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Assessment of an Increase in Boron and Arsenic Concentrations at the Discharge Area of Na-Borate Mine (Kirka-Eskisehir, Turkey)

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ABSTRACT

The Province of Kirka (Eskisehir, Turkey), located in the catchment of the Seydisuyu Plain, has one of the largest Na-borate deposits in the world. However, boron concentrations in surface and ground waters downstream of Kirka Province, the Seyitgazi Plain, have increased over the past twenty years. Seyitgazi plain has been widely irrigated from groundwater and Seydisuyu River. In this respect, quality of the river water directly affects groundwater quality in the Seyitgazi Plain since river water is the main supplier for irrigation water in the Seyitgazi plain in addition to groundwater which is extracted from the wells drilled in the Seyitgazi Plain. Thus, any mining activity built in the catchment area of groundwater poses potential risk for the quality of groundwater in the discharge area.

The Seydisuyu River is fed from Catören and Kunduzlar dam reservoirs which are located in the upper reaches of the Seyitgazi Plain. Chemical analysis of surface waters (n = 102) and groundwaters (n = 136) showed that boron concentrations in groundwater of the Seyitgazi Plain increased up to three to four times due to infiltration into the shallow aquifer system because the Seydisuyu River water is used for irrigation. Statistically, significant positive correlations were found between boron and arsenic due to deposition in the same playa lake. Since the boron bearing layers can contain arsenic minerals, arsenic can act in a tracer role for surplus boron concentrations in groundwater. Besides natural contribution, mining activities caused a substantial increase in boron and arsenic concentrations in the groundwater of the Seyitgazi Plain.

Key words: Kirka, Borax, Boron, Arsenic, Contamination, Groundwater

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1. INTRODUCTION

Boron is an element broadly distributed with low concentration in the environment. Minable deposits of borate minerals are rare and usually found in arid regions with a geological history of volcanic and/or hydrothermal activity (Mellor 1980). Boron can leach into groundwater from rocks and soils. Depending on forming condition, arsenic may accompany boron. Boron concentration in groundwater ranges from 0.3 to 100 mg l^{-1} throughout the world (Hem 1975), while it ranges from 0.1 to 1.5 mg l^{-1} in Europe (ECETOC 1997; WHO 1998). WHO (World Health Organization) and EPA (United States Environmental Protection Agency) recommend the limit for arsenic as 10 μg l^{-1} for safe drinking water.

Major borate deposits are found in Turkey, the USA, Argentina, Russia, Chile, China and Peru (Culver et al. 1994). The two largest producers are the USA and Turkey (WHO 1998). The borate deposits of Turkey are found mainly in five districts of Western Anatolia: Bigadiç, Kestelek, Sultançayır, Emet and Kirka Provinces. These areas were formed in a lacustrine environment during calc-alkaline volcanic activity periods in the Neogene (Palmer and Helvaci 1995, 1997). One of the commercial borate minerals is tincal, i.e., Na-borax, and is mainly found in Kirka Province, Turkey.

High boron in shallow groundwater generally originates either from upwelling geothermal waters or contamination, caused by mining acitivites (Smedley and Kinniburgh 2002; Younger et al. 2004). As a result of this, geothermal waters with high B concentrations dramatically affect the quality of shallow groundwater in Western Turkey

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(Gemici and Tarcan 2002; Vengosh et al. 2002; Baba et al. 2009). The pollution problem caused by boron mining activities has been studied before (DSI 1971, 1983; Urgüplü 1985; Onacak 1990; Wolkersdorfer 1996; Akbas 1998; Iller Bankası 2000; Rural Service of Eskisehir Research Institute 2001, 2002, 2003; Ugurluoglu 2004; Yasin and Yuce 2008). However, the origin of boron excess in groundwater has not been well addressed.

The study area is the Kirka province which has the biggest Na-Borate deposit in the world (Fig. 1a). The two dams, Catören and Kunduzlar, are located in the discharge area of Na-borate deposit and boron mining activities. The Catören

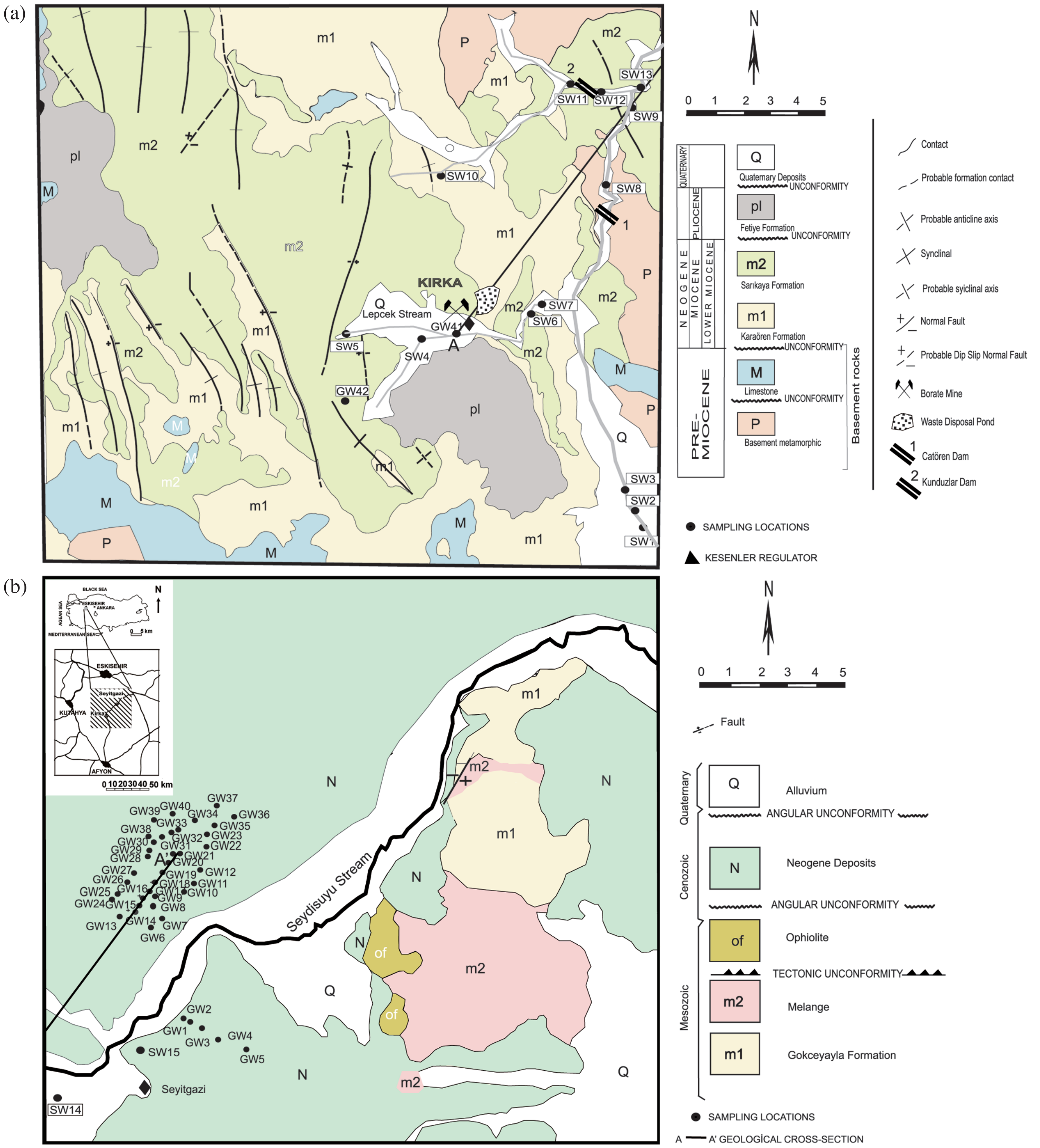


Fig. 1. (a) Geological Map of Kirka Basin (After Onacak 1990). (b) Geological Map of Seyitgazi Basin (After Ozcan et al. 1989).

dam's water forms the Seydisuyu River which flows to the Seydisuyu Plain. The Kirka Na-borate deposit was operated as an open-pit between 1971 and 1989 without tailing ponds, since then it has still been operated as the open-pit mine with the tailing ponds. Generally, the boron concentration in surface water was generally low up to the location of the Balik Bogazi stream (SW6) except for the period of 1979 - 1980 in which the mine activities were initiated at the recharge area of the Lepcek stream. Waste rock from ore has been deposited on the surface close to the mine. However, surface water in the study area was affected by leaching/seepage from the tailing ponds at the mine site. All shallow water has been collected and stored by the above-mentioned dams to supply irrigation water to the Seyitgazi Plain. After obtaining borax, resulting from the leaching process in the mining area, the solid waste has been dumped near surface water in the tailing area. There also exists two big tailings ponds to collect the leachates from the ore-deposits. Since the solid waste of Na-borate is easily soluble in water, it dissolves after rain and reaches the stream water near the Kirka mining area. Thus, boron concentration has increased in streams and creeks, especially during the wet seasons and all surface water recharge into the lake of the dams used for irrigation water in the Seyitgazi Plain. The Seyitgazi Plain is irrigated from the Catören and Kunduzlar dam lakes water as well as from wells (42 bores) that drilled to meet the deficiency of irrigation water. However, utilization of water having high boron concentration from Catören dam reservoir for irrigation purpose causes boron increment in groundwater at the discharge area, i.e., at the Seyitgazi Plain. Concordantly, boron concentration in the bottom sediments of the lake at the Catören dam was found to be 13.2 and 4 ppm for the lake at the Kunduzlar dam (Özkurt 2000). As a result, boron concentration in groundwater is higher than the allowable limit for irrigation purposes (> 3 ppm).

In addition to boron, arsenic was found in higher concentrations (>10 ppb) in groundwater samples from the bores at the discharge area of boron mine area. As is well-known, arsenic contaminated groundwater causes a serious health problem over a long-term. In this context, Unsal and Metintas (2002) determined some health problems such as pulmonary emphysema, asthma and bronchitis in the dwellers of Kirka Province where the level of boron was found to be equal or higher than 0.6 mg 1^{-1} were significantly greater than those in the other settlements where the level of boron was found to be lower than 0.6 mg 1^{-1}. Dissolution of the borate and a lesser amount of arsenic minerals in the boron bearing formation (Sarıkaya) or tuff through water-rock interaction, arsenic concentration increases in groundwater at the Seyitgazi Plain by use of irrigation water from the Catören dam reservoir. Groundwater extraction may also negatively affect arsenic mobilization in the downstream area of Kirka Province. Strontium was another trace element as remarkable concentrations in water resources with boron and arsenic.

To determine the hydrologic relations between water resources at the study area, in addition to hydrochemical studies, stable isotope and tritium analysis were analyzed, as well.

The aim of the study was to determine and evaluate the long-term geogenic effect of Kirka Na-borate mine activities on the quality of surface and groundwater at the discharge area, Seyitgazi Plain.

