

## Effects of the Contaminants from Turgutlu-Urganlı Thermomineral Waters on Cold Ground and Surface Waters

G. Tarcan, Ü. Gemici

Dokuz Eylül University, Geological Engineering Department, 35100 Bornova, İzmir, Turkey

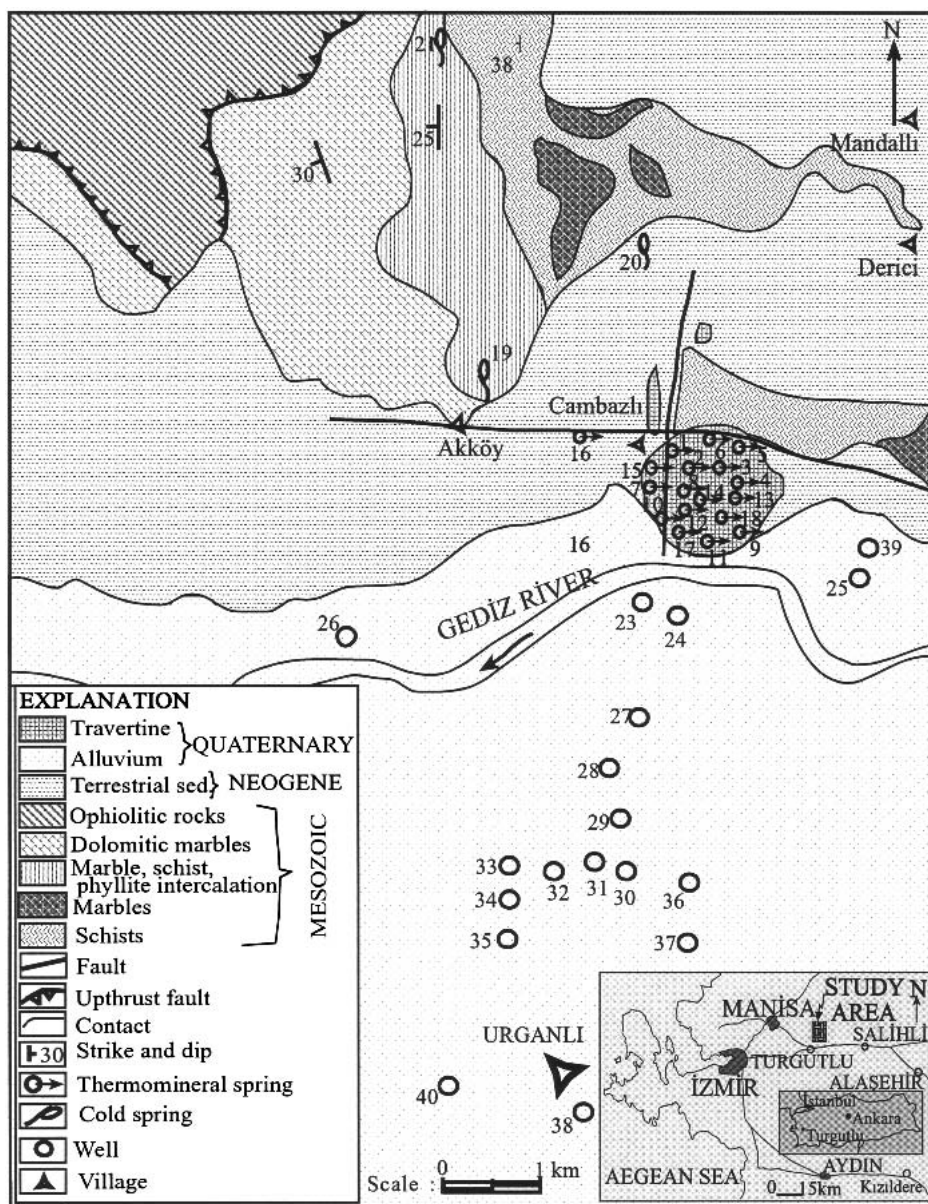
Received: 10 September 2004/Accepted: 7 January 2005

