Distribution of boron in thermal waters of western Anatolia, Turkey, and examples of their environmental impacts

Ünsal Gemici · Gültekin Tarcan

Abstract Boron concentrations of the CO_2-rich thermal waters in western Anatolia have a wide range of 1–63 mg/l. Cl/B molal ratios of high temperature waters (>150 °C) have low values ranging from 1 to 10. In low-temperature thermal waters (<150 °C), with the exception of samples that have some seawater, Cl/B ratios range from 2 to 88. The positive correlation between HCO_3 and B values for thermal waters means that B concentrations in thermal waters are also associated with the dissolution of carbonates. In addition to the water–rock interaction, boron in thermal waters is probably controlled by the contribution of B by degassing of magma intrusives. Sericite, illite and tourmaline minerals, which are abundant in Menderes Massif rocks, are considered to be the main reason for the high boron contents. High B concentrations of thermal waters causes environmental problems in groundwaters and surface waters in some agricultural areas of western Anatolia. Re-injection of thermal waters to the reservoir is the best way to dispose of the geothermal wastewater and prevent contamination problems.

Keywords Anatolia · Boron · Contamination · Thermal waters

Introduction

There are many geothermal fields and thermal springs in western Anatolia, Turkey (Figs. 1 and 2). Fluids emerging from some of these areas contain high boron concentrations and cause environmental problems for cold waters in agricultural areas where boron contaminates aquifers and soils. Several studies were carried out in these geothermal fields and the surrounding areas (Kasap 1984; Şimşek 1984; Şamilgil 1985; Yılmazer 1988; Tarcan 1995; Karamanderesi 1997; Yıldırım and others 1997; Mutlu 1998; Çetiner 1999; Tarcan and others 2000; Aksoy 2001; Gemici and Tarcan 2001; Tarcan and Gemici 2001; Vengosh and others 2002). The earlier studies mainly dealt with site descriptions, geological, hydrogeological and geochemical properties of the geothermal fields and they particularly focused on geothermal possibilities and geothermometer applications. Borate deposits were also investigated by Helvacı (1977, 1978, 1995) to evaluate their stratigraphy, mineralogy and genesis. Borate minerals (colomanite, ulexite, borax, etc.) are the major source of commercial boron (B) and are mainly concentrated in continental Tertiary deposits of western Anatolia (Floyd and others 1998). Isotopic geochemistry of these boron deposits were studied in detail by Palmer and Helvacı (1995, 1997). The aim of the present study is to examine the state of boron in the aquifers of the geothermal systems that occur in different geological environments and to determine its environmental impact.

For the study and comparison of chemical characteristics of the waters, the samples of thermal and cold waters in the geothermal fields were collected at different times during the year 2000. Samples were collected and stored in polyethylene bottles by the authors, and outlet temperature, pH and electrical conductivity were measured in the field. The remaining major chemical constituents were analysed in the DEU laboratory using standard methods described in APHA (1989). Na, K, Ca, Mg, Li and SiO_2 were determined by atomic absorption and/or atomic emission spectrophotometers. Cl and HCO_3 were determined by titration with silver nitrate and hydrochloric acid, respectively. SO_4 was determined by visible spectrophotometer with barium ions. Finally, boron was determined by colorimetric spectrophotometer using the carmine method. Additionally, chemical analyses of thermal waters were used from previous studies. All earlier and current analyses results were used to assess the water chemistry.

Geology and field descriptions

Turkey forms part of the Alpine–Himalayan orogenic belt and is a region of great tectonic complexity. The Menderes Massif, with its north-easterly-oriented elliptical shape,

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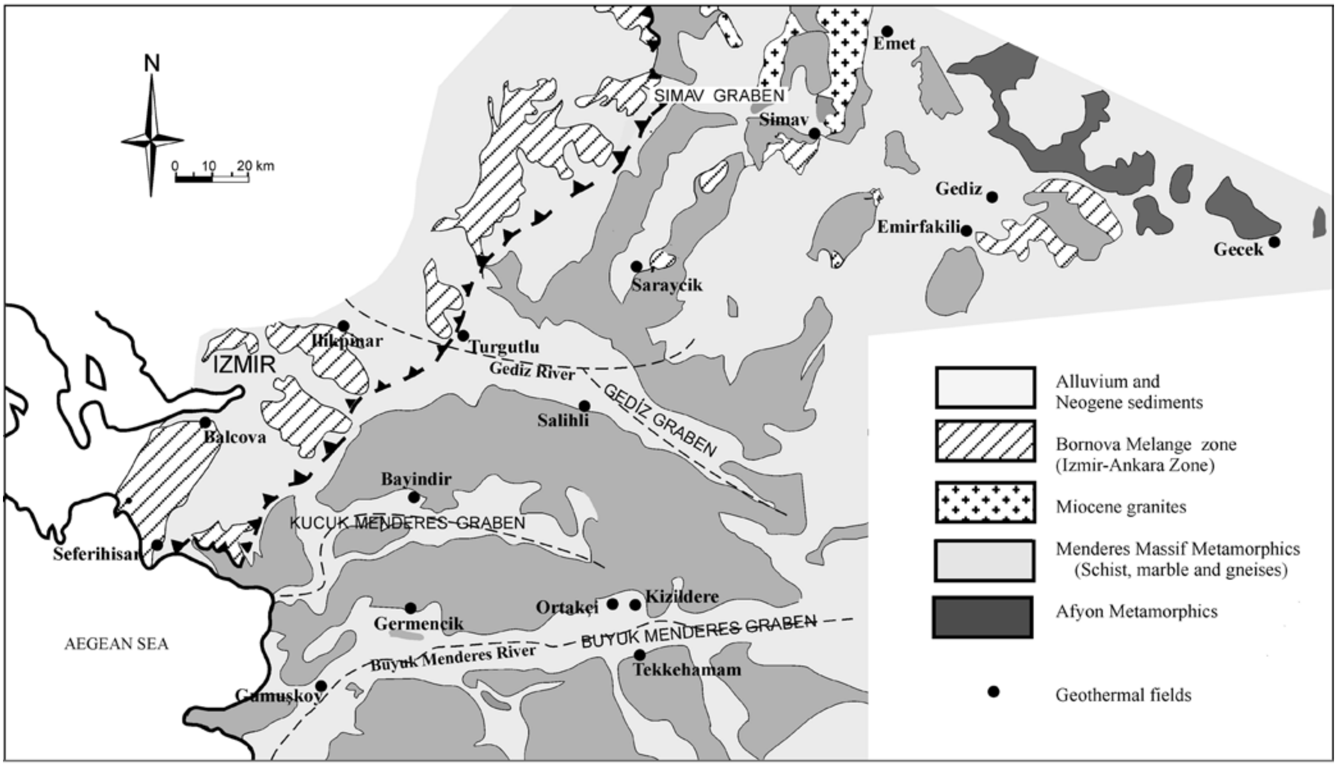

Fig. 1
Simplified geology map of western Anatolia (simplified after Okay 1984; Dora and others 1995) and locations of geothermal fields

has left a significant imprint on the geological evolution of western Turkey. From north to south, the Neogene grabens Simav, Gediz, K. Menderes, and B. Menderes divide the Menderes Massif into four sections (Dora and others 1995; Figs. 1 and 2). The basement of the study area consists of Menderes Massif rocks, and is made up of high to low grade metamorphics (gneiss, mica schists, phyllites, quartz schists, marbles) and granodiorite. In the eastern part of the study area Afyon metamorphic rocks outcrop. The non-metamorphic Mesozoic carbonates and Bornova melange that were deposited in flysch facies rest along a thrust fault on the top of the Menderes Massif (Fig. 1). The Bornova melange rocks are composed of shale and sandstone, which form the matrix with limestone mega blocks, mafic volcanic intervals and ophiolitic rocks. The age of the sandstone and shale and other components of the Bornova melange rocks vary from Upper Cretaceous to Palaeocene (Erdoğan 1990).