2. GEOLOGICAL SETTINGS

Geological maps of the study area are separately given as a recharge and discharge area in Figs. 1a and b, respectively. The basement rocks in the Kirka Plain contain Pre-Miocene units composed of metamorphics (probably Paleozoic) and Mesozoic limestone (Fig. 1a). Pre-Miocene units are overlain by Neogene units [Karaören Formation: continental and lacustrine tuff, Sarıkaya Formation: carbonate rocks, clay, borate, ignimbrite, tuff-zeolitic tuff (Helvaci and Alonso 2000), Fethiye Formation: re-sedimented tuff-tuffit, Quaternary deposits: alluvium] (Onacak 1990). The ignimbrite in the Kirka Region has high F and Rb concentrations; whereas the alkali lava suite has high Sr and Ba content (Floyd et al. 1998). The borate deposits formed in a lacustrine environment during periods of calc-alkaline volcanic activity in the Neogene. Actually, volcano-sedimentary sequence and alluvium form the main lithology in the Kirka area (Fig. 1a). The sequence consists predominantly of carbonate rocks, tuff, marl, tuffite, lenses of boron bands. The carbonate rocks are interbedded with various lithological units such as limestone, boron, tuff, tuffite and agglomerate as the lenses and thin bands. The basement units of the Seyitgazi Plain (Fig. 1b) are represented by Mesozoic aged Gökçeyayla formation (carbonate rocks), Melange (claystone, mudstone, sandstone), and ophiolite. The basement rocks are unconformably overlain by Neogene deposits (carbonate rocks, claystone with borate lenses, marl, agglomerate, tuff and tuffite) and Quaternary alluvium (Ozcan et al. 1989).

A stratigraphic section of the Kirka Provience and the general geologic cross-section of study area are shown in Fig. 2, respectively. The main boron mineral in the Kirka Province is borax; colemanite and ulexite are found in minor quantities. Other borate minerals such as pandermite, inyoite, meyerhofferite, tincalconite, kernite, hydroboracite, inderite, inderborite, kurnakovite, and tunnelite (Palmer and Helvaci 1995) have also been found in the Kirka Province. Sarıkaya formation is the source of borax deposit in the study area. This formation contains borate minerals that interlayered with claystones and tuffs, while a porcelanous limestone forms a cap-rock for borate zone.

The clay layers contain some volcanic tuff (frequently altered to zeolites), quartz, biotite, and feldspar. Na, Sr and

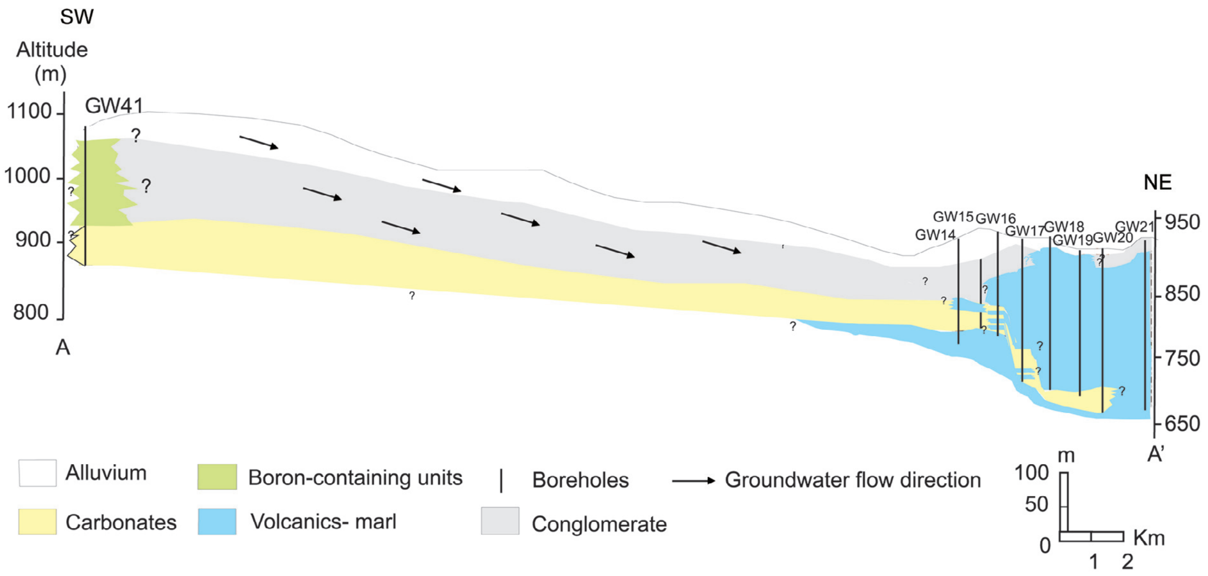


Fig. 2. Geologic cross-section of the study area. [Lithologic descriptions of the boreholes were defined according to the borehole logs provided by DSI (the Regional Directorate of State Hydraulic Works)].

B are originated from partial melting of lithosphere into magma and Ca derives from surrounding rocks, while Mg is sourced from ophiolite. Strontium is released to the surface because of hydrolysis of pyroclastic materials (Baysal 1972). These mixed fluids are discharged into the playa lake, concentrated by evaporation and formed borate deposits (Yalcin and Baysal 1991).

Alluvium is generally composed of fine-grained silt and sand materials along the Seydisuyu River. The sedimentary units form a poor aquifer condition because of fine detritic materials, which has lower permeability. The groundwater level depth in the study area varies from 9.5 to 32 m from the surface. Tuff, limestone and alluvium are aquifer units in the study area. Tuff and limestone aquifers are considered as a semi-confined aquifer while the alluvial aquifer is unconfined. The groundwater flow direction is from SW to NE. The map given in Fig. 3 shows that groundwater at the discharge area of Kirka is fed from the Seydisuyu River.

3. METHODS

The water samples, collected in wet and dry periods of 2007, were analyzed in the laboratories of Hacettepe University (HU), Ankara, Turkey. In addition to sampling campaigns performed in 2007, samples collected and analyzed by different governmental agencies between 1971 and 2003. In all, 102 surface waters and 136 groundwater samples were also evaluated in this paper. Groundwater samples were taken from DSI (The General Directorate of State Hydraulic Works) wells drilled in the Seyitgazi Plain. Boron contents of water samples were determined by the Carmine method using a spectrophotometer at the governmental agency, Rural Affairs Service of Eskisehir (RASE). This method was based on the color change of the solution (carminic acid and concentrated H_2SO_4) depending on the boron content of water samples. Intensity of color change

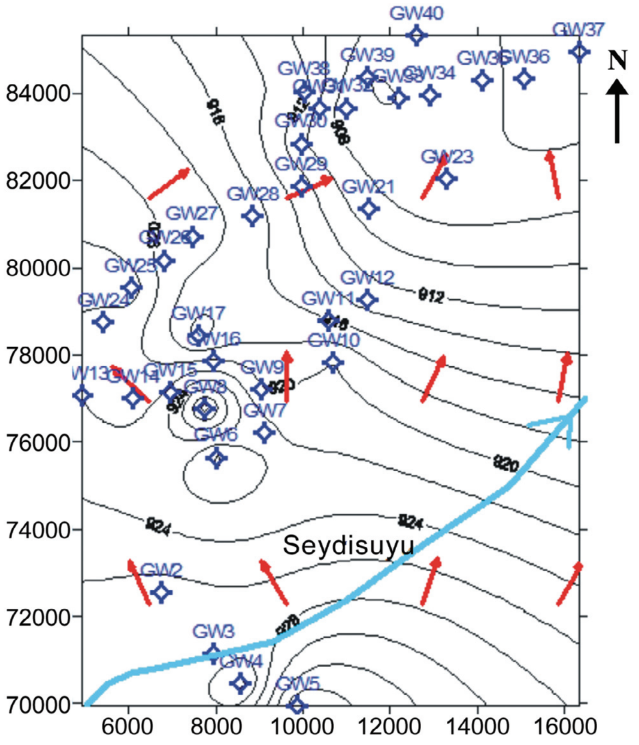


Fig. 3. Groundwater equipotential lines (modified from Ugurluoglu 2004; Ugurluoglu and Yuce 2004).

to red being consistent with the increasing boron content is measured by spectrophotometer. The carmine method (≤ 0.05 error limit) uses the complex of carmine (ananthraquinone dye) with boric acid in concentrated H_2SO_4 which has a 585 nm absorption maximum and 0.5 - 10 mg l^{-1} linear detection range. The direct (without matrix separation) determination of less than 0.5 mg l^{-1} by the carminic acid method is almost impossible in the presence of dissolved substances. The arsenic contents (2007) were carried out by ICP-MS in HU labs and its detection limit was near 0.5 µg l^{-1}. Samples were filtered by 0.45 µ and stabilized by ultrapure HNO_3 for arsenic analysis. Both analytical results in the RASE and HU Laboratories were consistent with each other.

Stable isotopes, $\delta^{18}O$ ve δ^2H, were analyzed using a thermo-chemical elemental analyzer (TCEA) coupled to a Thermo Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer through an open split interface at laboratories in Stable Isotope Ratio Facility for Environmental Research Department of Biology of the University of Utah (USA). Limits of precision were ±1 for δ^2H and ±0.2 for $\delta^{18}O$. Tritium was analyzed in the laboratory at Hacettepe University with a liquid scintillation counter (LSC) after electrolytic enrichment of the water samples with an error of ±0.8 Tritium Units Collected isotope samples were placed in a cold environment to eliminate evaporation effect till analyzing.

4. RESULTS AND DISCUSSION

4.1 Groundwater

A total of 136 groundwater samples were collected from the 42 deep bores drilled in the Seyitgazi Plain. The analytical results of groundwater samples performed between 1971 and 2003 and relatively recent (2007) were given in Table 1, respectively. The minimum, maximum and average concentrations are presented in Table 2. The boron concentration varies from below the detection limit to 7.82 ppm.

Table 1. Analytical results of groundwater samples.

No	Sample Date	pH	EC mho/cm	Na$^+$	K$^+$	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl$^-$	SO_4^{--}	B (ppm)	As	Sr	δ^{18} O	δD	T
GW1	1990 W											0.03					
GW1	2003 D	7.90	327	11.9	5.7	31.7	17.2	16.0	152.6	18.3	5.4	0.66					
GW2	1990 D											0.17					
GW2	1999 D											0.43	0.013				
GW2	2003 D	7.98	323	17.5	7.0	32.1	17.0	15.0	166.3	18.6	9.1	0.52					
GW2	2007 W	7.37	418	12.3	4.2	49.2	21.0	0.0	265.8	5.8	11.0	0.08	0.008	0.54	-8.34	-71.2	1.87
GW2	2007 D	7.37	451	14.6	5.8	40.3	19.4	0.0	235.8	8.1	18.0	0.13	0.020	0.68	-9.48	-71.5	0.49
GW3	1990 D											0.39	0.010				
GW3	2000 D											0.11					
GW3	2003 D	8.05	355	15.2	6.5	39.6	17.6	12.0	189.2	19.5	9.6	0.54					
GW4	1990 D											0.11					
GW4	1999 D											0.17	0.010				
GW4	2001 D											0.10					
GW4	2003 D	8.03	440	21.9	5.7	42.1	25.5	8.0	205.4	27.2	43.2	0.46					
GW5	1990 D											0.11					
GW5	1999 D											0.14					
GW5	2001 D											0.10					
GW5	2003 D	8.00	605	35.4	3.5	88.2	18.2	6.0	292.9	33.7	75.9	0.53					
GW6	1997 D											0.78					
GW6	2003 D	7.70	465	19.0	5.7	56.1	23.4	6.0	244.1	27.5	35.8	0.89					
GW7	1997 W											0.69					
GW7	1999 D											0.68	0.013				
GW7	2000 D											0.50					
GW7	2003 D	7.83	397	15.0	5.5	45.8	22.5	10.0	199.3	21.3	34.9	0.96					
GW8	1997 W											0.98					
GW8	2003 D	8.00	430	46.8	4.5	41.1	13.4	9.0	219.7	23.0	36.0	1.23					
GW9	1997 W											0.92					
GW9	2003 D	7.80	830	90.1	4.3	84.2	23.4	6.0	302.0	34.6	193.5	1.80					
GW10	1997 W											1.60					
GW10	2003 D	7.75	660	60.1	4.5	73.1	21.9	6.0	329.5	26.6	88.0	1.18					