Turkey has many thermomineral springs whose numbers attained about one thousand and two hundreds, related to the favorable geological conditions resulted from young tectonic and volcanic activities. Most of the thermomineral waters in Turkey are situated in Western Turkey; Turgutlu-Urganlı spa is one of them. Thermomineral springs in the spa area are well distributed and emerge as natural springs with outlet temperatures between 20°C and 77°C, and 50–100 L/s total discharges. Local people use these springs for greenhouse heating, bathing, washing and balneological purposes, and occasionally drink as mineral waters and to cure, and sometimes irrigate gardens, and several springs supply thermal water to the spa facilities. The thermomineral waters of the Turgutlu-Urganlı spa are mostly appropriate for bathing, swimming and greenhouse heating and balneological purposes. But, they are not appropriate to be used for any drinking and irrigating purposes due to the contaminant chemicals such as boron, strontium, lithium, iron and lead. In addition, these springs discharge permanently unchecked into agricultural areas and to the Gediz River. They can cause some environmental problems for cold ground waters and surface waters as its waters flow uselessly. Because its salinity and boron content are high and harmful for the vineyards and orchards in the area. This paper discusses the hydrogeochemical characteristics and water quality of the thermomineral aquifers as well as cold aquifers, in the Turgutlu-Urganlı area.

### MATERIALS AND METHODS

The study area is located in the Gediz Graben that is one of the important Western Turkey grabens, occupying approximately 160 km<sup>2</sup> (Fig. 1). 40 water points were selected as reference points and 18 thermomineral springs (samples from 1 to 18), 3 cold springs (samples from 19 to 21), a river (sample 22), 18 cold wells (samples from 23 to 40) were sampled for chemical analysis in July 1992 (Table 1). Samples were stored in polyethylene bottles. Outlet temperature, pH, and electrical conductivity (EC) were measured in situ. The remaining chemical constituents (Na, K, Ca, Mg, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, SiO<sub>2</sub>, B, Fe, Sr, Li, Mn, Ni, Pb) were analyzed in the Dokuz Eylül University Laboratory, with standard techniques (APHA 1989). Cl and HCO<sub>3</sub> were determined by titration with silver nitrate and hydrochloric acid, respectively. SO<sub>4</sub> was determined by visible spectrophotometry. Atomic absorption

Correspondence to: G. Tarcan



**Figure 1.** Hydrogeological map of the Turgutlu-Urganlı spa area (after Tarcan 1995; Tarcan and Filiz 1997).

spectrophotometry and/or atomic emission spectrophotometry determined Na, K, Ca, Mg, Li, Mn, Ni, Pb and SiO<sub>2</sub>. Finally, boron was determined by colorimetric spectrophotometry using the Carmine Method. Aquachem (Calmbach 1997) computer program was used to assess hydrogeochemical properties.