Most of the thermal waters originate from Menderes Massif metamorphics, which discharge from the rims of east–west-trending faults that form Büyük Menderes, Küçük Menderes, Gediz and Simav grabens (Fig. 2). The

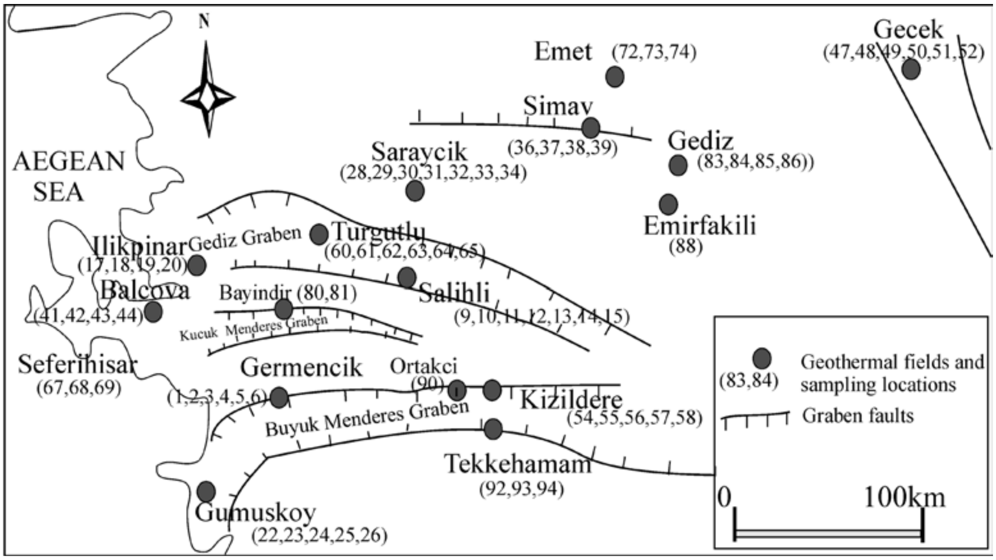

Fig. 2
General tectonic map and the locations of the sampling points

circulation of the thermal water is closely related to major faults and fractured zones. Fractured rocks of the Menderes Massif, such as quartz schists, gneiss and granodiorite, and karstic marbles, shale, sandstone and limestone mega blocks of Bornova melange and non-metamorphic Mesozoic carbonates are the reservoir rocks. Relatively impermeable Neogene sedimentary units occur in different facies in the northern and southern parts of the Gediz graben and the northern parts of Büyük Menderes graben, and these rocks cap the geothermal systems. An increasing geothermal gradient from the effects of graben tectonism may be the heat source of the geothermal systems. Thermal waters from Gümüşköy, Germencik, Kızıldere, Tekkehamam, Ortakçı, Bayındır, Salihli, Turgutlu Simav, Saraycık, Gediz, Uşak-Emirfakı and Gecek fields are hosted by Menderes Massif rocks (Figs. 1 and 2). The chemical properties of waters from these geothermal fields are presented in Table 1.

Gümüşköy thermal waters are of Na–Ca-Cl–HCO_3 type with 40 °C discharge temperature. They are used for balneological purposes. Thermal waters hosted by Menderes Massif metamorphics have around 10 mg/l boron concentrations. Germencik geothermal field is considered to have the highest potential (approximately 100 MW/e) in Turkey. Temperatures reach 232 °C in deep wells and 60 °C in springs. New power plant construction has been planned at this field. Na-Cl–HCO_3-type thermal waters from deep wells have high boron contents of 41–43 mg/l. In Kızıldere geothermal field, electricity generation by geothermal energy is available with an installation capacity of 20 MW/e. There are a series of drilled wells that reaching temperatures of 240 °C. Na-HCO_3–SO_4-type thermal waters with boron concentrations of 20–25 mg/l create environmental problems because of the high discharge rates. Tekkehamam and Ortakçı fields are located in the Büyük Menderes graben, near the area of Kızıldere field. Tekkehamam thermal springs have 83–98 °C discharge temperatures and Na-SO_4–HCO_3-type waters and with boron contents of about 17–18 mg/l. Ortakçı thermal spring discharges at a temperature of 52 °C, is of Na-HCO_3–SO_4 type and contains 8 mg/l boron. Bayındır thermal waters (45 °C), found in Küçük Menderes graben, have been used for bathing and medicinal purposes in resort spas since 1857. Na–Ca-HCO_3–SO_4-type waters contain boron concentrations lower than 1 mg/l. In Salihli geothermal field there are a series of hot springs with temperatures of 40–90 °C, which are used for balneological purposes and have deep wells with temperatures that reach 155 °C. The Na-HCO_3-type thermal waters of the Salihli geothermal field have significant boron values of 23–65 mg/l. The thermal waters of Turgutlu, which are hosted by Menderes Massif rocks, are obtained from springs with temperatures of 75–78 °C. Studies are being carried out for heating purposes by drilling deep wells. Boron concentrations are around 8–13 mg/l. Simav geothermal field has thermal springs between 51–90 °C. Na-HCO_3–SO_4-type thermal fluids from deep wells with temperatures of 163 °C are used for balneological and district heating purposes. Although the temperatures are quite high, boron concentrations are lower than those of the other high-temperature geothermal waters emerging from the Menderes Massif rocks. Boron concentrations are around of 1–2 mg/l. Gediz thermal waters, which are obtained from spa resorts, are physically divided into two groups. Gediz Murat Dağı spa waters (samples 83 and 84) with temperatures of 38–45 °C have Ca-SO_4 type waters with about 2 mg/l boron contents. Gediz Abide spa waters (samples 85 and 86) with 75–92 °C temperatures reflect Na-SO_4–HCO_3 type and have about 7.5 mg/l boron. Uşak Emirfakı spa (38 °C) contains Ca–Na-SO_4–HCO_3-type thermal waters and about 3.5 mg/l boron. The Na-Cl–HCO_3-type thermal waters of Gecek (Afyon) field, obtained from springs and deep wells at 92 °C, are used for balneological purposes. Boron concentrations reach to 10 mg/l. The Saraycık geothermal system is located in the northern part of the Menderes Massif. Saraycık geothermal field is one of the youngest areas and is controlled by Quaternary volcanism. Na-HCO_3–SO_4 type thermal waters with temperatures ranging form 40 to 74 °C and has boron concentrations of 13–35 mg/l. Emet geothermal waters with a temperature of 54 °C are of Ca–Mg-SO_4–HCO_3 water type. Although there are colemanite deposits within the Neogene terrestrial sediments around the Emet region, the thermal waters of the Emet area have lower boron concentrations of around 1.5 mg/l. Some thermal springs were generated by movements of NW–SE-trending faults during the Gediz earthquake in 1970 (Helvacı 1977). Seferihisar, Balçova and Ilıkpınar geothermal areas, which are located in the western part of the study area, are Bornova melange rocks that were deposited in flysch facies including mainly sandstone and shale intercalations. The Ca–Mg-HCO_3-type of Ilıkpınar (Manisa) thermal waters with 27 °C discharge temperatures has low boron concentrations. These waters are suitable for use as potable and irrigation water and they supply some of the water demand of Manisa vicinity. The Balçova geothermal field is one of the most important geothermal fields in Turkey with a 140 °C deep well temperature. Thermal waters are used for balneological and district heating. Na-HCO_3–Cl-type thermal waters with 8–14 mg/l B concentrations create significant problems in groundwater that is used for agricultural purposes. The Seferihisar geothermal area consists of Na-Cl type waters with high ion concentrations because of a seawater contribution. Deep well temperatures of fluids that are planned to be used for heating reach 120 °C. Boron values are 17 mg/l.