Table 1. (Continued)

No	Sample Date	pH	EC mho/cm	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	B (ppm)	As	Sr	δ^{18} O	δD	T
GW11	1997 D											0.89					
GW11	2001 D	7.70	630	25.3	5.5	40.1	52.3	12.0	231.9	26.6	124.0	0.06					
GW11	2003 D	7.78	678	72.3	5.8	55.4	26.9	9.0	267.0	33.2	127.3	0.76					
GW12	1997 D											1.37	0.028				
GW12	1999 D											1.86					
GW12	2000 D											1.74					
GW12	2001 D	7.75	785	52.7	5.7	65.6	21.9	6.0	134.4	44.3	185.4	0.68					
GW12	2003 D	7.93	670	90.0	4.8	53.1	17.8	10.0	268.5	39.6	110.6	1.77					
GW13	1990 W											1.00					
GW13	2001 D	7.70	630	29.0	6.7	40.1	29.2	0.0	286.8	19.5	27.9	0.00					
GW14	1990 W											1.37					
GW14	2007 W	7.40	863	75.7	4.3	69.8	29.3	0.0	294.2	12.1	183.1	1.43	0.024	0.80	-9.56	-66.4	1.82
GW14	2007 D	7.26	714	42.4	4.8	56.2	24.4	0.0	286.0	11.4	103.8	1.35	0.020	0.79	-9.02	-66.9	0.91
GW15	1990 W											1.64					
GW15	1999 D											1.70	0.017				
GW15	2003 D	7.83	413	40.7	4.1	42.3	13.7	7.5	233.4	19.9	22.8	1.93					
GW16	1990 W											1.60					
GW16	2001 D	7.70	680	43.0	5.9	60.1	28.6	0.0	292.9	28.4	85.0	0.00					
GW16	2003 D	7.85	485	31.4	4.7	60.1	18.5	6.0	238.0	23.0	60.5	1.31					
GW17	1990 W											0.90					
GW17	2001 D	7.80	570	34.7	6.3	69.1	24.3	0.0	311.2	30.1	56.2	0.00					
GW17	2003 D	7.70	447	26.7	5.7	57.8	16.6	8.0	252.2	23.6	23.5	1.66					
GW18	1990 W											0.76					
GW18	1999 D											2.94	0.016				
GW18	2001 D	7.70	695	37.1	7.0	63.1	35.2	0.0	137.3	27.5	226.5	0.48					
GW18	2003 D	7.50	540	26.9	8.6	74.2	19.4	6.0	201.4	21.3	124.0	1.21					
GW18	2007 W	7.27	674	28.3	7.1	73.1	27.3	0.0	253.9	8.6	120.4	0.83	0.014	0.80	-8.66	-69.6	0.19
GW18	2007 D	7.31	707	24.6	6.1	68.4	25.6	0.0	261.0	9.4	135.1	0.88	0.020	0.89	-9.53	-68.7	0.29
GW19	1990 W											0.50					
GW19	1999 D											4.30	0.026				
GW19	2001 D	7.80	560	16.3	5.1	52.1	29.8	6.0	305.1	17.7	9.1	0.00					
GW19	2003 D	7.73	838	95.7	6.1	70.1	22.5	10.5	344.8	27.0	139.6	1.40					
GW20	2001 D	7.65	735	26.7	7.0	73.1	31.3	6.0	146.5	26.6	202.3	0.00					
GW20	2003 D	7.70	655	41.4	8.9	80.9	22.2	6.0	288.3	23.9	110.2	1.41					
GW21	1990 W											0.95					
GW21	2001 D	7.75	690	23.7	8.4	73.7	19.1	3.0	140.4	23.9	159.3	0.51					
GW21	2003 D	7.65	610	35.7	9.4	77.2	22.6	6.0	233.4	26.1	131.5	1.23					
GW22	1990 D											0.40					
GW22	1999 D											4.30	0.018				
GW22	2001 D	7.70	735	25.9	10.0	67.1	29.5	6.0	149.5	24.8	183.0	0.41					
GW22	2003 D	7.40	517	32.3	8.9	64.5	18.8	6.0	229.8	24.8	83.1	1.04					
GW22	2007 W	7.35	617	27.2	7.4	66.9	21.1	0.0	229.1	9.5	102.5	0.51	0.016	0.68	-9.21	-71.5	0.54
GW22	2007 D	7.33	628	24.9	7.4	60.1	19.5	0.0	220.1	11.7	109.3	0.55	0.020	0.70	-9.78	-74	0.28
GW23	1997 D											0.36					
GW23	1999 D											2.66	0.015				
GW23	2000 D											0.45					
GW23	2001 D	7.70	530	19.5	4.7	70.1	23.1	12.0	170.9	24.8	119.0	0.08					
GW23	2003 D	7.80	470	41.6	8.0	44.6	17.0	9.0	219.7	36.3	34.4	0.79					
GW24	2001 D	7.83	657	34.6	7.0	68.5	27.1	10.0	250.2	40.2	84.9	0.57					
GW25	1989 W											0.42					
GW25	2001 D	7.80	673	24.0	6.1	63.5	38.1	10.0	262.4	32.5	93.6	0.49					
GW26	2001 D	7.90	635	30.1	5.9	64.6	31.9	9.0	262.4	32.8	85.6	0.29					
GW26	2003 D	7.53	608	41.4	6.8	68.6	25.2	9.0	219.7	30.6	130.3	1.58					

Table 1. (Continued)

No	Sample Date	pH	EC mho/cm	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	B (ppm)	As	Sr	$\delta^{18}O$	δD	T
GW27	2001 D	7.83	563	19.2	4.8	62.5	26.1	8.0	219.7	35.5	65.2	0.50					
GW27	2003 D	7.53	730	38.3	6.2	94.7	30.1	9.0	299.0	29.7	143.3	1.35					
GW28	1990 W											1.00					
GW28	2001 D	7.83	670	34.1	7.0	68.8	32.8	8.0	252.2	35.5	115.0	0.38					
GW28	2003 D	7.90	820	104.1	6.4	70.6	23.2	12.0	347.8	23.9	161.1	1.24					
GW29	1999 D											0.81	0.010				
GW29	2001 D	7.78	713	22.6	8.2	80.7	34.3	7.5	192.2	44.8	162.3	0.24					
GW29	2003 D	7.65	855	59.7	8.5	100.4	32.2	10.5	331.0	46.5	162.8	1.17					
GW30	2001 D	7.80	703	21.8	6.5	79.2	25.5	6.0	244.1	39.9	130.5	0.38					
GW30	2003 D	7.78	758	62.5	7.2	85.2	27.1	9.0	312.7	32.3	146.8	1.22					
GW31	1989 D											0.25					
GW31	2001 D	7.77	650	23.7	5.9	78.5	25.5	6.0	260.4	39.0	78.4	0.02					
GW31	2003 D	7.93	495	23.5	8.0	54.9	26.4	9.0	227.3	32.4	57.7	0.81					
GW32	1989 D											0.50					
GW32	2002 W	7.78	638	25.6	7.5	65.1	32.8	6.0	199.8	28.4	143.0	0.22					
GW32	2003 D	7.85	510	25.8	8.4	65.1	21.0	12.0	204.4	23.9	90.7	0.71					
GW33	2001 D	7.80	673	23.9	8.3	74.5	27.3	8.0	240.0	35.5	96.9	0.38					
GW33	2003 D	7.60	553	28.2	9.3	58.8	29.8	10.0	229.8	27.8	94.4	1.21					
GW34	1997 D											0.73					
GW34	1999 D	7.80	700	17.5	9.0	74.2	29.2	6.0	231.9	33.7	103.0	1.86	0.013				
GW34	2000 D											0.31					
GW34	2001 D	7.70	665	21.2	6.5	74.2	34.6	9.0	250.2	38.1	104.0	0.28					
GW34	2003 D	7.93	537	30.1	8.1	64.8	21.3	10.0	219.7	34.9	76.1	1.19					
GW35	1997 W											0.62					
GW35	2001 D	7.70	753	26.3	9.1	78.7	34.8	4.5	181.5	34.1	196.0	0.41					
GW35	2003 D	7.78	583	23.7	9.1	75.7	25.1	12.0	231.9	32.4	95.4	1.20					
GW36	1997 D											0.57					
GW36	1999 D											0.42					
GW36	2001 D	7.77	600	21.7	6.1	58.8	31.2	8.0	225.8	31.3	84.0	0.54					
GW36	2003 D	7.73	525	26.2	7.2	61.6	24.3	13.5	251.7	31.0	45.6	1.40					
GW37	1997 W											0.41					
GW37	1999 D											1.46	0.011				
GW37	2001 D	7.63	597	24.8	6.1	56.1	30.8	4.0	250.2	25.4	77.5	0.29					
GW37	2003 D	7.73	420	21.2	5.4	46.3	21.7	21.0	209.0	28.8	10.7	1.08					
GW38	1997 W											0.19					
GW38	1999 D											0.50	0.017				
GW38	2001 D	7.77	593	29.9	8.3	57.1	21.5	4.0	240.0	33.1	54.3	0.19					
GW38	2003 D	8.00	505	31.3	5.1	56.1	19.9	16.5	207.5	30.6	53.6	1.21					
GW39	1997 D											0.29					
GW39	1999 D											0.36	0.011				
GW39	2001 D	8.10	515	19.8	6.5	61.6	19.7	18.0	201.4	26.6	51.6	0.09					
GW39	2003 D	7.85	483	25.2	6.4	58.1	21.0	12.0	187.6	35.5	67.7	0.89					
GW40	1997 D											0.35					
GW40	1999 D											0.50	0.012				
GW40	2001 D	8.15	525	23.3	7.0	59.1	20.7	15.0	198.3	23.9	69.6	0.02					
GW40	2003 D	7.85	485	25.9	7.2	56.4	21.7	7.5	190.7	32.4	78.2	0.96					
GW41	2002 W	7.90	460	7.6	3.1	61.1	24.9	24.0	244.0	7.1	24.5	3.95					
GW41	2003 W	7.92	370	10.8	3.2	41.9	23.3	7.2	229.4	15.6	5.8	6.49					
GW41	2003 D	7.80	363	10.8	3.2	39.4	24.2	12.0	213.5	17.3	5.5	7.82					
GW41	2007 W	7.28	428	10.7	2.5	45.5	27.0	0.0	278.7	3.3	6.2	6.32	0.028	3.16	-9.44	-68.7	0.8
GW41	2007 D	7.41	435	9.3	2.5	52.6	26.6	0.0	273.6	6.9	14.1	6.26	0.030	3.61	-9.98	-69.6	0.37
GW42	1988 D											6.90					
GW42	1989 W											7.50					

Table 2. The results of the minimum, maximum and average concentrations of boron values in groundwater.