**Table 1.** Chemical characteristics of the water samples (concentrations are in mg/L unless otherwise specified).

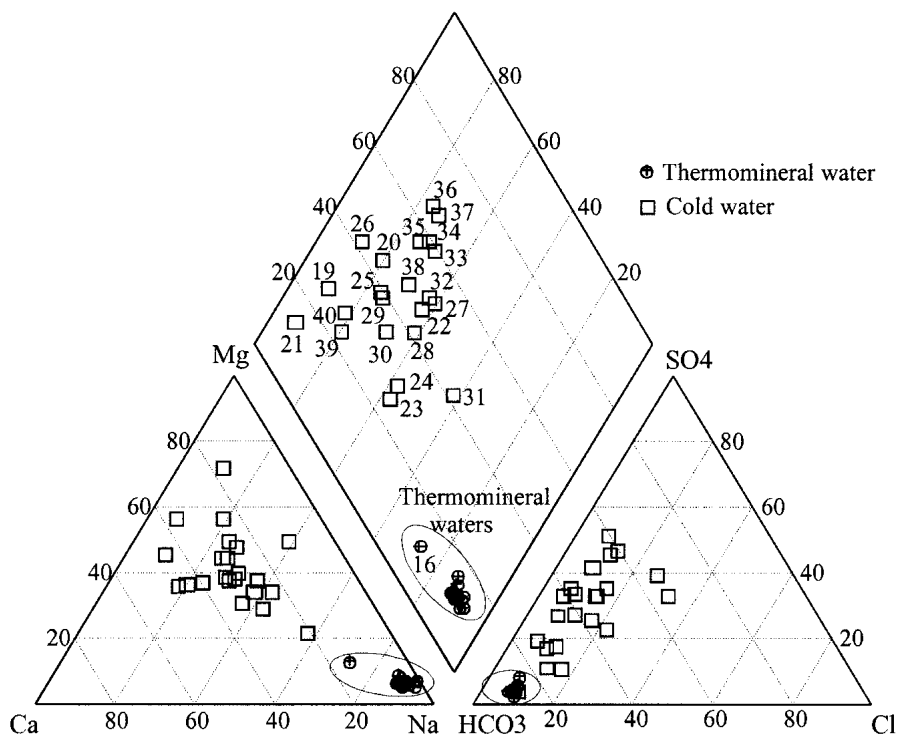
No	t (°C)	pH	EC μS/cm	Na	K	Ca	Mg	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	SiO <sub>2</sub>	B	Fe	Sr	Li μg/L	Mn μg/L	Ni μg/L	Pb μg/L
1	76	7.36	2160	525	50	16	19	73	1356	70	72.7	12.0	0.28	3.76	1433	2	174	71
2	70	7.37	2135	528	50	16	19	73	1359	58	70.6	9.0	0.28	3.02	1424	2	158	73
3	76	6.92	2206	515	49	20	21	74	1422	60	70.6	8.0	0.23	2.66	1424		147	73
4	75	6.67	2500	527	49	24	29	75	1516	122	68.5	13.0	0.34	2.74	1433	4	174	68
5	73	6.75	2232	533	50	23	23	74	1507	61	68.5	10.0	0.13	3.04	1496	9	152	73
6	32	7.00	2190	530	50	27	24	74	1517	66	59.9	9.0	0.25	2.52	1433	12	179	79
7	77	6.72	2306	514	49	19	22	73	1424	59	70.6	10.0	0.20	2.80	1415	2	163	68
8	64	6.61	2200	529	50	32	22	73	1514	54	68.5	11.0	0.19	2.63	1424	15		65
9	40	6.69	2224	551	52	26	25	78	1533	54	66.3	12.0	0.29	2.63	1460	2	158	82
10	55	6.73	2211	554	52	22	21	85	1523	53	68.5	9.0	0.25	2.85	1460		130	84
11	47	6.67	2192	530	30	28	18	74	1484	59	68.5	9.0	0.34	2.91	1500	34	190	84
12	49	6.58	2250	523	50	30	21	73	1480	51	68.5	8.0	0.14	2.58	1500	18	147	82
13	60	6.95	1991	519	49	28	19	79	1550	64	68.5	6.0	0.15	2.85	1451	2	120	83
14	56	6.70	2065	535	51	27	20	74	1512	50	62.0	7.0	0.13	2.63	1500	5	179	
15	26	7.65	2200	616	73	4	27	92	1615	38	74.9	0.0						84
16	31	6.76	2363	436	46	77	42	73	1725	62	47.1	10.0	0.32	2.62	1484	37	147	84
17	20	7.09	2066	502	52	21	25	75	1368	77	66.3	10.0	0.18	3.95	1342	2	152	79
18	21	7.45	2417	650	63	14	20	93	1684	54	74.9	10.0		3.92	1794		152	84
19		7.04	701	12	2	48	30	19	251	46	17.1	0.6	0.19	0.76	85		38	43
20		7.23	1667	78	52	88	124	162	701	228	20.5	0.3	0.06	1.50		140	71	73
21		7.65	575	10	1	46	44	21	339	13	12.8	0.0						
22		7.71	800	60	9	36	33	37	246	123	18.2	1.2	0.06	1.20	78		43	41
23		6.70	800	76	4	45	28	17	350	72		0.0						
24		6.93	640	70	7	34	30	32	325	64	40.6	0.0						
25		7.27	919	51	3	56	49	35	325	116	27.8	1.8	0.05	1.08	78		49	46
26		7.37	944	27	1	35	92	61	362	127	29.9	1.1	0.06	0.98	14		14	46
27		6.90	800	65	4	17	44	42	231	133	36.4	0.0						
28		6.85	1000	105	7	68	51	35	412	188	32.1	0.7	0.06	0.93	20		38	43
29		6.75	950	53	5	79	45	22	389	169	17.1	0.0						
30		7.30	1095	83	5	73	55	34	510	168	40.6	0.0						
31		7.50	1100	225	6	71	45	38	574	277	34.2	0.0						
32		7.40	1250	100	6	78	45	39	374	249	34.2	0.0						
33		7.50	1130	100	9	83	69	39	350	352	36.4	0.0						
34		7.20	1090	75	5	76	55	51	283	258	36.4	0.0						
35		7.20	1040	63	5	64	58	44	288	241	34.2	0.0						
36		7.15	1110	48	4	47	54	89	201	184	40.6	0.0						
37		7.10	1200	64	5	55	62	129	239	182	42.8	0.0						
38		7.32	500	32	4	31	22	28	178	88	17.1	0.0						
39		7.65	990	49	2	95	48	44	464	54	19.3	0.0						
40		7.75	789	32	1	72	34	45	344	42	25.7	0.0						
a												0.30				50		15
b	25	6.8< 9.2>	2000	175	12	200	50	600		250		2.0	0.20			50	50	50
c		6.5< 8.5>				200	150	250		250						100	20	10

