# Hydrogeochemical study of the Resadiye (Tokat) geothermal field, Turkey

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#### Abstract

Resadiye Cermik travertine area is one of the main natural heritages located within the Kelkit valley in the Middle of the Black Sea geographical region of Turkey. It is covered by the widespread natural, white travertines, which are acquired immediately on deposition from hot spring waters. Defination of the physico-chemical characteristics of the hot waters, factors affecting the travertine deposition, sources of pollution and protection were the main objectives of this study. Thermal water emanates from a N25W-N65W oriented tension fracture which is located within the North Anatolian Fault Zone. The composition of waters in Resadiye is governed by water-rock interactions. They are bicarbonate waters but do not reflect a peripheral or steamheated origin. The silica geothermometer gives temperature ranging from 51 to 96°C. These hot waters are of meteoric origin and circulation in the systems is closely related to tectonic activity.

Keywords: hydrogeochemistry, thermal waters, Resadiye, Turkey.

# **1** Introduction

The study area is within the Tokat-Resadiye town boundaries and encompasses 2 km<sup>2</sup>. Resadiye spa is immediately west of Resadiye town (see Figure 1). The town was established within the Kelkit Valley. The North Anatolian Fault Zone (NAFZ) passes through the Kelkit Valley and has prime importance for our study. The hot waters of the Resadiye discharge from the branches of the NAFZ in this area. These waters emerge from more than 10 different places around the spa. Their temperatures are between 38-49°C and the discharge rate is 3 l/s. One well is situated northwest of Resadiye spa. The temperature of the water at the wellhead is 50°C and the discharge rate is 30 l/s. The discharge mechanism of the thermal springs and their relationship with meteoric waters are important since the groundwater circulation system in the area is not known in detail. Hydrogeochemical and isotopic investigations have been carried out not only to provide information on the origin of the Resadiye thermal springs and their position in the ground water circulation system, but also to lead to the development of new groundwater wells in the area for domestic purposes.

# 2 Geological outlook

Upper Jurassic-lower Cretaceous Zinav Limestone exposed on the western bank of the Kelkit River is the oldest unit in the area. It is composed of whitish micritic, biomicritic, sparitic and detritic limestone and has a thickness of 150-200 m (Seymen, 1975). Limestone is extremely laminated, brecciated and fractured, and open spaces are filled with calcite and silica cement. The upper part of the unit is unconformably overlain by the Nebiseyh formation (Kocak and Erzenoglu, 1987). The Nebiseyh formation is of Turonian to early Campanian age is made of clayey limestone and marl that are interlayered with tuffaceous levels. It is thickly fractured and has a thickness of 150-200 m. Nebiseyh formation sits conformably on the Kapakli Formation.



Figure 1: Geological map and conservation area of Resadiye Spa and adjacent areas.



Figure 2: Geological cross section of the Resadiye Spa area.

#### LEGAND



The Kapakli Formation is of early Maastrichtian age and consists of volcanic rocks of andesitic composition. Volcanic units widely covering the area have thickness of 200-1000 m. Alteration of volcanics have produced vast amount of bentonite occurrences. Alluvium consisting of gravel, sand and silt comprise the youngest units in the study area. Travertine deposits exposed along the Kelkit valley are associated with modern spring activity. Among them Cermik travertine, with a thickness up to 60 m, is the largest deposit in the area (Seymen, 1975).

### **3** General hydrogeology

The main aquifer supplying hot water to the Resadive thermal springs is the Zinav Limestone. This unit has abundant fractures and dissolution cavities. Dissolution cavities in karstic or fractured limestones usually account for high permeability and hence allow transmitting considerable volumes of water making it an important aquifer. The Nebiseyh and Kapakli Formations have low permabilities. These units form the overburden layer, which is needed for the occurrence of the thermal springs (Figure 2). The alluvium deposits of the Kelkit Valley may also host good aquifer. Borehole S-1, about 450 m NW of the Resadive Spa, was opened by MTA (General Directorate of Mineral Research and Exploration) for the utilization of thermal waters for bathing. The discharge of water from the permeable zone was measured as 30 l/s. The temperature of the water ranges from 48° to 50°C. Resadive thermal waters also emanate in E-W direction along NAFZ and also from N25W-N65W-trending fracture zone immediately west of the Resadive town. These water springs emerge from more than 10 different places around the Resadive spa. Their discharge rate is 3 l/s, and the temperatures range between 38° and 49°C. Travertines precipitating from thermal waters form a dome-like formation (~0.5 km<sup>2</sup>). In places, travertine deposits are translucent. Depending on the water flow, kidney stony and stalagmite type morphologies are observed. At present, most of thermal waters discharge from the lower levels of the travertine dome. Gas also emanates from near the top of the deposit. Travertine deposition blocks fluid paths causing the springs to migrate over time. The deposition rate of travertine is greatest at the rim of the terraces, where out gassing of CO<sub>2</sub> is enhanced by turbulent flow. However, the deposition rate is also significantly high where the water flow has high velocity and the flow thickness is small. Spring locations are also sensitive to seismic activity (Seymen, 1975).