Sample No	Boron (ppm)		
	Average	Minimum	Maximum
GW1	0.34	0.03	0.66
GW2	0.31	0.08	0.52
GW3	0.49	0.39	0.54
GW4	0.21	0.10	0.46
GW5	0.22	0.10	0.53
GW6	0.83	0.78	0.89
GW7	0.71	0.50	0.96
GW8	1.10	0.98	1.23
GW9	1.36	0.92	1.80
GW10	1.39	1.18	1.60
GW11	0.57	0.06	0.89
GW12	1.48	0.68	1.86
GW13	0.50	0.00	1.00
GW14	1.38	1.35	1.43
GW15	1.76	1.64	1.93
GW16	0.97	0.00	1.60
GW17	0.85	0.00	1.66
GW18	1.18	0.48	2.94
GW19	1.55	0.50	4.30
GW21	0.90	0.51	1.23
GW22	1.54	0.40	1.04
GW22	0.53	0.51	0.55
GW23	0.41	0.08	0.79
GW24	0.57	0.57	0.57
GW25	0.45	0.42	0.49
GW26	0.93	0.29	1.58
GW27	0.93	0.50	1.35
GW28	0.87	0.38	1.24
GW29	0.74	0.24	1.17
GW30	0.80	0.38	1.22
GW31	0.36	0.02	0.81
GW32	0.48	0.22	0.71
GW33	0.79	0.38	1.21
GW34	0.87	0.28	1.86
GW36	0.73	0.42	1.40
GW37	0.81	0.29	1.46
GW38	0.52	0.50	1.21
GW39	0.41	0.09	0.89
GW40	0.46	0.02	0.96
GW41	6.09	3.95	7.82
GW42	6.91	6.90	7.50

Increase in pH value of groundwater may facilitate the mobilization of boron, locally (Demirtas 2006). Multiple correlation analysis was computed by Excel and the relationships between ions of groundwater samples were denoted on the wet (Tables 3a and b) and the dry periods (Tables 3c and d). Boron shows a strong positive correlation with sodium in groundwater.

The dissolution of sulfate mineral increased during the wet period. Concordantly, the correlation coefficients (r) of SO_4 with Ca and Mg were 0.84 and 0.91 for the wet periods. The correlation coefficients between Na and B in the wet season were eventually higher ($r = 0.92$) than the dry season ($r < 0.50$) as a result of increasing solubility by rainfall. Based upon all of analytical results of groundwater samples showed that boron concentration has increased since 1989 (Fig. 4); in particular, the years between 1990 and 1999, B concentrations increased 2.5 to 10 times higher from the initial concentrations in groundwater (except for GW2, GW14 GW22) at the Seyitgazi Plain. The arsenic concentration also increased in groundwater which exceeded the allowable limit of 10 $\mu g\ l^{-1}$ (EPA 2001) in the 14 wells out of 16 (Table 1). There is a strong correlation between arsenic, strontium and boron concentrations both in the wet and dry periods (Tables 3b and d). Arsenic concentrations are 25 $\mu g\ l^{-1}$ in the Seydisuyu stream, 26 $\mu g\ l^{-1}$ in the public water-supply system and 30 $\mu g\ l^{-1}$ in the well no. GW41 that are higher than the allowable limit for drinking purposes. The previous studies have also revealed that As and Sr concentrations in water resources around boron deposit areas are generally higher (Helvaci and Alonso 2000; Helvaci et al. 2004; Gemici et al. 2008; Zheng and Liu 2009).

A borax mine is located in the catchment area of the Catören and Kunduzlar dams. Boron is leached from the mine through rainwater and discharges into streams which recharge the lake at the Catören dam. Irrigation canals in the study area were constructed to provide irrigation water for the Seyitgazi Plain. Thus, water comes from Catören and Kunduzlar dams are conveyed via canals to the Seyitgazi Plain for irrigation. However, water high in boron content is infiltrated into aquifer system in the Seyitgazi Plain. Eventually, the boron level in groundwater in some parts of Seyitgazi Plain exceeds the recommended limit for irrigation purposes (10 $\mu g\ l^{-1}$, EPA 2001) due to percolation of the Catören reservoir's water into groundwater. For this reason, the boron concentration in groundwater of the Seyitgazi Plain has increased since 1989 and is still increasing in both catchment and disharge areas due to haphazard deposition of borate waste at the tailing of the mine site. As a result, most of the groundwater samples were over than the allowable boron limits for irrigation and drinking purposes according to the WHO, 2006. Particularly, the boron concentration in the wells, GW34, GW35, GW36, GW38, GW39 and GW40, increased up to three times, or even four higher than the initial concentration in consistence with the location of filtered shallow levels in the water wells (Fig. 5). However, boron concentrations in the wells, GW19 and GW20 which their filtered level were installed in relatively deeper depth, also increased in time due to the over-exploitation even. On the other hand, none of the deep wells at the Seyitgazi Plain were cut in boron bearing layers. Therefore, the high boron content of groundwater at the Seyitgazi Plain was sourced from irrigation water recharged by the Catören dam. As a result, boron increment in the groundwater in the Seyitgazi Plain was due to the infiltration of irrigation water provided from the Catören dam with a higher boron concentration.

Mineral equilibrium coefficients are a useful key for predicting the presence of reactive minerals and estimating mineral reactivity for future in a groundwater system. By using the saturation indices, one can easily predict the reactive minerals in host rocks, mineral dissolution and precipitation rates from the chemical analytical results of groundwater without examining on rock samples (Deutsch 1997). According to saturation index approach, groundwater was

Table 3a. Correlation values of groundwater (wet period) (2002 - 2007) (n = 7) (values less than 0.5 were omitted).

	pH	EC	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}
Na^+		0.92								
Ca^{++}		0.82	0.54	0.51						
Mg^{++}	0.67	0.60			0.51					
CO_3^{--}	0.97					0.70				
HCO_3^-			0.58							
Cl^-	0.96					0.81	0.97			
SO_4^{--}		0.95	0.79		0.84	0.76			0.50	
Bor		0.91	0.92		0.69			0.65		0.74

Table 3b. Correlation values of groundwater (wet period) (2007) (n = 5) (values less than 0.5 were omitted).

	pH	EC	Na^+	K^+	Ca^{++}	Mg^{++}	HCO_3^-	Cl^-	Bor	As
Na^+	0.58	0.94								
Ca^{++}		0.87	0.65	0.77						
Mg^{++}		0.57	0.58							
HCO_3^-						0.70				
Cl^-	0.56	0.93	0.87	0.54	0.87					
SO_4^{--}		0.99	0.90		0.91			0.96		
As						0.67	0.52		0.86	
Sr									0.99	0.80

Table 3c. Correlation values of groundwater (dry period) (2001 - 2007) (n = 66) (values less than 0.5 were omitted).

	pH	EC	Na^+	Ca^{++}
Na^+		0.56		
Ca^{++}		0.73		
Mg^{++}		0.50		
CO_3^{--}	0.56			
HCO_3^-			0.56	
SO_4--		0.84		0.68

Table 3d. Correlation values of groundwater (dry period) (2007) (n = 5) (values less than 0.5 were omitted).

	pH	EC	Na^+	K^+	Ca^{++}	Mg^{++}	HCO_3^-	Cl^-	Bor
Na^+		0.87							
Ca^{++}		0.77							
HCO_3^-						0.86			
Cl^-		0.81	0.84	0.66					
SO_4^{--}		0.96	0.72	0.60	0.86			0.79	
Bor	0.59					0.68	0.51		
As	0.72					0.57			0.98
Sr	0.69					0.62			0.99

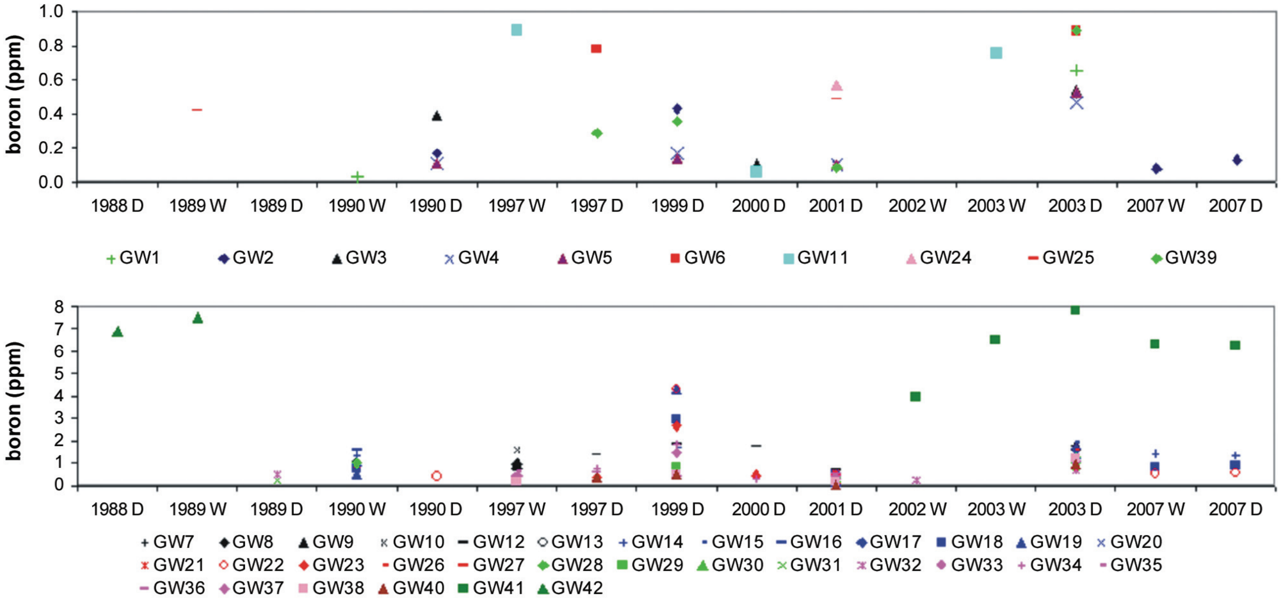


Fig. 4. Boron variations of groundwater in time.

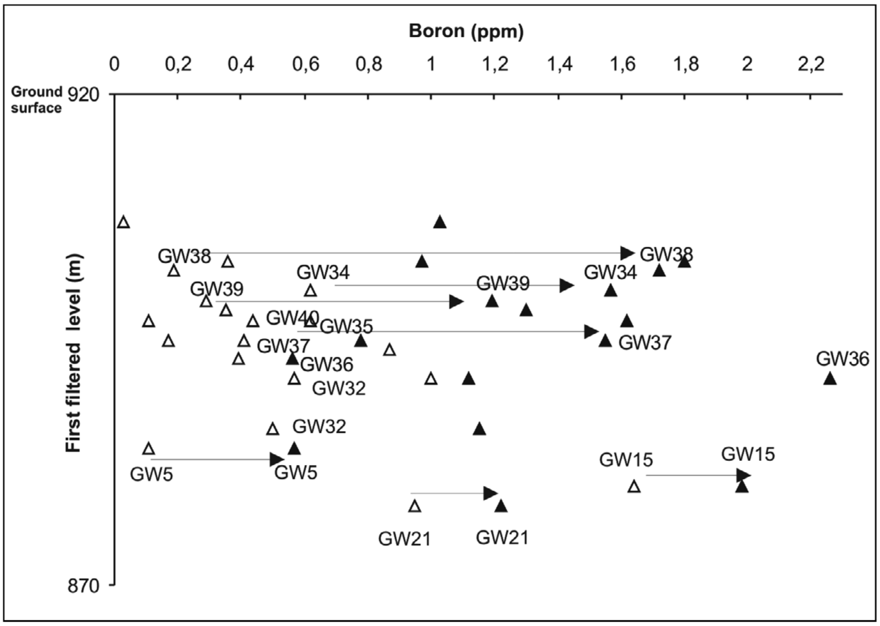


Fig. 5. Boron concentration as a function of time for first filtered level (modified from Ugurluoglu 2004). △: initial boron concentrations of groundwater when boreholes were drilled; ▲: boron concentrations in 2003 (August/September); ——►: relative boron increment rate.

almost supersaturated with respect to calcite and dolomite at the sampling temperatures (Fig. 6a). However, gypsum and anhydrite were under-saturated at the discharge temperature (Fig. 6b).

