_3AsO_3). Oxidation to the +5 state (arsenate) takes place when geothermal fluids react with atmospheric oxygen (Brown, 1995). As minerals are uncommon in geothermal reservoirs. Instead As is incorporated in pyrite or iron

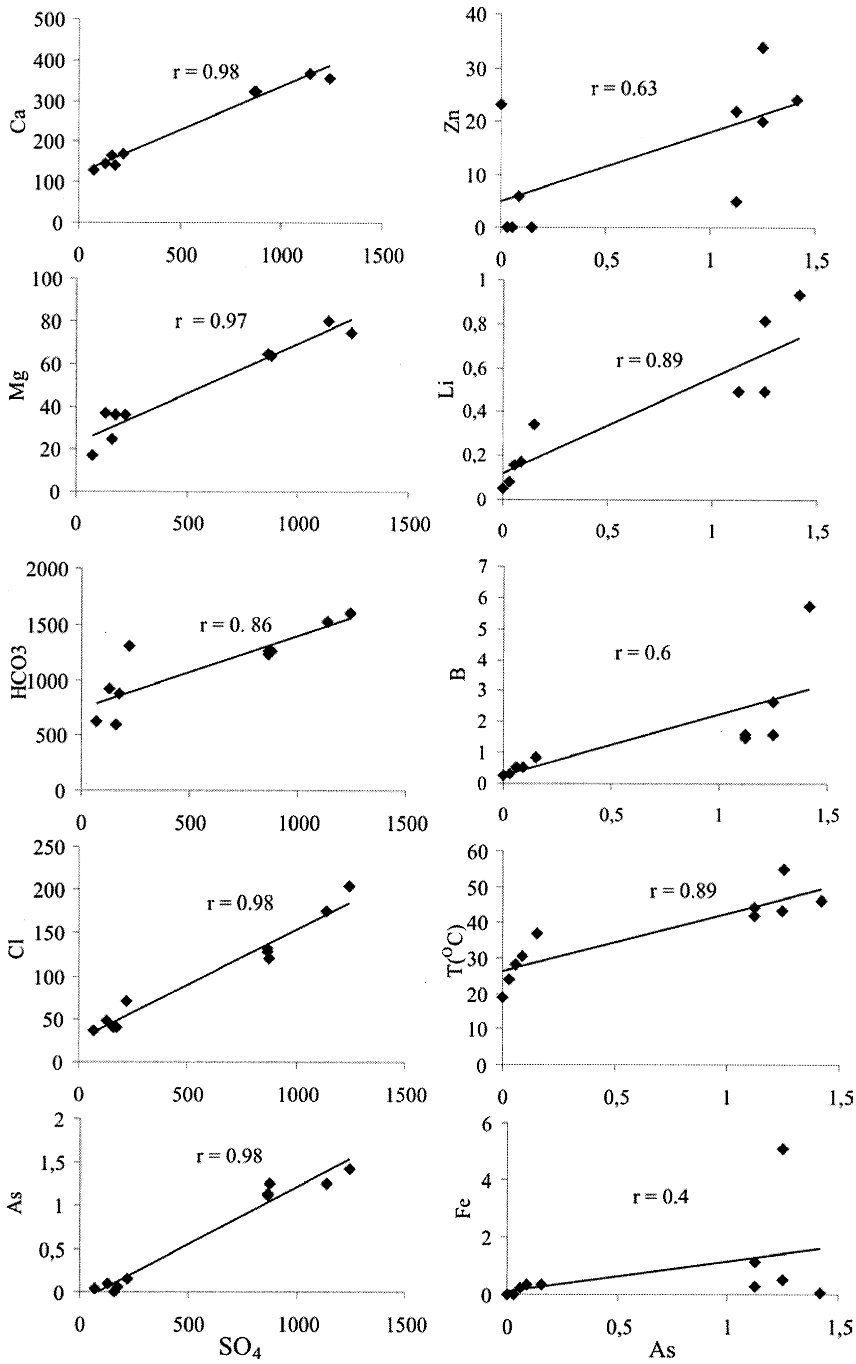

Figure 4. Relations of some ions for water samples (in mg/L).

oxides (Ballantyne and Moore, 1988). Arsenic concentrations of thermal waters from the study a rea vary between 30 and 1471µg/L. Thermal waters around the Heybeli spa (samples 1, 2, 3, 4 and 6; first group) have significantly higher As concentrations (1122-1417 µg/L). The second group waters have lower As values of 30-152 µg/L (Table 1). As contents of the thermal waters are above the drinking water standards, 50 µg/L (TS 1997) and, 10 µg/L WHO 1993). Discharges of thermal waters around Afyon more or less affect the quality of groundwaters (Doğdu and Bayarı 2002). Groundwaters around Heybeli spa are slightly effected chemical pollutants from the thermal waters. Thermal waters from the Heybeli Spa geothermal area are suitable for space heating, greenhouses, bathing, swimming and balneological purposes. However, some major (Ca, Mg, Na and SO4), and secondary ion concentrations especially As have values that are not suitable to be used as mineral water. Although the thermal waters from the Heybeli spa have benefits of curing various ailments, their usage as mineral water and drinking to cure may cause adverse effects on human health with over use.

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