### 4 Results of hydrochemical and isotopic analysis

### 4.1 Water samples and analytical methods

Water samples for both chemical and isotopic analyses were collected from the springs and well in February 2000 and again in June 2000. Samples were collected twice in order to assess the possible influence of precipitation on the spring water types and flow paths. All the analyses were done in the State Hydraulic Works (DSI) Laboratory of Turkey, Ankara (Table 1). Although chemical analyses of the spring waters have been published (Kocak and Erzenoglu, 1987), no previous isotopic analyses of the groundwater of the investigation area are available.

### 4.2 Hydrochemical evaluation

The total dissolved solids of the Resadiye water range from 3563 to 5990 mg/l. The waters are colourless and odourless but contain  $CO_2$  gas. At the point of discharge, a deposit of iron oxide is visible. The dominant ions are Na and HCO<sub>3</sub>. The source of

Na may be from alteration of Na-plagioclase in the volcanic rock in the area. Clay minerals also enhance exchange of Na with Ca.  $HCO_3$  results from interaction of  $CO_2$ -rich water with limestone.

Location	Kelkit	Resadiye cold water		S-1 well		Resadiye thermal spring	
name	stream						
Date	10.2.2000	10.2.2000	22.6.2000	10.2.2000	22.6.2000	10.2.2000	22.6.2000
T(°C)	4.56	14.9	-	48.2	49	47.3	46.5
PH(25°C)	7.4	6.9	6.7	6.6	6.6	6.4	6.4
Ca	51	208	180	260	314	260	330
Mg	15.8	52.8	89.8	63.7	176	72.8	156.6
Na	26.4	68.3	64.2	819	510	799	500
Κ	1.5	6.9	8.6	34	40	33	40
Cl	15.6	49.7	37.3	830.7	805.8	830.7	791.6
$SO_4$	19.8	292	275	140	111	103	96
HCO <sub>3</sub>	88.4	640.5	774.7	1739	1739	1769	1699
$SiO_2$	-	-	-	45	45	45	40
Li	-	-	-	1.00	1.1	1.2	1.4
В	-	-	-	-	-	28	30
EC	558	1660	1710	5328	5329	5154	5146
(µmho/cm)							
<sup>18</sup> O %o	-10.7	-11.42	-11.48	-12	-13.03	-12.6	-12.33
D %0	-68.49	-70.33	-82.12	-79.41	-93.46	-79.7	-94.28
T(TU)	$15.25 \pm 1.10$	$7.45 \pm 1.05$	$7.00 \pm 1.30$	$4.80 \pm 1.05$	$0.15 \pm 1.20$	$3.15 \pm 1.05$	$0.00 \pm 1.20$

Table 1: Chemical composition of waters from the study area (in mg/l).

Table 2: Geothermometry results of thermal water samples from the study area.

Geothermometer	S-1 well	Resadiye thermal water	Reference	
T (°C)	50	46	Measured	
$SiO_2$ (quartz, no steam loss)	94	82	Fournier et al, 1973	
$SiO_2$ (quartz, no steam loss)	82	70	Arnorsson et al, 1983	
SiO <sub>2</sub> (chalcedony, no steam loss)	64	51	Fournier et al, 1973	
$SiO_2$ (chalcedony, no steam loss)	65	54	Arnorsson et al, 1983	

No	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	Quartz	Chalcedony	Halite
Kelkit stream	-0.60	-0.76	-1.70	-2.32	-2.58			-7.90
Resadiye cold	0.31	0.16	0.24	-0.93	-1.18			-7.07
water								
S-1 well	1.15	1.02	2.34	-1.30	-1.36	0.50	0.14	-4.89
Resadiye	1.16	1.03	2.36	-1.33	-1.43	0.43	0.06	-4.87
thermal water								