4.2 Surface Water

A total of 102 surface water samples were collected from the 15 different locations in the study area. Previous (1971 - 2003) and relatively recent (2007) analytical results of surface water samples are given in Table 4 respectively. The minimum, maximum and average boron concentrations in surface waters are presented in Table 5. The minimum and maximum boron concentrations in the surface water ranged from 0.04 to 68 ppm. The highest boron concentration was found at location SW5 by 68 ppm. It is obvious that the boron concentration has increased since 1999 (Fig. 7). Paralleling the boron increase, the arsenic concentration in surface water was also higher than allowable limits for drinking water according to TS 266 (Table 4). This higher arsenic concentration in surface water was most probably due to the dissolution of realgar and orpiment minerals in Na-borate ore-deposit in the study area. Statistical analytical results of major ion and boron concentration of water were given in Tables 6a and c for the wet and dry seasons (Table 6b). Surface water results are in agreement with those from groundwater results and show a strong positive correlation of boron with Na for the both periods.

Boron concentrations in surface water and groundwater decreased with an increase in the distance from the borate mine area, and concentrations in the dry period were much higher than those in the wet period (Fig. 8).

4.3 Groundwater-Surface Water Interaction

Boron concentrations increased to 7 ppm in the Karaören stream (SW3) as a result of the discharge of solid waste of Na-borate which was rapidly dissolved by the rainfall. The boron values in SW6 and SW7 were highly elevated in 2007. The average and maximum boron values in the samples taken from the discharge water of Catören Dam were 6.43 and 9.71 ppm, respectively (Table 5). Whereas those values were 1.69 and 2.58 ppm in the sample from discharge of the Kunduzlar Dam (SW12). The average boron value in the water at the meeting point of these two dams' reservoirs (SW13), which forms the Seydisuyu River, was observed as 3.56 ppm (maximum 6.20 ppm). The Seydisuyu River runs

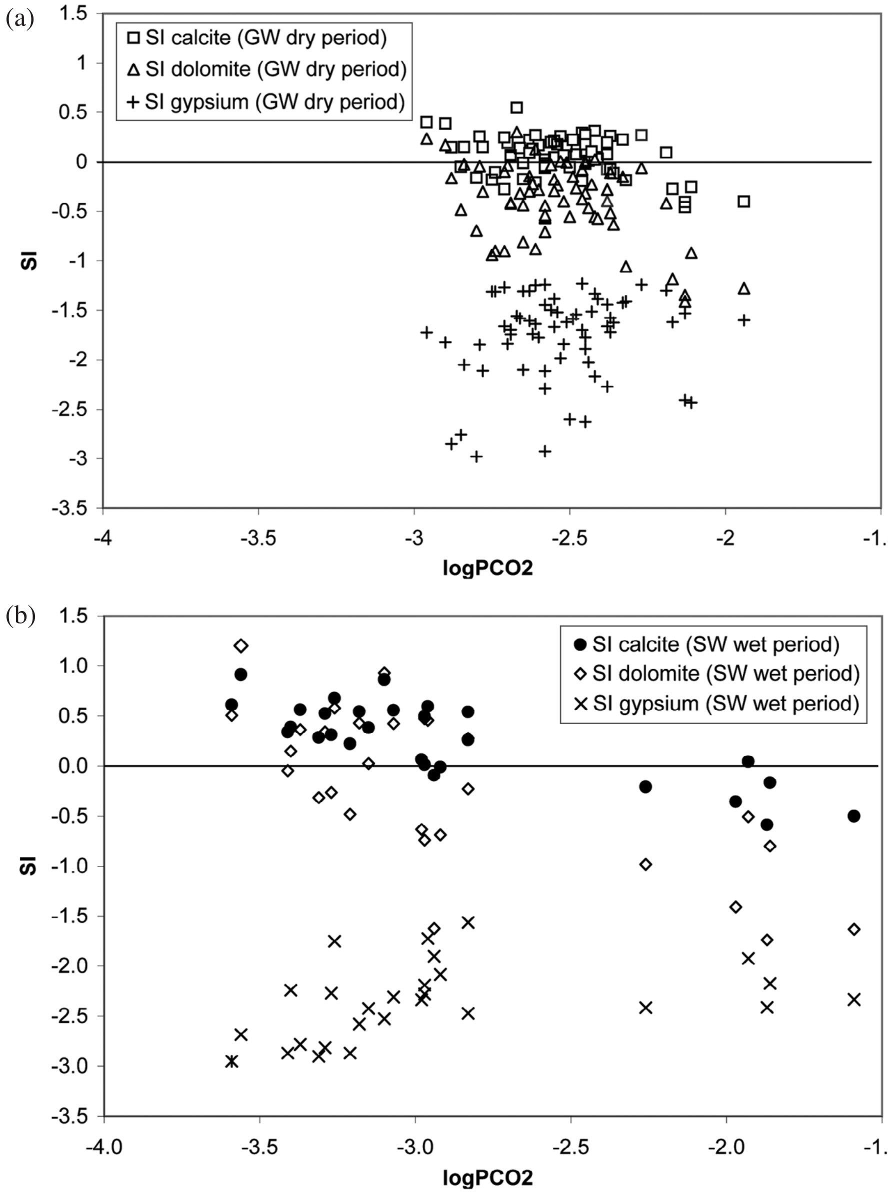


Fig. 6. (a) Chemical equilibrium of groundwater samples on saturation diagram showing relative mineral saturations in wet period. (b) Chemical equilibrium of surfacewater samples on saturation diagram showing relative mineral saturations in wet period.

Table 4. Analytical results of surfacewater samples.

No	Sampling Date	pH	EC mho/cm	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	B	As	Sr	$\delta^{18}O$	δD	T
SW1	2002 W	8.20	510	7.6	5.9	72.1	18.2	6.0	237.9	10.7	56.6	0.56					
SW1	2003 W	8.10	320	5.6	4.2	60.3	6.8	10.8	178.1	11.7	14.9	1.20					
SW1	2003 D	8.23	335	7.3	5.8	54.1	10.8	18.0	172.3	17.3	6.8	1.58					
SW2	2002 W	8.40	520	6.4	5.9	68.1	14.6	18.0	176.9	14.2	54.2	0.64					
SW2	2003 W	8.08	242	5.1	2.9	41.9	6.9	3.6	145.2	11.7	6.0	1.33					
SW2	2003 D	8.10	390	8.8	4.0	54.9	12.1	12.8	180.7	18.2	6.8	1.85					
SW3	2002 W	8.40	520	8.5	7.8	73.1	15.2	18.0	262.3	14.2	8.2	0.68					
SW3	2003 W	8.00	268	6.7	5.5	45.9	6.9	4.8	159.8	13.9	5.9	1.35					
SW3	2003 D	8.18	303	14.8	7.9	43.1	9.1	18.0	152.5	18.6	5.8	2.06					
SW3	2007 W	7.27	448	8.3	5.3	57.5	14.8	8.5	261.3	1.4	0.2	0.04	0.007	0.23	-9.45	-65.74	4.62
SW3	2007 D	8.17	350	12.7	5.1	32.8	15.9	9.3	182.4	7.5	17.6	6.85	0.020	0.76	-6.7	-52.91	5.78
SW4	2002 W	8.10	520	6.0	3.5	71.1	13.4	12.0	244.0	14.2	9.6	1.09					
SW4	2003 W	8.04	266	6.0	2.9	42.7	10.3	4.8	161.0	11.7	8.9	2.14					
SW4	2003 D	7.95	365	9.5	3.4	53.1	16.4	21.0	201.3	12.4	7.2	4.36					
SW5	1971 W											18.75					
SW5	1979 W											68.00					
SW5	1979 D											58.90					
SW5	1980 W											56.50					
SW5	1980 D											57.00					
SW5	1989 W											22.80					
SW5	2002 W	8.20	480	9.4	3.1	55.1	21.3	24.0	213.5	10.7	18.7	1.38					
SW5	2003 W	8.10	348	5.4	3.7	61.5	10.7	7.2	206.2	18.1	7.2	2.47					
SW5	2003 D	8.15	378	7.1	4.1	59.6	15.5	21.0	196.7	22.2	5.5	4.19					
SW6	2003 W	8.70	390	37.6	4.5	44.1	9.7	72.0	91.5	15.1	20.4	24.03					
SW6	2003 D	8.40	593	56.8	9.0	56.9	21.9	42.0	274.5	35.1	21.7	31.11					
SW6	2007 W	7.31	643	36.8	5.8	60.5	27.3	0.0	390.2	10.4	25.0	36.05	0.075	2.92	-9.4	-65.63	1.65
SW7	1988 K											1.80					
SW7	1989 W											2.25					
SW7	1999 W											7.80					
SW7	2000 W											3.12					
SW7	2000 D											3.75					
SW7	2001 D	7.65	533	14.2	4.9	66.6	21.9	6.0	195.2	27.1	81.8	3.94					
SW7	2002 W	8.00	583	42.1	6.0	65.8	15.4	34.0	172.8	20.2	96.0	19.73					
SW7	2002 D	8.54	418	17.0	5.7	50.5	13.4	10.8	197.6	17.1	20.4	5.55					
SW7	2003 W	8.74	410	41.2	5.3	46.5	13.6	55.2	164.7	22.7	9.0	18.25					
SW7	2003 D	8.30	323	20.0	6.4	44.9	8.8	28.5	143.4	20.4	5.8	28.98					
SW7	2007 W	6.99	574	26.9	5.0	62.7	20.4	0.0	340.6	8.4	15.8	19.48	0.056	2.38	-9.25	-65.97	2.64
SW8	2001 D	8.34	440	15.9	6.5	43.7	20.8	15.8	122.7	22.7	75.4	4.21					
SW8	2002 W	8.43	333	13.6	5.5	41.3	11.0	23.0	120.0	15.1	26.1	5.42					
SW8	2002 D	8.74	338	16.1	5.9	38.6	9.8	15.6	114.1	20.1	30.0	5.43					
SW8	2003 W	8.48	320	17.6	6.1	42.7	10.8	19.8	159.8	18.5	6.7	8.76					
SW8	2003 D	8.46	290	16.5	5.8	39.1	7.5	28.5	123.6	16.6	4.3	9.85					
SW8	2007 W	7.52	396	15.0	4.8	48.6	15.8	0.0	247.7	6.9	14.9	5.52	0.018	0.67	-9.86	-55.92	5.16
SW9	1988 D											4.80					
SW9	1989 W											3.20					
SW9	2000 W											4.17					

Table 4. (Continued)