Water chemistry

The chemical composition of the thermal and cold waters are given in Table 1. The Piper diagram (Fig. 3) illustrates that cold waters are characterised dominantly as Ca–Mg–HCO_3 type, largely as a function of their host rocks. High-temperature geothermal waters (>150 °C) are mainly of Na–HCO_3 type. Figure 3 shows that thermal waters vary from Ca–Mg- to Na-rich waters. Their water types are a

Table 1
Chemical properties of natural waters in western Turkey (in mg/l). *s* Hot spring; *w* drilled well; *c* cold groundwater

Location	No.	T (°C)	pH	Na	K	Ca	Mg	Cl	HCO_3	SO_4	B	Cl/B (molal)	Li	Water type	Ref.[a]
Germencik	1s	60	6.66	1,199	125	69	25	1,212	2,426	66	41	9		Na-HCO_3–Cl	a
	2s	50	6.9	1,101	109	66	58	1,115	2,355	144	45	7.5		Na-HCO_3–Cl	a
	3w	200	8.5	2,050	85	3.2	1	1,747	2,123	66	63	8.44	7.2	Na-HCO_3	b
	4w	200	8.5	1,355	45	6.4	1	1,586	1,324	37	45	10.7	8	Na-Cl–HCO_3	c
	5w	231	8	2,810	191	4.2	2	1,948	1,531	168	63	9.42	7.4	Na-Cl–HCO_3	b
	6w	231	8.7	1,600	145	6	1.2	1,790	900	24	50	10.9	18	Na-Cl–HCO_3	c
Salihli	9w	85	6.3	462	55	130	13	69	1,378	125	65	0.32		Na–Ca-HCO_3	d
	10w	95	6.03	431	50	31	13	90	1,220	100	31	0.88		Na-HCO_3	
	11w	155	7.8	680	70	42	6	115	1,983	34	67	0.52		Na-HCO_3	
	12s	51	6.03	199	24	134	23	37	1,076	81	13	0.86	1.8	Na–Ca-HCO_3	
	13s	42	5.98	500	62	45	15	68	1,513	119	23	0.9	1.8	Na-HCO_3	
	14s	90	4.85	426	51	10	9	64	1,080	107	38	0.51	1.84	Na-HCO_3	
	15c	16	6.76	29	4	26	16	16	204	92	3	1.62	0.08	Mg–Ca–Na-HCO_3–SO_4	
Ilıkpınar	17w	24	7.5	12.2	1.1	86.4	19.7	15	305	35	0.67	6.8	0.05	Ca–Mg-HCO_3	e
	18s	27	7.4	11.3	0.8	116.4	5.8	12	370.8	44	0.67	5.45		Ca-HCO_3	
	19c	16	7.2	7	0.4	117.2	11.9	13	370.8	25	0.32	12.37	0.05	Ca-HCO_3	
	20w	27	7.2	9.7	2.6	100	19.2	14	382	33.3	0.32	13.31	0.1	Ca–Mg-HCO_3	
Gümüşköy	22w	39	6.7	867	77	161	55.7	957	1,098	103	11	26.49		Na-Cl–HCO_3	f
	23s	39	6.7	1,141	110	103	36	1,418	927	51	10	43.18		Na-Cl–HCO_3	
	24w	39	6.68	803	104	257	38	1,348	982	39	10	41.05		Na–Ca-Cl–HCO_3	
	25c	19	7.54	13.6	1.34	187	33.3	113	441	62	2.2	15.6		Ca–Mg-HCO_3–Cl	
	26s	26	7.4	45	4.6	223	41	96	732	20	2.29	12.77		Ca–Mg-HCO_3	
Saraycık	28w	74	7.3	1,159	118.9	98.4	7.3	130	2,647	585	17.9	2.21	1.67	Na-HCO_3–SO_4	g
	29w	51	6.9	987	126	97.6	27.7	130	2,713	544	35	1.13	1.76	Na-HCO_3–SO_4	
	30c	19	6.8	75	13.9	192.4	113.2	28	996	154	1.5	5.68		Ca–Mg-HCO_3	
	31w	55	7.1	1,050	118	90.4	26.2	130	2,718	602	18.6	2.13	1.74	Na-HCO_3–SO_4	
	32s	41	6.8	1,088	114	73.6	27.5	200	2,528	590	13.3	4.58		Na-HCO_3–SO_4	
	33c	18	7.6	89	18	84.8	9	28	402	55	1.4	60.9		Ca–Na-HCO_3	
	34w	40	7.5	1,287	117	90	3.1	132	2,459	534	14	2.87		Na-HCO_3	
Simav	36w	163	8.74	506.4	55.3	11.6	4.9	80	678.3	471.2	2.69	9.06	0.42	Na-HCO_3–SO_4	h
	37w	160	8.84	532.3	62.3	6.4	5.8	80	651.5	455.9	1.08	22.55	0.41	Na-HCO_3–SO_4	
	38s	78	9.2	529.5	48.4	1.6	3.9	71	588	424.3	1.31	16.5	0.35	Na-HCO_3–SO_4	
	39c	13	7.21	27.2	17.6	107.6	38.2	31	419.7	80.7	0.1	94.4	0.05	Ca–Mg-HCO_3	
Balçova	41w	114	8.6	400	28	12	7	213	494	176	13.5	4.8	1.6	Na-HCO_3–Cl	i
	42w	140	7.7	395	24	27	2.7	176	62	143	13	4.9	1.5	Na-Cl–SO_4	
	43w	122	9	440	31	8	4	223	467	169	14	4.85	1.7	Na-HCO_3–Cl	
	44w	115	8.4	420	32	10	8.5	216	488	219	13.6	4.84	1.6	Na-HCO_3–Cl–SO_4	
Gecek	47w	88	6.7	1,600	144	214.6	30	1,754	1,628	494	8.6	62	1.5	Na-Cl–HCO_3	j
	48w	92	6.7	1,750	158.7	78.8	9.96	1,862	1,294	536.6	10	56.7	1.6	Na-Cl–HCO_3	
	49w	62	6.95	1,300	101.7	205	36.5	1,261	1,397	450.2	8.2	46.8	1.9	Na-Cl–HCO_3	
	50w	87	7.1	1,700	156.8	105.8	18.9	1,842	1,350	513.6	9.6	58.4	1.6	Na-Cl–HCO_3	
	51w	51	6.4	780	64.1	135.8	32.9	812	1,025	236.6	4.4	56.2	0.9	Na-Cl–HCO_3	
	52c	14	6.95	13.1	1.4	110	16.2	29.1	281	45.1	0.1	88.6	0.1	Ca-HCO_3	

Table 1
(Contd.)

Kızıldere	54w	196	8.97	1,220	116	1.2	0.36	124	1,150.1	560	20.4	1.85	3.9	Na-HCO$_3$–SO$_4$	k
	55w	207	8.96	1,410	152	1.2	0.2	144	1,746	737	24.4	1.79	4.5	Na-HCO$_3$–SO$_4$	
	56w	202	9.3	1,275	140	1.2	0.24	729	1,148.2	735	25	8.88		Na-Cl–HCO$_3$–SO$_4$	
	57s	100	7.9	1,200	110	5.1	1.4	100	1,484.4	680	21	1.45		Na-HCO$_3$–SO$_4$	
	58c	16	7.6	11.9	1.5	65	1	7.5	183.9	23	0.3	7.6		Ca-HCO$_3$	
Turgutlu	60s	75	7.36	525	50	16	19	73	1,256	70	12	1.87	1.43	Na-HCO$_3$	l
	61s	78	6.92	515	49	20	21	72	1,422	60	8	2.7	1.42	Na-HCO$_3$	
	62s	72	6.67	527	49	24	26	75	1,516	122	13	1.7	1.44	Na-HCO$_3$	
	63s	78	6.72	514	49	19	22	73	1,424	59	10	2.2	1.42	Na-HCO$_3$	
	64c	18	7.27	51	3	56	49	35	245	216	1.8	5.9	0.08	Mg–Ca–Na-SO$_4$–HCO$_3$	
	65c	18	7.37	27	1	35	92	61	362	127	1	18.5	0.01	Mg-HCO$_3$–SO$_4$	
Seferihisar	67s	75	6.05	6,021	823	562	612	11,048	391	204	17	197.9		Na-Cl	m
	68s	70	6.71	2,507	2.1	63	851	4,049	659	347	13	94.85		Na–Mg-Cl	
	69s	72	6.63	6,797	781	751	1,829	12,647	366	597	15	256.76		Na–Mg-Cl	
Emet	72s	43	7.11	18.8	5	230.8	45.2	11	295.2	541.9	1.4	2.39		Ca–Mg-SO$_4$–HCO$_3$	n
	73s	54	7.1	12.7	3.29	176.8	32.3	11	324.5	319.7	1.48	2.26		Ca–Mg-SO$_4$–HCO$_3$	
	74s	13	7.25	13.3	4.22	298.8	49.6	13	273.3	749.8	5.2	0.76		Ca–Mg-SO$_4$–HCO$_3$	
Bayındır	80s	45	6.96	211.4	9.7	54.8	6.9	17	659	66	0.7	7.4		Na–Ca-HCO$_3$–SO$_4$	n
	81s	45	7.04	191.7	9.8	56.1	10.4	14	691	148	0.8	5.3		Na–Ca-HCO$_3$–SO$_4$	
Gediz	83s	45	7.3	45	3.2	544	50	9	100	1,386	1.2	2.3		Ca-SO$_4$	n
	84s	38	7.3	45	3	443	53	7	124.4	1,226	1.2	1.8		Ca-SO$_4$	
	85s	75	7.3	624	94	139	57	103	969	1,269	7.6	4.1		Na-SO$_4$–HCO$_3$	
	86s	92	6.9	614	91	166	49	104	1,083	1,228	7.6	4.2		Na-SO$_4$–HCO$_3$	
Uşak-Emirfakı	88s	38	6.5	361	42	326	45	51	991	1,030	3.4	4.6		Ca–Na-SO$_4$–HCO$_3$	n
Ortakçı	90s	52	8.03	306	27	40	19	25	529	384	8.3	0.9		Na-HCO$_3$–SO$_4$	n
Tekkehamam	92s	83	7.6	1,823	106	18	9	106	2,164	1,958	17.7	1.8		Na-SO$_4$–HCO$_3$	n
	93s	98	7.0	917	78	58	13	105	615	1,613	17.9	1.8		Na-SO$_4$–HCO$_3$	
	94c	18	7.86	82	12	124	61	60	381	370	3.6	5.1		Ca–Mg–Na-SO$_4$–HCO$_3$	
Seawater	100		8.5	10,365	569	454	1,437	21,800	103	3,210	3.4	1,941		Na-Cl	n