The source of Cl may be rainwater or evaporitic deposits. The results show that the Resadiye spa water and the water from well S-1 are similar in origin. These waters are Na-Ca-HCO<sub>3</sub>-Cl-As-B-CO<sub>2</sub> bearing (IAH, 1979). From Cl- SO<sub>4</sub>- HCO<sub>3</sub> triangular diagram (Figure 3) Resadiye thermal and mineralised waters and well S-1 are bicarbonate-rich waters. They are near neutral pH, low in chloride and the major cation is sodium. The reservoir rocks in the Resadiye are composed of limestone. The water emerging from such a reservoir is naturally rich with calcium and bicarbonate ions as in the studied water. Also these waters contain a slightly high concentrations of sulphate, the source of which maybe the oxidation of H<sub>2</sub>S gas escaping from magma, and/or dissolution of minerals like gypsum and celestite (SrSO<sub>4</sub>). It is concluded that the relative abundance of SO<sub>4</sub> and HCO<sub>3</sub> in the Resadiye Turkish

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geothermal water in relation to Cl, is a reflection of the sedimentary rocks in these areas but not that their abundance reflects a peripheral or steam heated origin. Based on Figure 4 all the data points plot in the area of immature waters, therefore solute geothermometry is not likely to yield meaningful equilibration temperatures. The only option is to use silica geothermometers (Table 2). Clearly, the estimated subsurface temperatures range from 51 to 94°C for the study area. The thermal waters derive from conductive heating and geothermal gradient. The recharge probably derives from higher elevation to the north and south of the Resadiye. These waters seep into the subsurface system along fault and fracture zones, get heated and discharge at the surface.





Figure 4: Plot of Na -K-Mg

Mineral saturation indices for a number of hydrothermal minerals potentially present in the reservoir were calculated at measured surface temperatures by the PHREEQC computer code (Parkhurst and Appello, 1999). Results are presented in Table 3. Thermal waters from the well and springs of the area are undersaturated with respect to gypsum, anhydrite, and halite. They are oversaturated or nearly in equilibrium with respect to calcite, aragonite, dolomite, quartz, and chalcedony indicating that these minerals will have a thermodynamic tendency to precipitate at the point of sampling. Scaling of carbonate minerals is expected for all the thermal waters. These results coincide with the field observations. Water from the well causes scaling during extraction. Some inhibitors are used to prevent scaling in the well.

#### 4.3 Isotopic evaluation

In the <sup>18</sup>O-D diagram all the waters fall close to meteoric water line ( $\delta D = 8\delta^{18}O + 10$ ) of Craig (1961), indicating that the springs and well waters are mainly fed by meteoric water Resadiye thermal waters lie over the (+) positive side of the meteoric water line, which belongs to the Eastern Mediterranean basins ( $\delta D = 8\delta^{18}O + 22$ ) of Gat and Carmi (1970). Also thermal spring and well have a lighter isotopic composition than cold spring and stream. This would be an indicator of the effect of continental rains (Figure 4). As the North Anatolian Fault Zone (NAFZ) passes through the Kelkit valley, the surface water reaches Kelkit stream leaves the stream through fault, fracture and by streambed infiltration, without a significant amount of evaporation. Enrichment in <sup>18</sup>O values would be expected had the stream water been exposed to the atmosphere for a long period. They are affected, to a great extent, by meteoric waters.

Three different groundwater circulation systems have been distinguished by the following factors; depth of ground water circulation system, trelative residence time between the samples, effect of altitude, and recharge area. The first circulation system is characterized by only shallow circulation. The stream belongs to this group. The intermediate group is characterized by continental recharge, relatively higher recharge elevation, and longer residence time. The Resadiye cold-water spring is in this group. The third group is characterized by the deepest and longest circulation system and higher recharge elevations. The Resadiye thermal water spring and S-1 drilling well are typical examples for this group (Figure 5). Based on the results of isotopic data, Resadive thermal waters are of meteoric origin. The circulation velocity of these waters, which have hardly any tritium in the ground, is very low (Table 1) and their minimum age is 50 years. Their reservoir temperatures are not very high. Using all of this set of data along with elevation- $\delta^{18}$ O data, the surface waters that infiltrate the aquifer system probably reach the well and springs in a long time. In addition, Resadive thermal water spring has a higher elevation of recharge area than the S-1 well and the recharge elevation of the Resadive thermal spring is over than 958 m, whereas the S-1 drilling well recharged at an elevation of 925 m or more.