Sample numbers are the same, as the locality numbers shown in Fig. 1. EC: electrical conductivity, pH: -log H in standard unit, t (°C): measured outlet temperature of the thermomineral waters (temperatures of cold samples were accepted as 18°C), a: USEPA (1994), b: TS-266 (1997), c: WHO (1996). Blanks show no data, the values of zero (0.0) refer to under the detection limits.

## RESULTS AND DISCUSSION

The Menderes Massif rocks, consisting of from bottom to top of schists, marbles, marble-schist-phyllite intercalation and dolomitic marbles, form the basement of the study area. Ophiolitic rocks, which outcrop in the İzmir-Ankara zone, overlie the dolomitic marble of the Menderes Massif rocks with a low angle upthrust fault. These ophiolitic rocks consist of serpentinised ultrabasics, cherts, sandstone-shale interbedded, limestone, and their complex. The Neogene sediments, which consist of conglomerates, sandstones, claystones, marls and lacustrine limestones, cover all the above units, discordantly. Quaternary alluvium and travertines are the youngest deposits in the study area (Fig. 1). All thermomineral springs discharge from travertines, but their feeding aquifers are inside the Menderes Massif rocks (marbles, and marble-schist-phyllite intercalation). Permeability within the Menderes Massif rocks is highly variable and is related to rock and fracture types. Mesozoic carbonates (marbles and dolomitic marbles) of the Menderes Massif rocks are highly fractured and karstified, and act as a karstic aquifer for both cold waters and thermomineral waters depending upon location. Schists and phyllites are relatively impermeable basement rocks. Where poorly permeable and impermeable rocks, such as schist and phyllite units, underlie the karstic and fractured aquifers at depth, natural springs are confined to fault and fracture zones and discharge thermomineral waters. Clayey levels of the Neogene sediments occur as impermeable barrier rocks. Sandy and gravelly and limestone levels of this Neogene unit contain minor aquifers. It is possible to withdraw groundwater with low flow rates from 5-15 meters deep shallow wells. Alluvium is the most important and favorable unit for cold groundwater production. It is possible to lift groundwater with 5-30 L/s discharges from 20-150 meters deep wells. As with many other geothermal areas in Western Turkey, the circulation of thermomineral springs in Turgutlu-Urganlı area is closely related to major fault and fracture zones. Fractured rocks of the Menderes Massif, such as quartz schists, karstic marbles, and dolomitic marbles are the aquifer for the thermomineral springs in the area. Since the clayey levels of the Neogene sediments are relatively impermeable, they act as the system cap rock. The thermomineral waters are fed by meteoric waters, as proved by  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  isotopic data (Tarcan and Filiz 1997). Meteoric waters penetrated through the discontinuities are heated in reservoir rocks, and move up to the surface along the faults.