[a] *a* Khayat (1988); *b* Kasap (1984); *c* Şimşek (1984); *d* Tarcan and others (2000); *e* Gemici and Filiz (2001); *f* Tarcan and Gemici (2001); *g* Gemici and Tarcan (2001); *h* Gemici and Tarcan (2002); *i* Erişen and others (1998); *j* Mutlu (1998); *k* Yıldırım and others (1997); *l* Tarcan (1995); *m* Filiz and Tarcan (1993); *n* this study

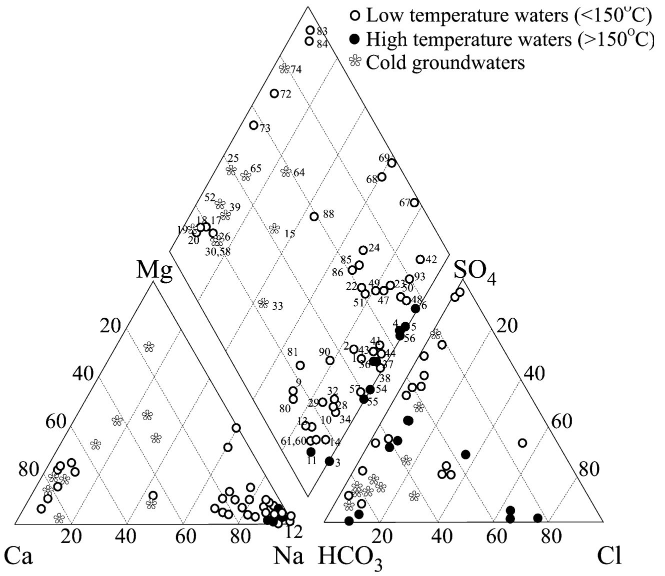

Fig. 3
Distribution of thermal and cold groundwaters from the study are in a Piper diagram

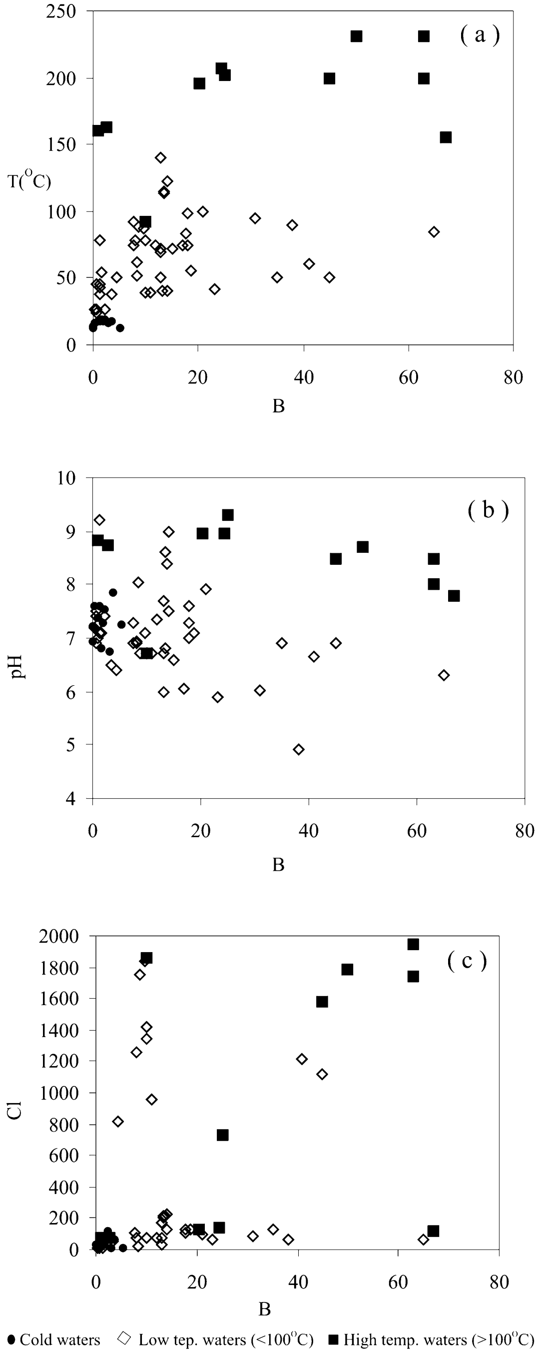

Fig. 4
Relation between B concentrations and **a** temperature, **b** pH and **c** Cl contents of cold and thermal waters in western Anatolia (values are in mg/l)

result of rock dissolution and ion exchange reactions in the aquifer at high temperatures. Lower temperature geothermal waters (<150 °C) are of various types. Although the expected type of thermal waters in the aquifer is initially Na-HCO_3, mixing during upflow, and re-equilibration processes causes Na–HCO_3-type waters to change into various types. In spite of mixing, the main ions are Na and HCO_3 in lower temperature thermal waters.

Some thermal waters with Na-Cl-HCO_3 have remarkable Cl contents such as the samples from Kızıldere and Gecek (Table 1). The relatively high Cl contents of these waters indicate that waters are fed from deep reservoirs at high temperatures with minimal groundwater mixing. Boron concentrations of thermal waters from western Turkey have a wide range of 1–63 mg/l. The Cl contents of these waters varies from 10 to 1,950 mg/l. However waters from Seferihisar geothermal area (Table 1) are different from those mentioned above. The Na-Cl-type geothermal waters of Seferihisar have a significant seawater contribution with boron concentrations varying between 13 and 17 mg/l. The Cl contents of thermal waters in which seawater contribution takes place reaches to 10,000 mg/l (Table 1). Generally, B and Cl concentrations of cold groundwaters have significantly lower values of 0.1–2 and 7–113 mg/l, respectively, than those of thermal waters. However, cold groundwaters contaminated with boron from geothermal fluids have higher values (such as in Büyük Menderes, Gediz grabens and Balçova plains).