**Resadiye waters.** 



### 5 Protection sites of thermal and mineral waters

In order to protect thermal springs from pollution and preserve their discharge rate and chemical composition, three boundaries for a protected area are suggested. For the Resadive spa, the protected area is based on geological and hydrogeochemical data of the springs (Ministerialblatt, 1968), (Figure 1).

Boundary 1: This boundary represents the 1<sup>st</sup> degree protection site. It was determined on the basis of travertine outcrops and the fault direction from which thermal and mineral waters issue. The extremely porous and permeable character of travertine is found to be a negative factor for determining of protection site. In this respect, 1<sup>st</sup> degree protection site was drawn at 10-60 m distance from fault and fractures.

Boundary 2: This boundary, also including the 1<sup>st</sup> degree protection site, comprises an area 50-150 m distant from the spring site. The boundary of this site was drawn on the basis of the estimated 50-day's groundwater travel time. This boundary intersects with

alluvium in the west and Resadiye-Aybasti to the east. Its northwest and southeast boundaries are drawn to include the fracture zone.

Boundary 3: This boundary, also including the  $2^{nd}$  degree protection site, extends to a distance of 100 and 150 m from northern and western parts of the  $2^{nd}$  protection site.  $3^{rd}$  degree protection site intersects with the  $2^{nd}$  degree protection site in the east while it extends to Kelkit stream in the south.

#### 5.1 Restrictions with protection sites

Protection measurements necessary for the outer belt should also be applied to the inner belts.

1<sup>st</sup> degree protection Site: entry to the zone should be restricted to authorized persons. It must be protected from any type of pollutant and other harmful materials. Except for structures for storage and capture of the thermal and mineral waters, no other facility and structure should be allowed. Whatever the reason is, no explosion can be made. No stone and material can be extracted. The area should be grassed. No fertilizer and pesticide should be used. Soil should not be cultivated. If the area is utilised for therapy, all necessary measures must be taken against pollution.

2<sup>nd</sup> degree protection Site: This area should be protected from any kind of harmful human impacts. For example, an existing building and its supplementary structures in the eastern part of the field should be removed. Trash and other waste material should be demolished. No stone and material should be extracted. Camping activity, vehicle washing, establishment of cattle markets and the opening of galleries and excavation should be prohibited.

**3<sup>rd</sup> degree protection Site**: In this site, all necessary measures must be taken against radioactive and chemical pollutants. Storage of petroleum, gas, textile and detergent products as well as production of battery, paint and explosive materials should be prohibited. New graveyard should be prohibited. If a proper sewage system is built, new settlement areas may be established. Drilling of water wells, any kind of underground works and explosions should not be allowed.

### 6 Increasing the discharge rate of the water

Resadiye Spa greatly contributes to the local economy of Resadiye. Thus to support the supply of increasing tourism, more thermal water must be secured, and this depends on the drilling of two new boreholes. Based on the field study two new wells (W-1, W-2) are suggested (Figure 1). Resadiye Municipality has initiated a geothermal heating project in 1992 (Orme Jeo, 1992). This project includes supply of water to 1000 new homes. Together with the S-1 borehole, these two boreholes should be sufficient. Used hot water must be re-injected to the subsurface via proposed new injection wells.

### 7 Results

The hydrogeological and isotopic evaluations have revealed three different ground water circulation systems in the area. A shallow zone characterized the first circulation system. The intermediate group is characterized by continental recharge, relatively higher recharge elevation, and longer residence time. The Resadiye cold-water spring is in this group. The third group is characterized by the deepest and longest circulation system with the longest residence time and higher recharge elevations. The Resadiye thermal water springs and S-1 well are typical examples for this. The springs are located on a major fault zone caused by intensive stress tectonic

movements in the Upper Jurassic- Lower Cretaceous and the Quaternary units. The thermal waters derive from conductive heating and geothermal gradient. The recharge probably derives from higher elevation to the north and south of the Resadiye. These waters get into the subsurface system along fault and fracture zones, get heated and discharge at surface. The most common ions in Resadiye thermal and mineralised water are sodium and bicarbonate. Based on the silica geothermometers, the estimated subsurface temperature range from 51 to 94°C. Thermal waters of well and springs are typically oversaturated with respect to calcite, aragonite, dolomite, and quarts minerals. Scaling of carbonate minerals is expected for thermal waters. To conserve the thermal waters, three protection areas are proposed. Two well sites are proposed for drilling to increase the water production in Resadiye.

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