Results of the chemical analyses are shown in Table 1 and main components are plotted on a Piper diagram in Fig. 2. The chemistry of cold waters and thermomineral waters in the study are clearly differentiated (Fig. 2). Chemistry of all thermomineral waters is dominated by Na and  $\text{HCO}_3$  ions (>80 %). They show high bicarbonate content between 1356 to 1725 mg/L and sodium content between 436 to 650 mg/L. Cold waters are mainly dominated by Mg, Ca, and  $\text{HCO}_3$  ions, although often they have not a dominant cation or anion. Although compositions of them vary from Mg, Ca,  $\text{HCO}_3$  to Mg, Ca, Na,  $\text{HCO}_3$ ,  $\text{SO}_4$  cold waters type is called Mg, Ca, and  $\text{HCO}_3$  for brevity. The chemistries of the cold waters are designated by the solubility reactions referred to the lithology type of the recharge area.



**Figure 2.** Piper trilinear diagram of the waters from the study area (numbers are the same as in Table 1 corresponding the locality numbers shown in Fig. 1).

However, if dissolved Mg, Ca and  $\text{HCO}_3^-$  in both cold and thermomineral water would derive from the dissolution of carbonate minerals, then the proportions of Ca and/or Mg versus  $\text{HCO}_3^-$  should be linear.

The correlation coefficients ( $r$ ) between Mg and  $\text{HCO}_3^-$ , and Ca and  $\text{HCO}_3^-$  ions for waters from the study area are  $-0,55$  and  $-0,59$  that indicate very poor fit and negative correlation (Table 2). Therefore, carbonate dissolution reactions for all the waters cannot only be dominant in the area. Nevertheless, geochemical processes for cold waters in the study area can partly be explained by the dissolution of carbonate minerals. Sodium-bicarbonate type waters are present only in the thermomineral aquifer in the study area. Data from the water points indicate a trend toward sodium predominance on cation plot, and toward bicarbonate predominance on the anion plot. Na- and  $\text{HCO}_3^-$ - rich thermal waters are a common thermomineral type, classically known as “Vichy type”. Sodium might derive from the dissolution of sodium bearing silicates or evaporate minerals in the thermomineral aquifers. But, no geologic evidence exists to indicate the presence of halite ( $\text{NaCl}$ ) in the aquifer system of the study area. The dissolution of sodic plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ) is likely, and generally invoked mechanism to explain the origin of these waters in many cases. Na and  $\text{HCO}_3^-$  ions are well correlated ( $r=0.98$ ) corresponding to linear

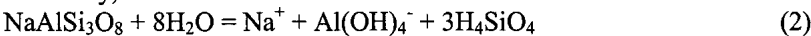
relationship in all the thermomineral water from the study area. In addition to these, SiO<sub>2</sub> and Na are significantly correlated (r=0.94). It could be a good model of dissolution of silicates by CO<sub>2</sub> rich thermal waters. Several authors suggest that aluminosilicate dissolution coupled with precipitation of secondary minerals may lead to the evolution of Na- and HCO<sub>3</sub><sup>-</sup> rich groundwater (Hanor 1980; Deutsch et al. 1982).

**Table 2.** Correlation coefficients ( r ) of chemical constituents for linear regression in waters from the Turgutlu-Urganlı field.

	pH	Li	Na	K	Mg	Ca	Sr	Mn	Fe	Ni	SiO <sub>2</sub>	B	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
	(40)	(22)	(40)	(40)	(40)	(40)	(23)	(15)	(22)	(21)	(40)	(23)	(40)	(40)	(40)
pH	1.00	-0.45	-0.42	-0.35	0.31	0.29	-0.19	0.22	-0.40	-0.55	-0.47	0.91	-0.45	0.23	-0.44
Li		1.00	0.99	0.97	-0.72	-0.57	0.90	0.52	0.68	0.95	0.94	-0.45	0.91	-0.70	0.99
Na			1.00	0.93	-0.63	-0.68	0.91	-0.96	0.69	0.94	0.94	0.92	0.51	-0.49	0.98
K				1.00	-0.42	-0.60	0.85	-0.06	0.51	0.83	0.85	0.78	0.66	-0.45	0.94
Mg					1.00	0.65	-0.59	0.95	-0.53	-0.62	-0.60	0.65	0.19	0.66	-0.55
Ca						1.00	-0.65	0.86	-0.39	-0.55	-0.58	-0.65	-0.15	0.63	-0.59
Sr							1.00	-0.70	0.63	0.86	0.90	-0.62	0.40	-0.56	0.87
Mn								1.00	-0.38	-0.73	-0.93	0.87	0.93	0.85	-0.78
Fe									1.00	0.73	0.63	-0.77	0.12	-0.55	0.69
Ni										1.00	0.88	0.30	0.37	-0.55	0.93
SiO <sub>2</sub>											1.00	0.90	0.51	-0.41	0.89
B												1.00	0.25	-0.62	0.90
Cl													1.00	0.06	0.52
SO <sub>4</sub>														1.00	-0.53
HCO <sub>3</sub>															1.00