No	Sampling Date	pH	EC mho/cm	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	B	As	Sr	$\delta^{18}O$	δD	T
SW9	2000 D											1.87					
SW9	2001 D	8.18	413	10.8	5.4	43.9	21.7	10.5	157.1	16.4	57.3	3.60					
SW9	2002 W	7.97	337	12.8	5.2	44.1	13.2	14.0	138.3	18.3	34.7	5.35					
SW9	2002 D	8.36	398	14.7	5.6	41.9	15.4	10.8	154.9	26.3	24.0	5.68					
SW9	2003 W	8.28	386	15.1	5.3	55.3	14.4	13.2	212.3	16.3	17.0	7.84					
SW9	2003 D	8.13	343	18.7	5.7	43.6	12.8	16.5	176.9	21.3	6.4	9.71					
SW10	1971 W											0.50					
SW10	1979 Y											2.50					
SW10	1979 K											2.36					
SW10	1980 Y											3.98					
SW10	1980 K											2.50					
SW10	1988 K											2.90					
SW10	1989 Y											3.30					
SW10	2001 K	8.13	515	7.5	4.5	52.9	30.4	12.0	176.9	19.6	82.9	2.27					
SW10	2002 Y	7.90	423	6.1	3.9	53.4	16.2	4.0	170.8	17.8	44.8	1.77					
SW10	2002 K	8.30	478	7.3	4.9	63.9	15.2	9.6	202.5	19.5	33.1	0.76					
SW10	2002 Y	7.20	480	6.2	4.7	62.1	20.7	12.0	244.0	10.7	23.5	2.72					
SW10	2003 Y	8.24	316	5.3	4.0	50.5	11.4	14.1	158.6	16.0	13.1	2.70					
SW10	2003 K	8.00	385	10.3	5.5	58.9	14.8	13.5	201.3	29.8	7.3	3.39					
SW11	1986 W											1.95					
SW11	1988 D											2.50					
SW11	1989 W											2.65					
SW11	2000 W											1.25					
SW11	2000 D											0.41					
SW11	2001 D	8.51	334	8.9	5.0	35.1	17.2	17.3	110.6	16.4	40.0	1.53					
SW11	2002 W	8.30	297	7.3	4.0	45.3	8.0	11.0	132.2	13.0	21.0	0.92					
SW11	2002 D	8.70	336	6.2	4.5	47.6	11.5	12.6	151.9	17.6	14.4	1.17					
SW11	2003 W	8.63	267	6.8	4.4	41.3	10.0	18.0	131.2	15.3	5.2	2.21					
SW11	2003 D	8.28	249	6.5	4.4	40.4	8.1	15.0	125.8	15.3	4.0	2.75					
SW12	1999 W											1.80					
SW12	2000 W											1.04					
SW12	2000 D											0.62					
SW12	2001 D	8.85	298	8.7	4.9	29.3	18.6	24.0	100.7	15.5	29.0	1.39					
SW12	2002 W	8.03	297	5.3	3.5	43.8	10.5	10.0	142.3	11.3	18.6	1.27					
SW12	2002 D	8.46	324	8.4	4.8	40.9	12.3	8.4	150.1	17.0	15.2	1.19					
SW12	2003 W	8.40	306	7.0	4.3	46.5	12.3	14.4	164.7	16.0	5.5	2.18					
SW12	2003 D	8.20	258	7.3	4.4	39.1	9.3	13.5	131.2	16.0	4.4	2.58					
SW12	2007 W	7.14	330	8.2	4.2	44.8	14.1	0.0	216.7	3.8	10.8	1.52	0.036	0.57	-7.36	-61.21	4.62
SW13	1999 W											8.00					
SW13	2000 W											2.08					
SW13	2000 D											2.50					
SW13	2001 D	8.38	378	9.6	5.4	37.4	18.1	10.5	129.6	17.3	45.2	2.25					
SW13	2002 W	8.00	313	6.9	3.8	45.8	9.3	10.0	134.2	13.0	26.2	1.84					
SW13	2002 D	8.36	368	11.6	5.3	45.1	13.3	10.8	147.6	30.6	16.3	2.55					
SW13	2003 W	8.34	340	10.0	4.9	50.5	13.9	16.8	184.2	16.0	9.1	4.97					
SW13	2003 D	8.08	295	9.4	5.0	45.1	10.6	10.5	161.7	19.1	5.9	6.20					

Table 4. (Continued)

No	Sampling Date	pH	EC mho/cm	Na^+	K^+	Ca^{++}	Mg^{++}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	B	As	Sr	$\delta^{18}O$	δD	T
SW14	2001 D	8.30	387	11.6	6.4	37.4	18.8	16.0	176.9	17.1	8.2	3.04					
SW14	2002 W	8.20	270	9.4	2.3	46.1	7.3	0.0	109.8	12.4	58.6	1.91					
SW14	2002 D	8.13	390	13.9	5.4	44.8	11.5	10.0	144.4	25.5	24.5	2.69					
SW14	2003 W	8.30	340	5.8	3.9	42.1	6.1	13.5	122.0	14.2	4.8	2.30					
SW14	2003 D	8.08	308	13.3	5.2	43.4	10.9	12.0	161.7	22.2	4.7	5.04					
SW15	2001 D	8.27	370	11.1	5.6	36.8	17.0	16.0	166.7	18.4	3.7	3.04					
SW15	2002 W	7.90	260	9.4	2.3	51.1	2.4	0.0	122.0	12.4	41.8	1.83					
SW15	2002 D	8.30	343	13.9	5.2	40.8	11.5	10.0	126.1	28.4	25.1	2.23					
SW15	2003 W	8.40	350	6.9	4.3	40.1	9.7	15.0	115.3	24.9	5.8	3.55					
SW15	2003 D	8.33	278	13.4	5.2	43.9	6.4	16.5	135.7	20.0	4.4	5.62					

Table 5. The results of the minimum, maximum and average concentrations of boron values in surface water (average values were calculated from different analytical results of the pertinent samples).

Sample No	Boron (ppm)				Sample No	Boron (ppm)			
	Average	Minimum	Maximum	n		Average	Minimum	Maximum	n
SW1	1.11	0.56	1.58	3	SW9	6.43	3.60	9.71	9
SW2	1.27	0.64	1.85	3	SW10	2.27	0.76	3.39	13
SW3	2.20	0.04	6.85	5	SW11	1.72	0.92	2.75	10
SW4	2.53	1.09	4.36	3	SW12	1.69	1.19	2.58	9
SW5	2.68	1.38	4.19	9	SW13	3.56	1.84	6.20	8
SW6	30.40	24.03	36.05	3	SW14	3.00	1.91	5.04	5
SW7	15.99	3.94	28.98	11	SW15	3.26	1.83	5.62	5
SW8	6.53	4.21	9.85	6					

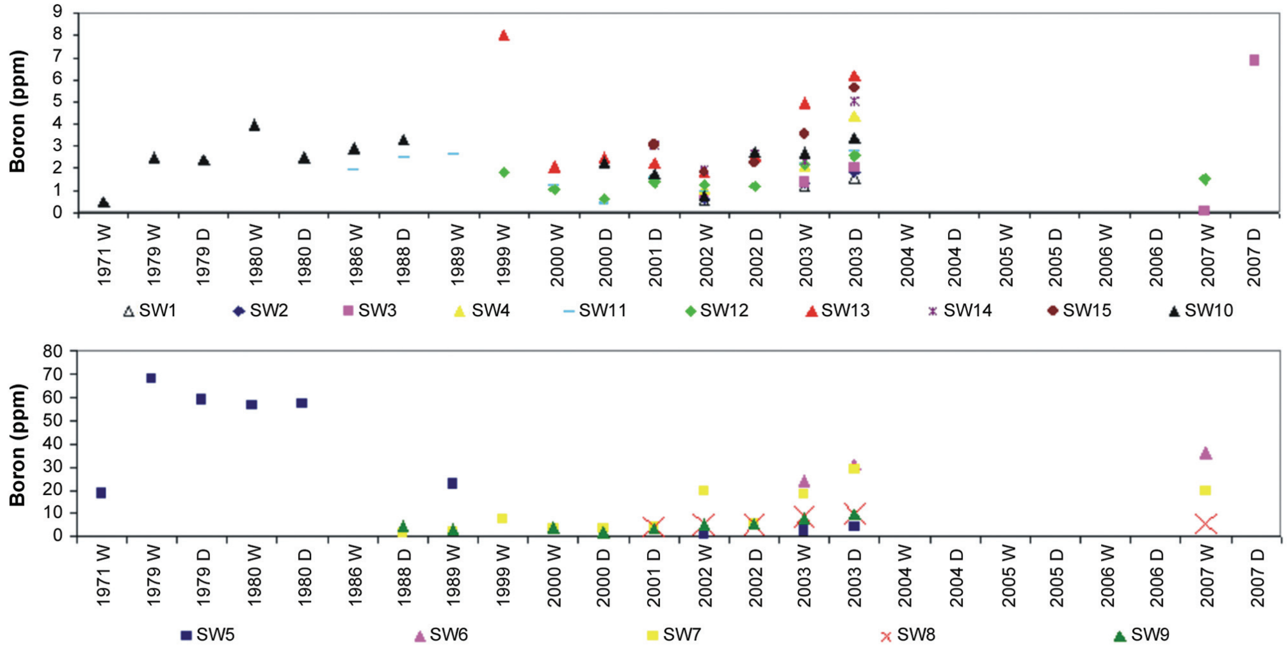


Fig. 7. Boron variations of surface water in time.

Table 6a. Correlation values of surfacewater (2001 - 2007) (wet period) (n = 35) (values less than 0.5 were omitted).

	pH	**EC**	**Na^+**	**Ca^{++}**	**Mg^{++}**
K^+		0.54			
Ca^{++}		0.78			
Mg^{++}		0.82		0.53	
CO_3^{--}			0.57		
HCO_3^-		0.74		0.65	0.81
Cl^-	0.67				
SO_4^{--}					
Bor		0.51	0.91		

Table 6b. Correlation values of surfacewater (2001 - 2007) (dry period) (n = 34) (values less than 0.5 were omitted).

	EC	**Na^+**	**K^+**	**Ca^{++}**	**Mg^{++}**	**CO_3^{--}**
Na^+						
K^+		0.77				
Ca^{++}	0.61					
Mg^{++}	0.77					
CO_3^{--}		0.67	0.52			
HCO_3^-	0.67			0.71		
Cl^-		0.53				
SO_4^{--}	0.63				0.75	
Bor		0.82	0.59			0.74

Table 6c. Correlation values of surfacewater (2007) (wet period) (n = 5) (values less than 0.5 were omitted).

	pH	**EC**	**Na^+**	**K^+**	**Ca^{++}**	**Mg^{++}**	**CO_3^{--}**	**Cl^-**	**SO_4^{--}**	**Bor**
Na^+	0.69									
Ca^{++}		0.86		0.79						
Mg^{++}		0.63		0.56	0.80					
CO_3^{--}	0.96		0.77							
HCO_3^-		0.59		0.72	0.85	0.97				
Cl^-	0.76		0.95				0.77			
SO_4^{--}			0.78					0.90		
Bor	0.58		0.97				0.67	0.86	0.70	
As							0.63			
Sr	0.57		0.98				0.68	0.87	0.70	0.99

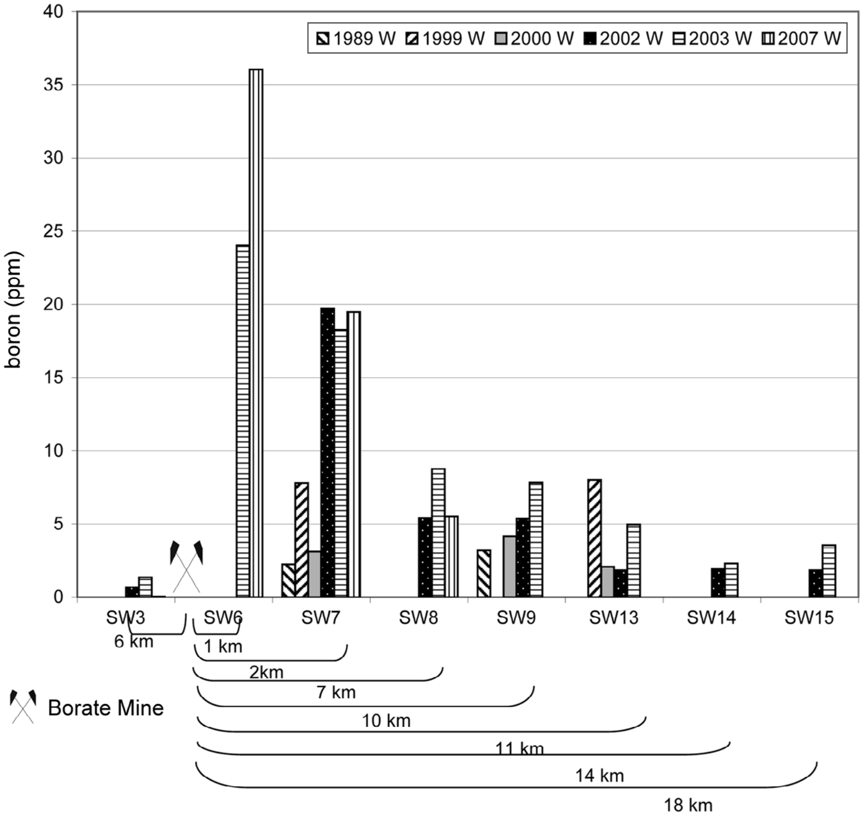


Fig. 8. Boron variations in distance from the Na-borate mine.

to the Kesenler regulator (Fig. 1) where the water is diverted into two irrigation canals as the right and left side (SW14 and SW15, respectively) on the Seyitgazi Plain. The average and maximum boron concentrations of surface water in the approach to the Seyitgazi Plain were 3 and 5 ppm in SW14 and 3.26 and 5.62 ppm in SW15, respectively. Thus, the boron concentration in the surface water at the discharge area of the Na-borate mine has been affected.