Ca–Mg–HCO_3 type cold waters turn into a Na–HCO_3 water type during deep circulation through to the geothermal aquifer. Absorption of CO_2-bearing gases or condensation of CO_2-rich geothermal steam in O_2-free environments controls the formation of Na-HCO_3-type waters. The acidity of the water is controlled by H_2CO_3, which converts feldspars to clays resulting in Na-HCO_3-type thermal waters. Because K and Mg are taken up in clays and Ca and SO_4 ions are relatively insoluble, the aqueous solution becomes rich is Na and HCO_3 (Ellis and Mahon 1977). The chemical processes mentioned above probably control the chemistry of groundwaters from their initial Ca–Mg–HCO_3 types to the Na–HCO_3 type in both low and high temperature geothermal areas of the study area.

Figures 4, 5 and 6 show the relations between B and some of the other ions and pH and temperature values of the natural waters in western Turkey. Boron and Cl concen-

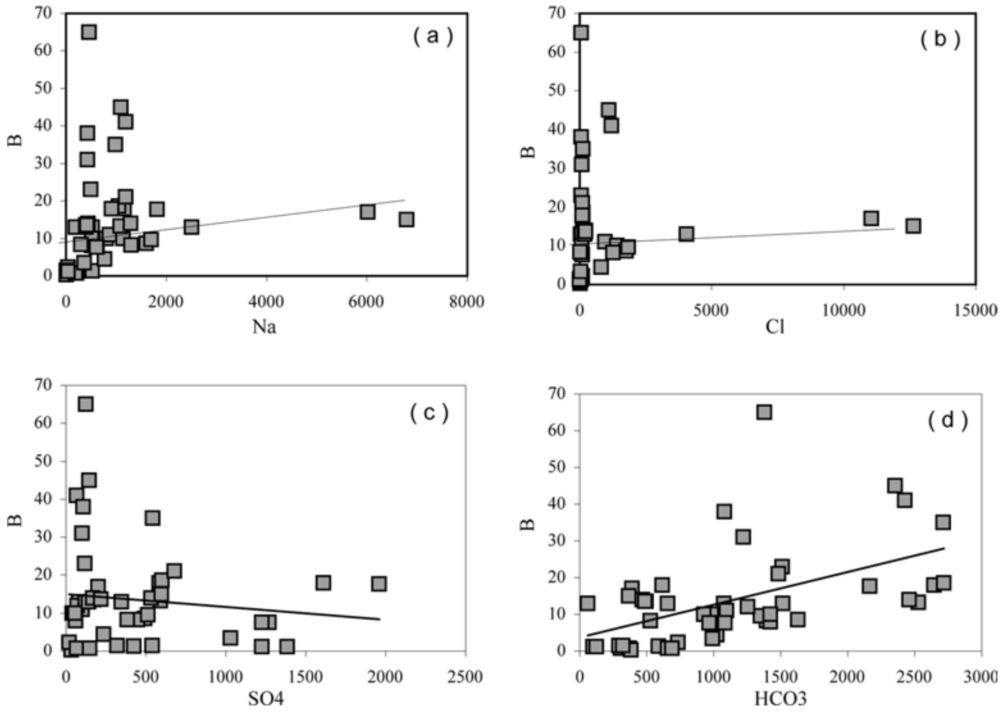

Fig. 5
Relations of some major ions for low temperature thermal waters (values are in mg/l)

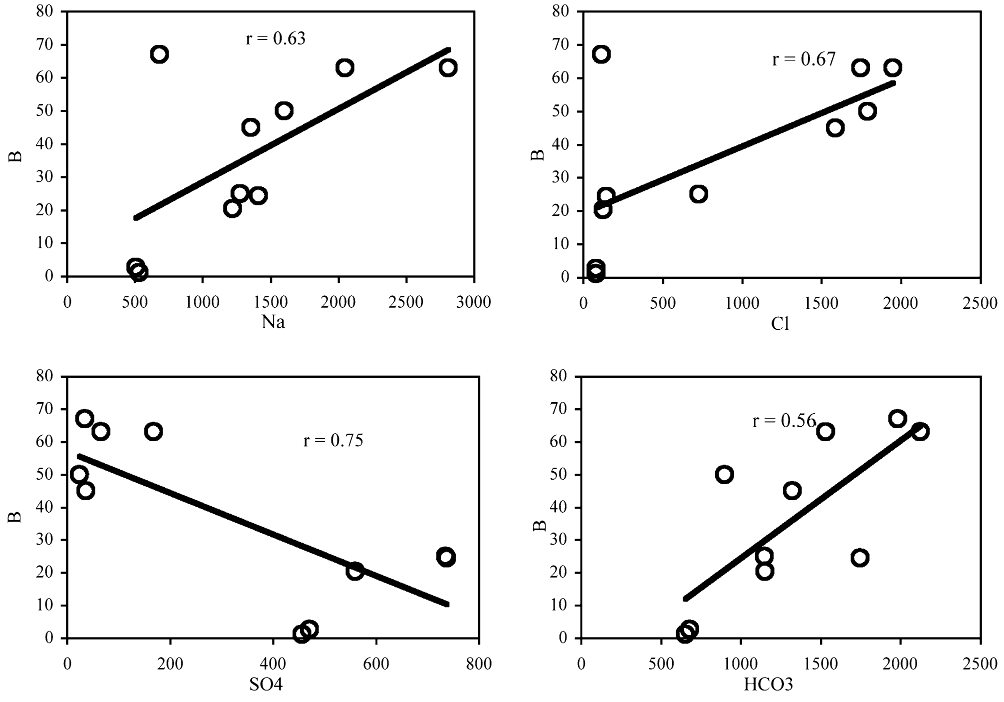

Fig. 6
Relations of some major ions for high temperature thermal waters (values are in mg/l)

trations of thermal waters increase with increasing water temperatures (Fig. 4a). This is evident in high temperature areas. However, the correlation for low temperature waters is not good because of mixing with groundwaters during the upflow to the surface. The dominant aqueous species of boron are undissociated boric acid, $B(OH)_3$ and the borate anion $B(OH)_4$,whose relative abundances are sensitive to pH. While at low pH $B(OH)_3$ predominates, at high pH (>8–9) $B(OH)_4$ is a primary anion (Barth 2000). As shown in Fig. 4b, most of the water samples have a pH value of ~7, which means that B is present mainly in the form of $B(OH)_3$.

A plot of B against SO_4 in high temperature waters demonstrates that B increases whereas SO_4 decreases (Fig. 6b). SO_4 concentration in thermal waters is likely to be controlled by the dissolution of gypsum and/or oxidation of pyrite. This inverse correlation may mean that the dissolution of gypsum and/or the oxidation of pyrite in host rock are not the primary effects in increasing B contents of waters.

There is a good correlation between HCO_3 and B values of both low and high temperature waters (Figs. 5d and 6d). This positive correlation with HCO_3 means that B concentrations in thermal waters are associated with the dissolution of carbonates. Gülensoy and Kocakerim (1977) experimentally demonstrated that the solubility of boron in water increases with increasing CO_2 content. Therefore, HCO_3 may be one of the important ions related to the high boron content in the thermal waters. The conditions that prevail in the formation of Na–HCO_3-type waters are related to the B enrichment in thermal fluids. For Na–HCO_3-type thermal waters, increasing Na concentrations can be used as an indicator of the degree to which water–rock interaction takes place. In addition to the water–rock interaction, some boron in thermal waters probably originates from the mantle or from metamorphism of marine sediments. Güleç (1988) and Ercan and others (1994) used $^3He/^4He$ data to detect the presence of mantle helium in thermal waters from western Anatolia and showed that helium is partly derived from the mantle. Boron isotopic data by Vengosh and others (2002) indicate either leaching of boron from the rocks, or $B(OH)_3$ degassing flux from the deep sources.