Total 40 data. Numbers in brackets suggest to the data points for regression, concentrations are in mg/L except pH, which is standard unit. The value 1.00 refers to best fit in linear regression and negative (-) values indicate inverse relationship between chemical species.

The suitable reaction for the dissolution of Na-silicates can be expressed by in a simplified way,



However, if silicate weathering had only been dominant reaction in the aquifer, there could have been indications of silicate deposition in the hot spring area. But, there are no silicate deposits and cementation near the thermomineral springs and their modern travertine deposition. Additionally, major oxide analyses (Tarcan 1995) show the evidently paucity of the percentage for the Na<sub>2</sub>O, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the modern travertine deposits of the study area. Therefore, not only silicate dissolution, but also additional effects could explain the origin and the evolution of the thermomineral waters in the study area. Another sodium supplier for the thermomineral waters might be cation exchange process between Ca and Na ions. Exchange would follow the generalized reaction;



where, M<sup>2+</sup> is Ca<sup>2+</sup> or Mg<sup>2+</sup> or other alkaline earth metals. Exchange sites may be both inside the Menderes Massif clays and/or the Neogene sediment clays at the

subsurface circulation paths of the thermomineral waters. The concept that Ca-Na exchange processes can play an important role in producing soft and high alkalinity water is not new. Several authors (Foster 1950; Krothe and Parizek 1979; Thorstenson et al. 1979; Chapelle and Knobel 1983; Siegel 1989) have described Ca-Na exchange processes in many aquifer systems elsewhere. Lee (1993), and Toran and Saunders (1999) suggested that both silicate dissolution and cation exchange mechanisms should be considered to understand the evolution of Na- and HCO<sub>3</sub><sup>-</sup> rich groundwater. They stated that a combination of cation exchange and silicate hydrolysis, in addition to carbonate dissolution and precipitation, occurred. As a result the combined effects of cation exchange and calcite, dolomite and silicates dissolution can explain the occurrence of this type water.

Thermomineral waters from Turgutlu Urganlı Spa are suitable for district heating and greenhouse, swimming, bathing and balneological purposes. But the chemical analyses (Table 1) revealed that the concentrations of EC, Na, K, Fe, Ni, Pb and B in thermomineral samples exceed the drinking water limits (USEPA 1994; WHO 1996; TS-266 1997). Fe contents are between 0.13 and 0.34 mg/L and slightly exceed the drinking standards. Especially, Ni (0.120-0.179 mg/L) and Pb (0.043-0.084 mg/L) concentrations are quite high. Boron concentrations (6-13 mg/L) also exceed remarkable drinking water standards. Therefore their usage as mineral water and drinking to cure may cause unhealthy effects on human with over use. Presently, the all constituents of all the cold waters (except for sample 20) are below the standard limits, and are appropriate for drinking and irrigation. However, discharges of thermomineral waters flow unchecked into the Gediz River and garden beds. For this reason the quality of surface waters and ground waters of cold aquifers in the study area can be effected chemical contaminants from the thermomineral waters. As a matter of fact the boron contents in some cold samples (samples 19, 20, 22, 25, 26 and 28) showed the evident of this effect.