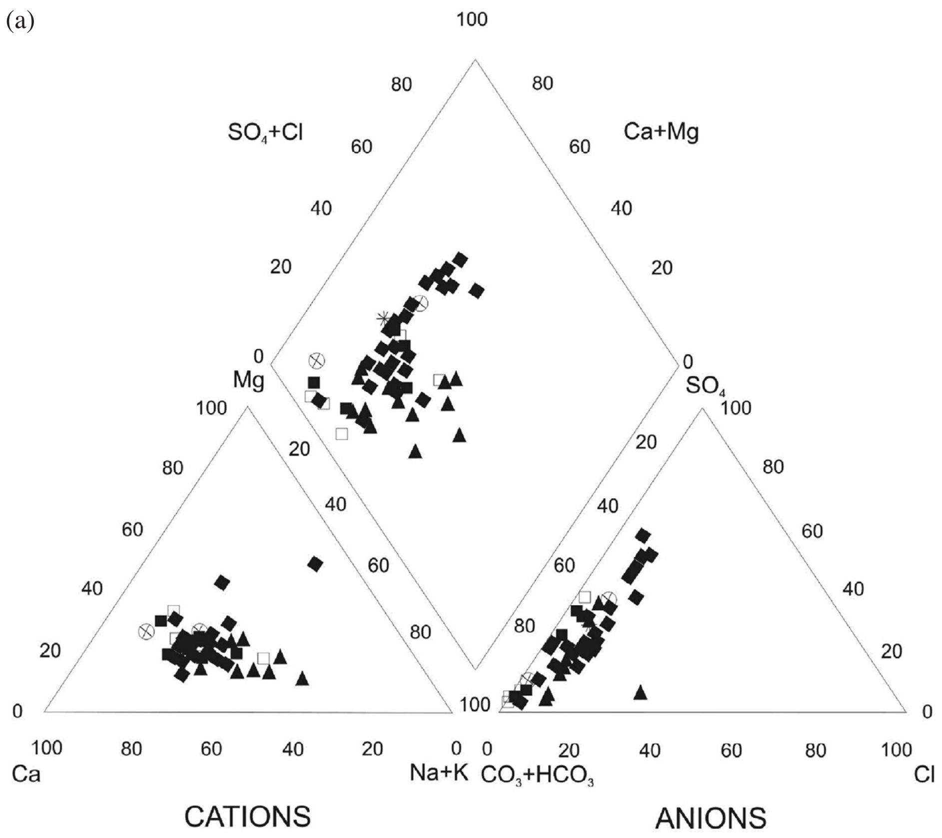
Both ground and surface water in the study area are generally of a Ca-HCO_3 type (Figs. 9a and b). Significant positive correlation was found between boron and arsenic and strontium in both for surface water and groundwater (Figs. 10a and b). Because arsenic and strontium salts are generally found in the same playa lake (i.e., Kirka borax province) as associated with boron. The positive correlation shows that increasing concentrations of one constituent are associated with increasing concentrations of another constituent and they may migrate under similar conditions (Senior and Sloto 2006). Boron concentration in water samples taken from the catchment area, SW7, SW8, SW9, SW12, SW13, SW14 and SW15, increased in the different rates (between 2 and 7 times) from the dry period of 2001 to the dry period of 2003. Parallel to the boron increase in surface water, boron also elevated in the dry period between 2001 and 2003. This may be indicative of the groundwater-surface water interaction in the study area. On the other hand, arsenic concentrations in surface water were in higher concentrations up to 0.075 ppm that is 7.5 times higher than the allowable limit for drinking water, given by WHO, EPA and TS 266.

4.3.1 Stable Isotopes and Tritium

Isotope samples were collected from the study area to determine relationships between groundwater and surface water as well as to identify that of recharge and discharge. The $\delta^{18}O$ values of the groundwater have varied from -8.66 to -9.86‰ for the wet season and from -9.02 to -9.98‰ for the dry season. However, there is a slight deviation in stable isotope values of surface water (in SW3) in the dry season due to the enrichment by the evaporation. The evaporation effect has also been seen for SW8 and SW12 even in the wet season (Fig. 11). In contrast to general expectations, groundwater at the Seyitgazi Plain has slightly more negative stable isotope values (GW22, GW18, GW14) in the dry period in comparision with those of the wet period. Given the seasonal variation in stable isotope values of groundwater, relatively positive values in the wet period may be due to the influence of surface water which infiltrated into the shallow aquifer system from the previous irrigation season (in the dry period) and that water from the lake of the Catören and Kunduzlar dams has more positive stable isotope values (SW8 and SW12) because of an evaporation effect (Fig. 11). However, above the Catören dam, surface water at the section of SW6 and SW7 are close to similar stable isotope values of groundwater at upstream (GW41) and downstream (GW2, GW14, GW18, GW22) areas (Tables 1 and 4). Tritium values of surface water are generally higher (between 4.62 and 5.78 T.U.) than that of groundwater which refer to a long residence time due to deep circulation at depth. Tritium values of surface water taken from SW6 and SW7, somehow, are of lower than aforementioned values for surface water. The lower tritium values at SW6 and SW7 (1.65 and 2.64 T.U.) may be due to the mixing of groundwater which has much lower tritium values. Possible interaction between groundwater and surface water at the upstream area of the dams are another alternative to explain high boron and arsenic concentrations in the dams' water besides directly leaching from boron disposal from the mining activites. The interaction of groundwater and surface water at SW7 and SW8 can also be seen in tritium - $\delta^{18}O$ and δD in Figs. 12a and b, respectively. One can easily recognize that all groundwater samples are almost clustered in the same area (icluding SW6 and SW7 at the some extent) which are distinctly plotted far from the surface water samples (SW3, SW8, SW8). In fact, stable isotope composition of groundwater at the Seyitgazi Plain during the dry season was expected to be notably enriched due to infiltration of irrigation water into the aquifer system. However, the enrichment in stable isotope values of groundwater at the Seyitgazi Plain was not strongly observed. Because, it is most possibly, irrigation water from the Catören dam was not available due to the extreme drought period in 2007. On the other hand, the stable isotope results of GW41 (located upstream of the Seyitgazi Plain), GW2, GW18 and GW22 (at the Seyitgazi Plain) have a similar stable isotope and tritium abundances. Therefore, this may imply that groundwater in the Seyitgazi Plain has been replenished from Kirka Province which is consistent with the conceptual model given in Fig. 2b.

5. CONCLUSIONS

The surface water and groundwater resources are contaminated by Na-borate mine activities in addition to the natural leaching from the boron-bearing formation at the catchment area of the study area. The analytical results of surface water and groundwater samples taken from the recharge and discharge areas demonstrate that boron concentrations have been increasing since 1989. The increasing boron concentration in the surface water is widely associated with the Na-borate mine, while the increase in groundwater is as a result of the utilization of surface water in a high boron concentration for irrigation purposes on the Seyitgazi Plain. The recent boron concentration in groundwater at Seyitgazi Plain is three-four times higher than initial boron contents (0.1 - 0.5 ppm). This higher boron content in the groundwater of the Seyitgazi Plain is mostly due to replenishment from surface water by the infiltration of irrigation water supplied



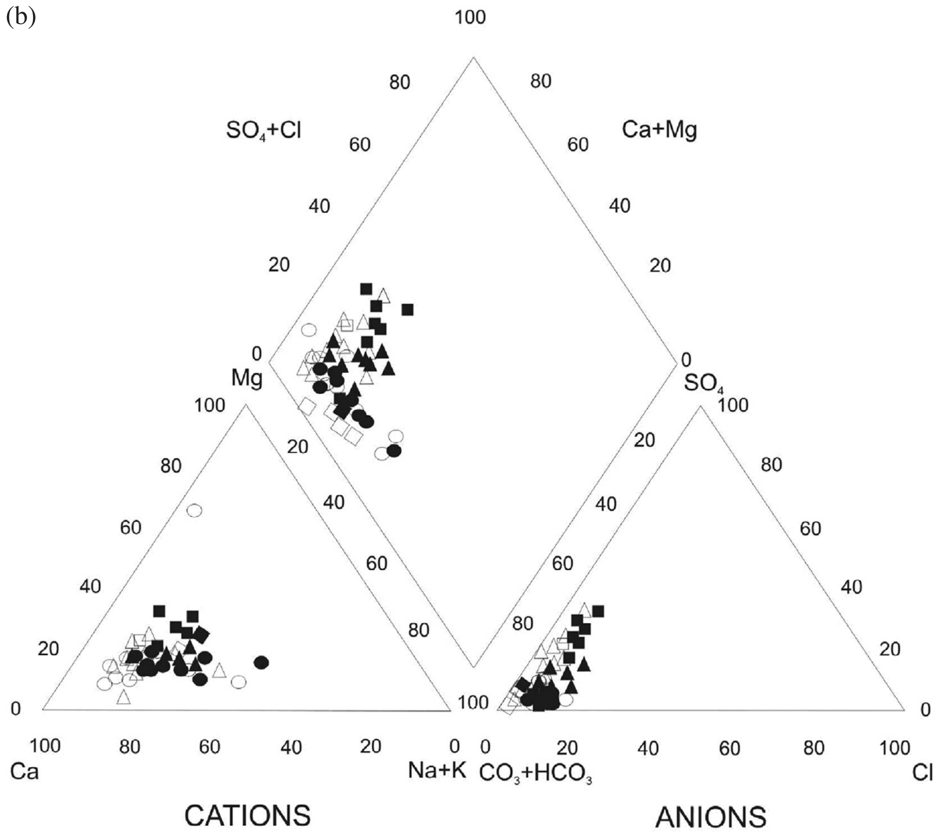


Fig. 9. (a) Piper diagram for groundwater. (b) Piper diagram for surfacewater.