Because Li is one of the alkali metals that are least affected by secondary processes, it may be used as a tracer for the initial deep rock dissolution processes to evaluate the possible origin of the other two important conservation constituents of thermal waters, Cl and B, (Giggenbach 1991). Figure 7 illustrates the relative contents of the thermal waters presented in Table 1. None of the waters plots close to the position of crustal rock. Cl and B contents of the thermal waters plot away from the position of crustal rock suggesting the addition of ions during rock dissolution processes. The locations of high temperature waters in Fig. 7 may be described as the dissolution of rock in deeply circulating groundwaters at high temperatures. Water samples 47, 48, 49, 50 and 51 from Gecek geothermal area plot close to the Cl corner, representing modification by absorption of low B/Cl magmatic vapours, or the effect of admixtures of B/Cl seawater. Thermal waters that plot close to the B corner represent the absorption of high B/Cl steam. Cl and B contents reflect their abundance in the rock with which the water reacted rather than the maturity of the system. This group could be considered as relatively young geothermal systems (Fig. 7).

Boron and Cl concentrations in geothermal waters are related to volcanic and sedimentary rocks. Thus, B and Cl contents and the Cl/B molal ratio could be used as an indicator to obtain information about the origin of thermal waters. The Cl/B ratio of natural waters has a wide range from less than 1 to 1,330 for seawater (Arnorsson and Andresdöttir 1995). Dissolution of Cl is easier than that of B from volcanic rocks. However, increasing temperature causes the Cl/B ratio to decrease and get close to the Cl/B ratio of aquifer rock (Ellis and Mahon 1967). The dominant source of Cl in non-thermal waters is from the atmosphere. B concentrations range from about 1 to 95 μg/l in precipitation (Fogg and Duce 1985). Most of the boron present in the atmosphere is in a gaseous state, primarily in the form of boric acid (Mather and Porteous 2001). The Cl/B ratio of non-thermal waters is expected to be similar to the Cl/B ratio of seawater. However, the cold groundwaters considered in this study have Cl/B ratios ranging from 0.1 to 2. This significant decrease is because B is contributed to cold groundwaters by the aquifer rock and in some areas by admixture of thermal waters.

Cl/B molal ratios of high temperature waters (>150 °C) have low values, ranging from 1 to 10, with high B contents that reach 67 mg/l. In addition to the water–rock interaction, degassing of magma intrusives may increase B content. Although water–rock interaction also increases

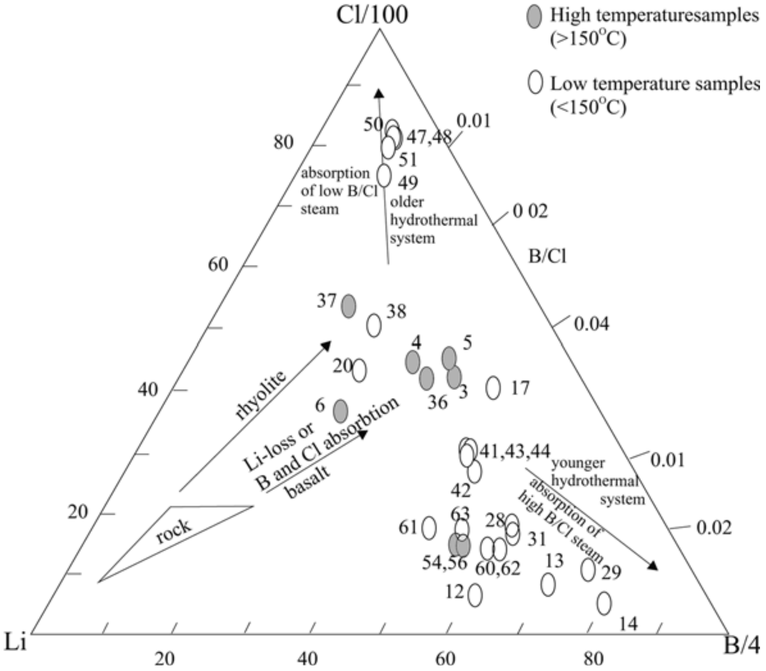

Fig. 7
Relative Cl, L and B contents of thermal waters from the study area (in mg/l). After Giggenbach (1991)

the Cl concentrations in deeply circulating thermal fluids at high temperatures, the contribution of Cl by degassing of magma is lower, resulting in relatively low Cl/B ratios (Table 1). In low-temperature thermal waters (<150 °C), with the exception of samples that have a seawater contribution, Cl/B ratios range from 2 to 88 (Table 1). Thermal waters with seawater mixing (Seferihisar) have Cl/B ratios of between 94 and 256. The seawater contribution to the thermal waters in Seferihisar is also supported by hydrogeochemical and isotopic investigations by Tarcan and others (1999).

The correlation between B and Cl illustrates the progressive rock dissolution and that B and Cl are released from rock during water–rock interaction in approximately stoichiometric proportions for high temperature waters (Fig. 6b). At lower temperature waters B, is taken up from solution to form secondary minerals, especially illite and mica (Seyfried and others 1984; Palmer and others 1987). These processes control the B contents of low-temperature thermal waters. Because the absorption of B by secondary minerals shows differences depending on the lithological characteristics of the aquifers, there is not a good correlation between Cl and B values of low-temperature thermal waters in western Turkey (Fig. 5b). There are mainly two reasons for why Cl/B ratios of high-temperature thermal waters are lower than that of water from lower temperature areas. Firstly, the contribution of B by degassing of magma intrusives in addition to the water–rock interactions of high-temperature fields and, secondly, B uptake into secondary minerals during weathering processes in lower-temperature fields.

Boron contamination in ground- and surface waters because of geothermal activities

High B concentrations of thermal waters causes environmental problems in groundwaters and surface waters in some parts of western Turkey. Boron is necessary in small quantities for growth of plants, but in larger concentrations it becomes toxic (Todd 1980). Plant boron resistance is divided into three groups according to the plant species. Relative tolerances for boron are classified as sensitive, semi-tolerant and tolerant. As a general classification, boron concentrations of groundwater exceeding 1 mg/l are harmful to plants (Richards 1954). In the following examples of ground and surface water use for irrigation, B contamination from geothermal activities are presented. The Gediz graben has an important role in agriculture in Turkey. Almost 75% of grape production in Turkey takes place on this plain. However, B contents of groundwaters create problems in agriculture. The distribution of B in groundwaters is presented in Fig. 8. The B distribution of groundwaters in Gediz graben is directly related to the geothermal fluids. The geothermal fluids contaminate groundwaters in different ways. Hot springs with a high content of B, which emerge along the rims of the Gediz graben (Fig. 2), have been mixing with groundwaters for years. The other probable reason is the recharge of the alluvium aquifer by thermal waters that rise to the surface along fractures of the host rocks under the alluvium. This may explain the high B contents of groundwaters in the middle of the graben (Fig. 9). Although the B content of groundwaters is less than 1 mg/l in a great part of the Gediz plain in some areas this value exceeds 3 mg/l. Right now, these highly B contaminated areas cannot be used for agricultural purposes. A part of water demand for irrigation is supported by drilled wells. This is the other reason for B contamination in groundwaters. The overpumping of wells in uncontaminated areas gives rise to the flow of B-contaminated groundwater to the uncontaminated areas. The alluvium aquifer has different levels of B concentrations. Alluvium aquifers are composed of alternating permeable and impermeable levels. Contaminated levels with boron are not clear because of mistakes in well projects. Consequently, the wells that cut the entire aquifer are formed at various levels with different B concentrations. Drilled wells cause these different groundwaters to mix with each other, resulting in an increase in B concentrations in uncontaminated areas (Fig. 9).