Local people use cold waters in the study area for drinking and irrigation purposes. One of the major environmental problems for cold waters in the study area is boron contamination of aquifers and soils. Because of the insufficient water supply from dams, since 1980, in the study area and nearby areas, ground water has been used in viniculture irrigation. Water taken from wells used for irrigation is known to create problems in the viniculture, which in brief is identified as the "boron problems". Boron is necessary in very small quantities for normal growth of plants, but in larger concentrations it becomes toxic. As a general classification, boron concentrations of groundwater exceeding 1 mg/L are harmful for plants (Richards 1954). As discussed before boron contents in thermomineral waters in the Turgutlu-Urganlı spa are quite high. Boron concentrations of waters from Gediz River (sample 22) and some wells (samples 25 and 26) that are between 1.1 and 1.8 mg/L exceed irrigation water standards, 1 mg/L (USEPA 1994). Because boron contaminants in thermomineral waters issuing from the Turgutlu-Urganlı spa affect the surface waters and cold aquifers in area close to spa area. The impact of boron on surface waters, aquifers and soils in Western Turkey and the origin of the boron in thermomineral waters were already discussed by Gemici and Tarcan (2002) in detail. Briefly, the combined effects of water-rock interaction and degassing of

magma intrusions can explain the boron content of thermomineral waters. To prevent boron contamination of cold waters used for irrigation purposes re-injection of all the disposal thermomineral waters to the thermomineral aquifer may be necessary.

## REFERENCES

- APHA (1989) Standard Methods for the Examination of Water and Wastewater, 19th edition. American Public Health Association, Washington DC
- Calmbach L (1997) AquaChem Computer Code-Version 3.7.42, Waterloo hydrogeologic. Waterloo, Ontario, Canada, N2L 3L3
- Chapelle FH, Knobel LL (1983). Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia aquifer. Maryland Ground Wat 21:343-352
- Deutsch WJ, Jenne EA, Krupka KM (1982) Solubility equilibria in basalt aquifers: the Columbia Plateau, Eastern Washington, USA. Chemical Geology 36, 15-34
- Foster MD (1950) The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains. Geochim Cosmochim Acta 1:33-48
- Gemici Ü, Tarcan G (2002) Distribution of boron in thermal waters of Western Anatolia, Turkey, and examples on their environmental impacts. Environ Geol 43:87-98
- Hanor JS (1980) The origin of high sodium bicarbonate waters in the Gulf Coastal Plain: a reassessment of role of carbonate dissolution and ion exchange. Geol Soc Am Abstracts with Programs 14:354
- Krothe NC, Parizek RR (1979) An anomalous occurrence of sodium bicarbonate water in a flood plain in a carbonate terrain. Ground Wat 17:595-605
- Richards LA (1954) Diagnosis and improvement of saline and alkali soils. Agriculture handbook no 60. US Dept Agriculture, Washington DC
- Siegel DI (1989) Geochemistry of the Cambrian-Ordovician aquifer system in the Northern Midwest, United States. US Geol Survey. Profes paper 1405-D
- Tarcan G (1995) Hydrogeological study of the Turgutlu Hot Springs. Ph.D. Thesis, Dokuz Eylül University, İzmir, Turkey
- Tarcan G, Filiz Ş (1997) Hydrogeology of the Turgutlu geothermal field. Turkish J Earth Sci 6:43-64
- Thorstenson DK, Fisher DW, Croft MG (1979) The geochemistry of the Fox Hills-Basal Hell Creek aquifer in Southwestern North Dakota and Northwestern South Dakota. Water Res 15:1479-1498
- Toran EL, Saunders JA (1999) Modeling alternative path of chemical evolution of Na-HCO<sub>3</sub>- type groundwater near Oak Ridge, Tennessee, USA. Hydrogeology Journal 7:355-364
- USEPA (1994) Drinking Water Regulations and Health Advisories, 202-260-7571, Washington, DC, U.S. Environmental Protection Agency
- TS-266 (1997) (Turkish drinking water standards) Sular-İçme ve kullanma suları. Türk Standartları Enstitüsü, Ankara, Turkey
- WHO (1996) Health criteria and other supporting information second ed. Guidelines for drinking water quality, vol. 2, World Health Organization, Geneva, Switzerland