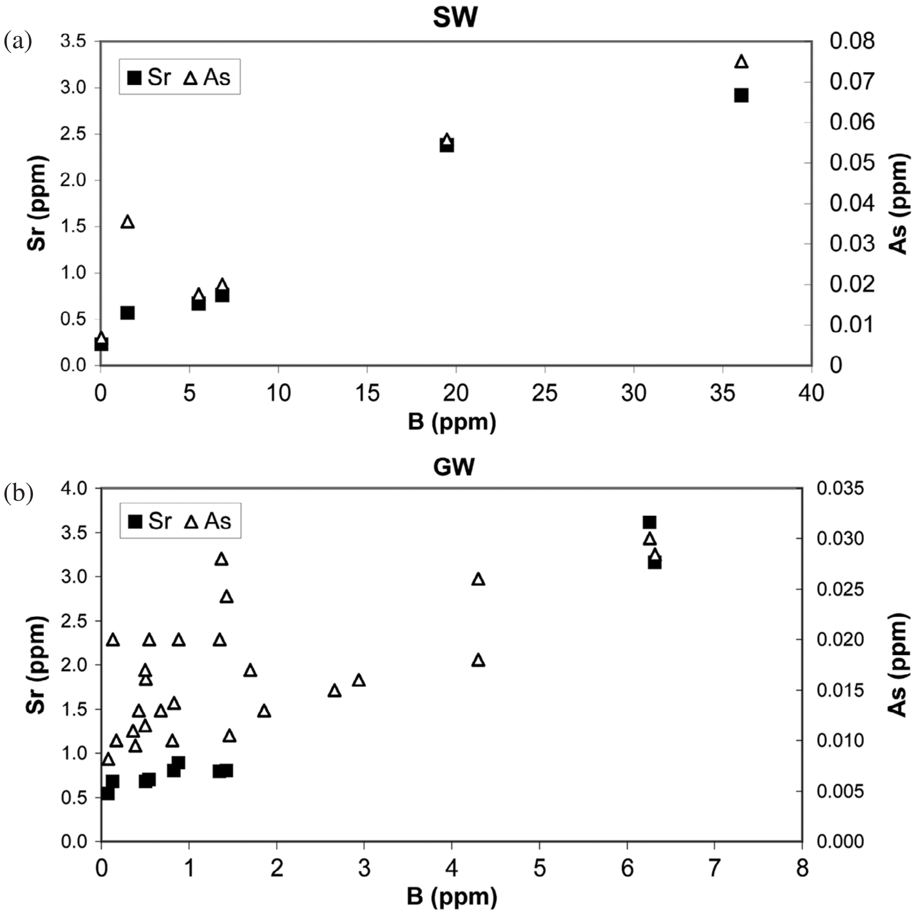


Fig. 10. (a) B-Sr-As graph for surface water. (b) B-Sr-As graph for groundwater.

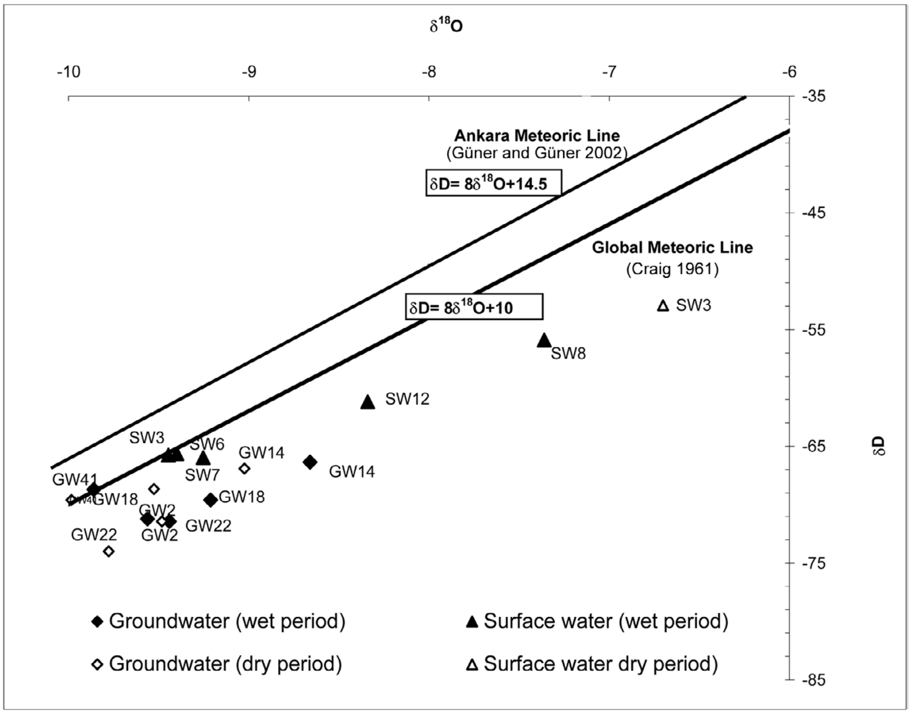


Fig. 11. $\delta^{18}O$-δD graph.

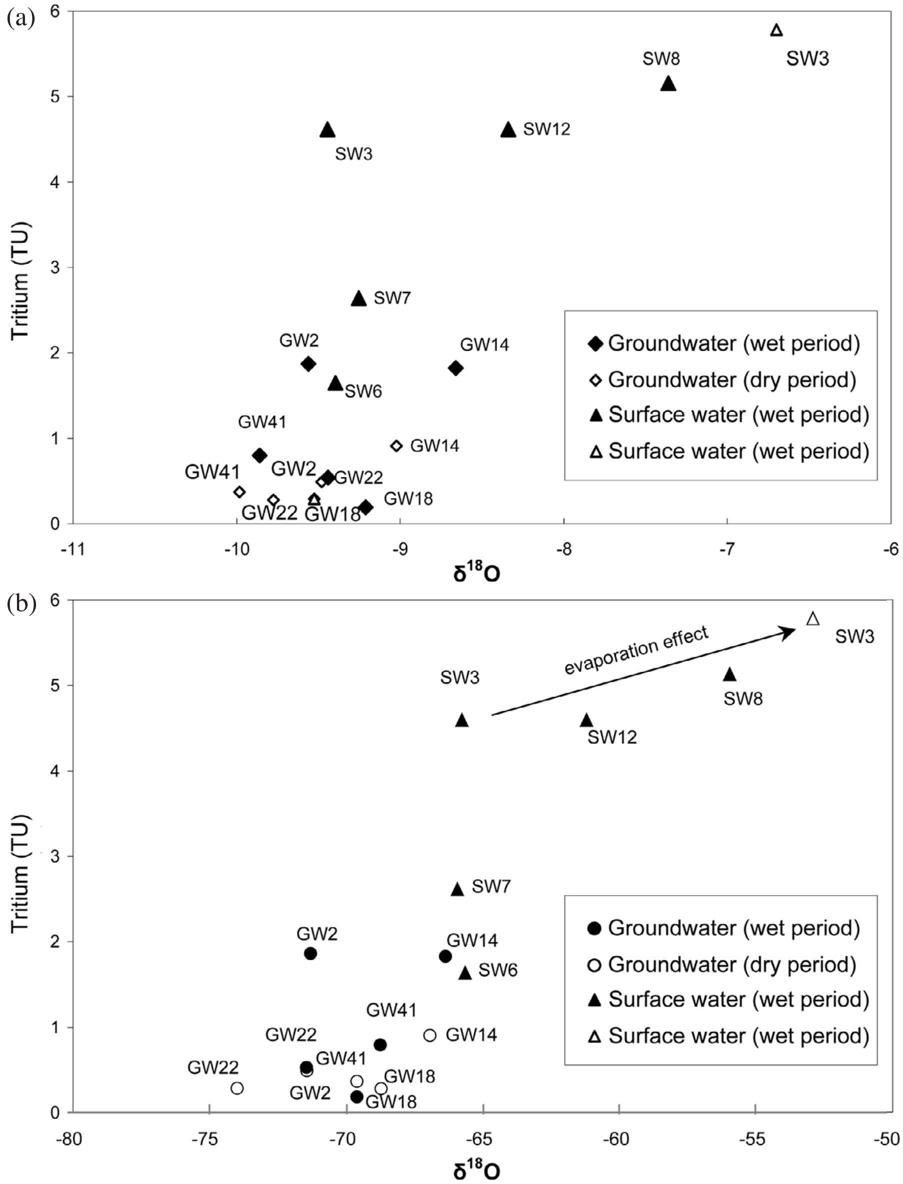


Fig. 12. (a) $\delta^{18}O$-^3H graph. (b) δD-^3H graph.

from the Catören dam located in the catchment area of the Seyitgazi Plain. Concordantly, between 2003 and 2007, boron concentration remarkably increased more than one ppm in groundwater in the Seyitgazi Plain. The boron concentration of the Seydisuyu River was also higher than the recommended limit for irrigation purposes which should be less than one ppm according to Ayers and Westcot (1976). High boron content in water resources in the study area are mostly related to the Na-borate mine activities at the Kirka Province. The arsenic concentration in the groundwater of the Seyitgazi Plain was also more than the allowable limit for drinking purpose which is recommended as 10 μg l^{-1} by EPA (2001). During the dry period, boron, arsenic and strontium contents in water were relatively higher than the wet period.

Groundwater in the study area is generally in Ca-HCO_3 type. The high pH value of water likely contributes to the mobilization of boron, locally. Irrigation from Catören dam's reservoir strongly affects the local geohydrochemical conditions and might be an important factor for boron mobilization in the study area.

Chemical analysis shows that the groundwater of the Seyitgazi Plain is influenced by the Na-borate mine activities in the catchment area. High boron concentration of surface water in the catchment area negatively affects the quality of groundwater of the Seyitgazi Plain by means of surface water-groundwater interaction since water with high boron content comes from the Catören dam used for irrigation purposes on the Seyitgazi Plain. Water-rock interaction within the Sarıkaya formation, which contains higher borate minerals, causes increasing boron concentrations in the groundwater in Kirka Province. Conformingly, the boron concentration reached up to 7.82 ppm in the deep well (GW41: 172 m) located near the Kirka boron mine area. After leaching Na-borate from the Kirka borate deposit, the disposal mine waste has been deposited in tailing areas next to the mine site. Since the mine waste has a higher boron content, it is readily dissolved in aquatic environment under the atmospheric condition (i.e., rain and snow). Eventually, this high boron-contained water is mixed with surface water (Özkurt 2000). Thus, boron concentration increases in the wet season in streams and creeks close to the tailing site. It is obvious that these streams and creeks recharge into the Catören dam's reservoir which is used for irrigation water on the Seyitgazi Plain. Because groundwater flow direction is from Kirka to Seyitgazi, it also contributes to the increase of boron content of the groundwater in the Seyitgazi Plain.

In conclusion, water coming from the Catören dam is recharged from the surface water in contact with the tailings of Kirka Na-borate mine. The groundwater flow direction from the Kirka to Seyitgazi Plain possibly contributes to the increase of boron content of the groundwater in the Seyitgazi Plain. Arsenic content in groundwater exceeds the WHO and EU limits for the safe drinking water standard (10 μg l^{-1}), especially for water from GW22 and GW26 at the discharge area of Kirka Province due to either naturally leached from tuff or boron-bearing formation. Isotope analytical results also confirm that groundwater at the Seyitgazi Plain are hydraulically linked with the ground water in Kirka Province. Therefore, any environmental contamination in the Kirka Province will affect the groundwater quality of the Seyitgazi Plain in addition to surface water influence. Periodically, water samples should be collected for monitoring boron and arsenic levels in the water resources as well as required precautions taken to prevent further water quality deterioration in the study area.

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