The Balçova plain is another area where thermal fluids cause boron contamination in groundwater. Similar to the Gediz graben, thermal springs from springs and wells recharge the alluvium aquifer (Fig. 10). As shown in Fig. 10, thermal fluids contribute to the aquifer from the bottom

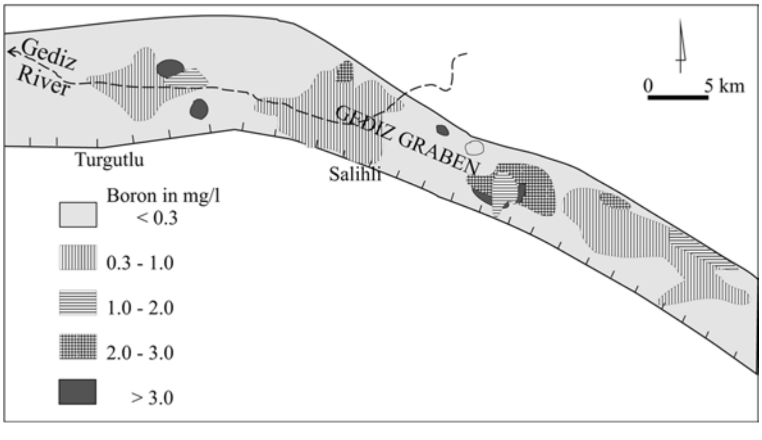

Fig. 8
Distribution of boron in groundwaters of Gediz graben (modified from Filiz and Tarcan 1997)

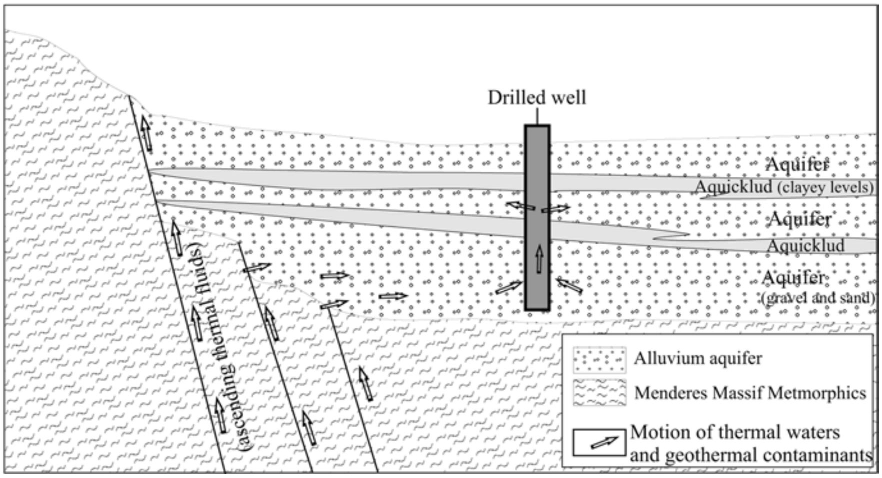

Fig. 9
Schematic model of the transportation of geothermal fluids and distributions of geothermal contaminants through the cold groundwater aquifers in and around the western Anatolia geothermal fields

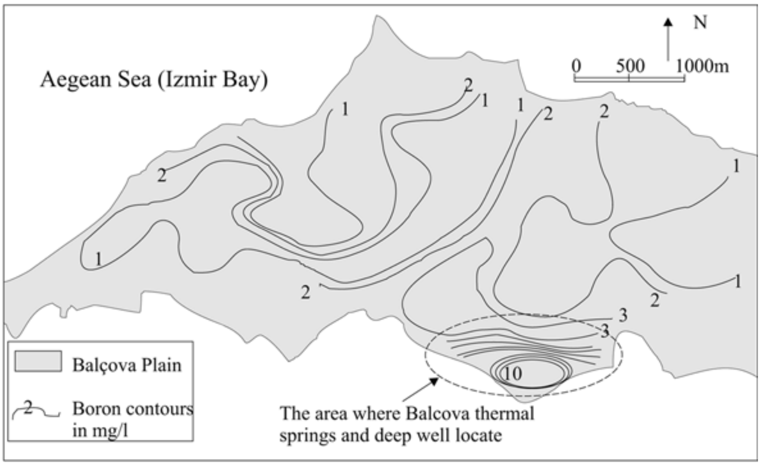

Fig. 10
Distribution of boron in cold groundwater aquifer in Balçova plain. Modified from Ylmazer (1988)

and are widespread in the aquifer. Warm waters (<50 °C) are obtained from some drilled shallow wells in the alluvium aquifer. Another factor that increases the boron content of groundwater is seawater intrusion in the northern part of the aquifer. Over pumping of wells near the coast causes seawater to penetrate through to the aquifer. Thermal waters with 140 °C bottom temperatures in Balçova thermal area are used for balneological purposes and district heating. A total of 10,000 residences are now heated by geothermal energy and studies are carried out to increase this to 50,000 residences, which may bring problems for the removal of wastewater after heating. Because the thermal waters contain boron at about 10 mg/l, admixtures of thermal fluids will increase the B content of cold groundwaters.

Contaminants in the geothermal water affect surface waters. Boron contamination in Büyük Menderes River (Fig. 1) is an example of surface water contamination because of the geothermal fluids. Büyük Menderes basin is one of the most important basins in Turkey, and river waters are used for irrigation. Waters from springs discharge to the Büyük Menderes basin (Fig. 2). The main source of the geothermal contaminants is caused by the spill of the fluids from the geothermal electricity generation plant in Kızıldere. A series of deep wells provides the high-temperature thermal fluids for plant. The B contents of thermal waters are about 20–25 mg/l. The discharge rate of water spilled from the power plant reaches 2,000 ton/h, with an average boron content of 23 mg/l. The average flow rate of the Büyük Menderes River over 17 years is 49.556 m^3/s (Şamilgil 1985). Dilution and sorption processes cause decreasing B concentrations in the downstream part of the river and B contents remain under 1 mg/l, which is the limit for use in agriculture. However, at times when drier climatic conditions prevail, the flow rate of the river decreases to 5.750 m^3/s. Because the dilution is less, the B concentration of the river reaches 2 mg/l, which becomes unsuitable for irrigation. This is why re-injection studies are being carried out by MTA (General Directorate of Mineral Research and Exploration of Turkey). Germencik geothermal field with a 232 °C bottom temperature is planned to generate electricity. The potential of this area (about 100 MW/e) is considered to be higher than that of Kızıldere (Yıldırım and others 1997). However, its B concentrations are also higher, reaching about 63 mg/l. Thus, the operation of both plants will cause a significant increase in B concentration of the Büyük Menderes River.

Conclusions

The metamorphic Menderes Massif mainly hosts the thermal waters. Although gneisses and schists generally have low boron contents, sericite, illite and tourmaline minerals that are abundant in the Menderes Massif rocks are considered to be one of the reasons for the high boron additions to thermal waters by water–rock interactions. There is a good correlation between HCO_3 and B values of both low and high temperature waters, which means that B concentrations in thermal waters are associated with the dissolution of carbonates. The conditions that prevail in the formation of Na–HCO_3-type waters are related to the B enrichment in thermal fluids. For Na–HCO_3-type thermal waters, increasing Na and HCO_3 concentrations can be used as an indicator of the degree to which water–rock interaction take place. Cl/B molal ratios of high temperature waters (>150 °C) have low values, ranging from 1 to 10. In addition to the water–rock interaction, degassing of magma intrusives may increase B content in high-temperature thermal waters. Cl/B ratios of lower temperature thermal waters have higher values than high-temperature waters. There are mainly two reasons for this. Firstly, the contribution of B from degassing of magma intrusives in addition to the water–rock interactions in high-temperature fields and, secondly, the uptake of B into secondary minerals during weathering processes in lower temperature fields.

The contribution of thermal waters to cold groundwater aquifers causes contamination to aquifers and surface waters. In particular, high discharge wastewater disposal from geothermal power plants and district heating systems increases the boron concentration of groundwaters and surface water. To prevent contamination of the cold waters used for irrigation in the study area, re-injection of thermal waters to the reservoir is necessary. This will also recharge the aquifers of the thermal waters.

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References

Aksoy N (2001) Balçova-Narlıdere jeotermal sisteminin izleyiciler ile incelenmesi (in Turkish). PhD Thesis, Dokuz Eylül University, Turkey

APHA (1989) Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, Washington, DC

Arnorsson S, Andsresdottir A (1995) Processes controlling the distribution of boron and chlorine in natural waters in Iceland. Geochim Cosmochim Acta 59(20):4125–4146

Barth SR (2000) Utilization of boron as a critical parameter in water quality evaluation: implications for thermal and mineral water resources in SW Germany and N Switzerland. Environ Geol 40(1–2):73–89

Çetiner L (1999) The hydrogeological study of the kızıldere (Denizli) geothermal field for reinjection purposes. PhD Thesis, Dokuz Eylül Üniversity, Turkey

Dora OÖ, Candan O, Dürr S, Oberhanslı R (1995) New evidence on the geotectonic evolution of the Menderes Massif. IESCA Proceedings, vol 1, pp 53–72

Ellis AJ, Mahon WAJ (1967) Natural hydrothermal systems and experimental hot water/rock interactions. Geochim Cosmochim Acta 31:519–538

Ellis AJ, Mahon WAJ (1977) Chemistry and geothermal systems. Academic Press, London

Ercan T, Matsuda JI, Nagao K, Kita I (1994) Anadolu'daki sıcak sularda bulunan doğal gazların izotopsal bileşimleri ve karbondioksit gazının enerji açısından önemi (in Turkish). Türkiye 6. Enerji Kongresi, 17–22 Ekim 1994, İzmir, Teknik Oturum Tebliğleri I, pp 197–207

Erdoğan B (1990) İzmir–Ankara Zonu'nun İzmir ile Seferihisar arasındaki bölgede stratigrafik ve tektonik evrimi (in Turkish). TAPG Bülteni 2(1):1–10

Erişen B, Akkuş I, Uygur N, Koçak A (1996) Türkiye Jeotermal Envanteri (in Turkish), MTA Genel Müdürlüğü, Ankara

Filiz S, Tarcan G (1993) Seferihisar (İzmir) güneyindeki jeotermal alanın hidrojeolojisi (in Turkish). Türkiye Petrol Jeologları Bülteni 5(1):87–112

Filiz Ş, Tarcan G (1997) High boron content in the aquifer system of the Gediz Basin (on the Aegean region of Turkey). IESCA-1995 Proceedings, vol 2, pp 681–692

Floyd PA, Helvacı C, Mittwede SK (1998) Geochemical discrimination of volcanic rocks associated with borate deposits: an exploration tool? J Geochem Explor 60:185–205

Fogg TR, Duce RA (1985) Boron in the troposphere: distribution and fluxes. J Geophys 90(2):3781–3796

Gemici Ü, Filiz S (2001) Ilıkpınar ve Akpınar (Manisa) karstik kaynaklarının hidrojeolojisi (in Turkish), 1. Çevre ve Jeoloji Sempozyumu-Yeraltı Suları ve Çevre Sempozyumu. 21–23 Mart 2001, Bildiriler, pp 321–330

Gemici U, Tarcan G (2001) Hydrogeochemistry of the Saraycik geothermal area (Manisa) Western Turkey. Water–Rock Interaction 2001, Villasimus, Italy, 10–15 June 2001, Proceedings, vol 2, pp 831–834

Gemici Ü, Tarcan G (2002) Hydrogeochemistry of the Simav geothermal field, western Anatolia, Turkey. J Volcanol Geotherm Res (in press)

Giggenbach WF (1991) Chemical techniques in geothermal explanations. In: D'Amore F (coordinator) Application of geochemistry in geothermal reservoir development. UNITAR/UNDP Publications, Rome, pp 119–142

Güleç N (1988) The distribution of helium-3 in western Turkey. Bull Mineral Res Explor (MTA Dergisi) 108:35–42

Gülensoy H, Kocakerim M (1977) Uleksit mineralinin karbondioksitli sularda çözünürlüğü (in Turkish). MTA Derg Sayı 89:34–44

Helvacı C (1977) Geology, mineralogy and geochemistry of the borate deposits and associated rocks at the Emet Valley, Turkey. PhD Thesis, University of Nottingham, Nottingham, UK

Helvacı C (1978) A review of the mineralogy of the Turkish borate deposits. Mercian Geol 6:257–270

Helvacı C (1995) Stratigraphy, mineralogy, and genesis of the Bigadiç borate deposits, western Turkey. Econ Geol 90:1237–1260

Karamanderesi İ H (1997) Geology and hydrothermal alteration processes of the Salavatlı-Aydın geothermal field. PhD Thesis, Dokuz Eylül University, İzmir, Turkey

Kasap İ (1984) Geothermal resource evaluation of Germencik-Omerbeyli (Western Anatolia) Geothermal Field of Turkey. Seminar on Utilization of Geothermal Energy for Electric Power Production and Space Heating, 14–17 May, Florence

Khayat JR (1988) Germencik-Kizilcapinar (Aydin) ve cevresinin hidrojeolojik incelenmesi, sıcak ve soğuk suların jeokimyasal yorumlanması (in Turkish). Yüksek Lisans Tezi, Dokuz Eylül Üniversitesi, İzmir

Mather JD, Porteous NC (2001) The geochemistry of boron and its isotopes in groundwaters from and non-marine sandstone aquifers. Appl Geochem 16:821–834

Mutlu H (1998) Chemical geothermometry and fluid-mineral equilibria for the Ömer-Gecek thermal waters, Afyon area, Turkey. J Volcanol Geotherm Res 80(3–4):303–321

Okay AI (1984) Distribution and characteristics of the north-west Turkish blue schists. Reprinted from Dixon JE, Robertson AHF (eds). The geological evolution of the eastern Mediterranean. Special publication of the Geological Society, no 17. Blackwell, Oxford, pp 455–465

Palmer MR, Helvacı C (1995) The boron isotope geochemistry of the Kırka borate deposits, western Turkey. Geochim Cosmochim Acta 59:3161–3169

Palmer MR, Helvacı C (1997) The boron isotope geochemistry of the Neogene borate deposits of western Turkey. Geochim Cosmochim Acta 61:3599–3605

Palmer MR, Spivack AJ, Edmond M (1987) Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clays. Geochim Cosmochim Acta 51:2319–2323

Richards LA (1954) Diagnosis and improvement of saline and alkali soils. Agriculture handbook no 60. US Dept Agriculture, Washington, DC

Şamilgil E (1985) Jeotermal uygulamalarda çevre sorunları (in Turkish). İstanbul Üniv Müh Fak Yerbilimleri Dergisi 5(1–2): 1–106

Seyfried WE, Janecky DR, Mottl ML (1984) Alteration of the oceanic crust: implication for geochemical cycles of lithium and boron. Geochim Cosmochim Acta 48:557–569

Şimşek Ş (1984) Aydin-Germencik-Ömerbeyli Geothermal Field of Turkey. Seminar on Utilisation of Geothermal Energy for Electric Power Production and Space Heating, 14–17 May 1984, Florence. Sem. ref. no EP/SEM.9/R.37

Tarcan G (1995) Hydrogeological study of the Turgutlu Hot Springs. PhD Thesis, Dokuz Eylül University, Graduate School of Natural and Applied Sciences, İzmir

Tarcan G, Gemici U (2001) Hydrogeochemistry of the Gumuskoy and Sazlikoy geothermal fields, Aydin, Turkey. Water–Rock Interaction 2001, Villasimus, vol 2, Italy, 10–15 June 2001, Proceedings, pp 931–934

Tarcan G, Filiz Ş, Gemici Ü (1999) Balçova-Seferihisar (İzmir) jeotermal alanlarında karşılaştırılmalı hidrojeokimyasal incelemeler ve jeotermometre uygulamaları (in Turkish). 1. Batı Anadolu Hammadde Kaynakları Sempozyumu Bildiriler Kitabı, 8–14 Mart-İzmir, pp 346–358

Tarcan G, Filiz S, Gemici Ü (2000) Geology and geochemistry of the Salihli geothermal fields, Turkey. In: Proceedings of WGC-2000 World Geothermal Congress 28 May–10 June, 2000 Congress Kyushu-Tohoku, Japan, pp 1829–1834

Todd DK (1980) Groundwater hydrology. Wiley, New York

Vengosh A, Helvacı C, Karamanderesi I H (2002) Geochemical constrains for the origin of thermal waters from western Turkey. Appl Geochem 17(3):163–183

Yıldırım N, Demirel Z, Doğan AU (1997) Geochemical characteristics and re-injection of the Kızıldere-Tekkehamam geothermal field. GEOENV'97, İstanbul

Yılmazer S (1988) Balçova Kaplıcalarının (İzmir) hidrojeolojisi ve jeokimyasal özellikleri (in Turkish), Doktora tezi, Fen Bilimleri Enstitüsü, Akdeniz Üniversiesi, Isparta