

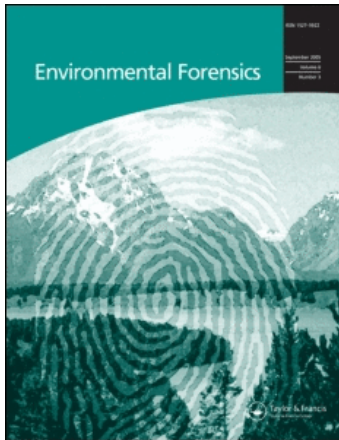
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Hydrochemical and Isotopic Composition of Tuzla Geothermal Field (Canakkale-Turkey) and its Environmental Impacts

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Tuzla is an active geothermal area located in northwestern Turkey, 80 km south of the city of Canakkale and 5 km from the Aegean Coast. Geothermal brine, deriving from this area, contains an abundance of NaCl and a water temperature of 173°C (T1 well at 814 m depth) is typically encountered. The aim of this study was to determine the hydrogeochemical properties of the geothermal brine using both chemical and isotopic data, and to investigate the origin of the geothermal brine in the Tuzla area and the environmental impacts of Tuzla Geothermal Field (TGF). Both geothermal brine and shallow groundwater in the area are of meteoric origin. Isotope results indicate that the hot saline waters (brine) in the Tuzla geothermal field originate from connate water along faults. As the saline water rises to the surface, it mixes with shallow groundwaters in various ratios. In addition, the high sodium (Na) and chloride (Cl) content in the Tuzla Stream, fed from the Tuzla geothermal brine during the dry season, cause an increase in sodium and chloride concentrations in the shallow groundwaters by infiltration into the aquifer. Moreover, salt accumulation on the surface is observed due to the uncontrolled artesian flow of geothermal brine, which adversely affects the salinity of shallow groundwater.

Keywords: Tuzla, geothermal fluid, hydrogeochemistry, oxygen-18, deuterium, tritium

Tuzla Geothermal Field (TGF) is located in northwestern Turkey, 80 km south of the city of Canakkale and 5 km from the Aegean Sea (Figure 1). Tuzla is an active geothermal area hosted by rhyolite lava and pyroclastic deposits. Geothermal brine is found in a shallow volcanic reservoir at a depth of between 330–350 m and a deep granite reservoir at a depth of 1,020 m (Vengosh et al., 2002). TGF is an interesting area in Turkey from the point of its temperature and dissolved ions in the water. At the surface, the waters reach temperatures between 32°C and 86°C. The chloride concentration of Tuzla geothermal brine reaches 68,256 mg/L, which is nearly twice the concentration of seawater, and is termed “brine” water. The total outflow of water from approximately 100 springs in the TGF field is estimated to be close to 50 L/s. The sodium and chloride concentrations reach up to 16,963 mg/L and 68,256 mg/L, respectively.

Geothermal studies on the TGF have been ongoing since 1966. The general geological and volcanological characteristics have been studied by Samilgil (1966), Erdogan (unpublished data, 1966 *MTA Report* [Geothermal energy possibility of survey and tectonic mapping of Tuzla hot springs and surrounding]), Urgun (1971), Ongur (unpublished data, 1973 *MTA Report*

[Volcanology and geological report of Canakkale Tuzla geothermal area, Ankara]), and Alpan (1975). Geophysical surveys were carried out by Demiroer (unpublished data, 1971 *MTA Report* [Resistivity survey of Tuzla-Kestanbol hot springs and surrounding]) and Ekingen (1972). Ten thermal gradient wells were drilled from 50–100 m depth in 1974 based on the result of geological and geophysical surveys. Temperatures of up to 145°C were observed at 50 m depth in some of these wells, and, due to vigorous boiling, blowouts were observed (Karamanderesi and Ongur, 1974). Two deep exploration wells (with a depth range of 814–1020 m) were drilled in 1982 and 1983. The reservoir depth is in the range of 333–553 m in volcanic rock with a temperature of 174°C, a production rate of 130 tonnes/hr, and steam fraction of 13%. The general characteristics of alteration in this field were described by Gevrek and Sener (1985). Hydrothermal alteration mineral assemblages indicate a geothermal fluid with temperatures of 150°C–220°C (Sener and Gevrek, 2000). Conformably, Mutlu and Gulec (1998) calculated the reservoir temperature of Tuzla to be between 187°C–212°C using different geothermometers (Table 1). The nature and origin of the thermal springs in the Tuzla area have been described by Mützenberg (1997). The environmental properties of the Tuzla geothermal field were described by Baba (2003), Baba and Ozcan (2004), and Baba et al. (2005). Tarcan (2005) emphasized that the Tuzla hot brine water has a high scaling tendency. According to previous studies, Tuzla geothermal brine originates from the dissolution of marine

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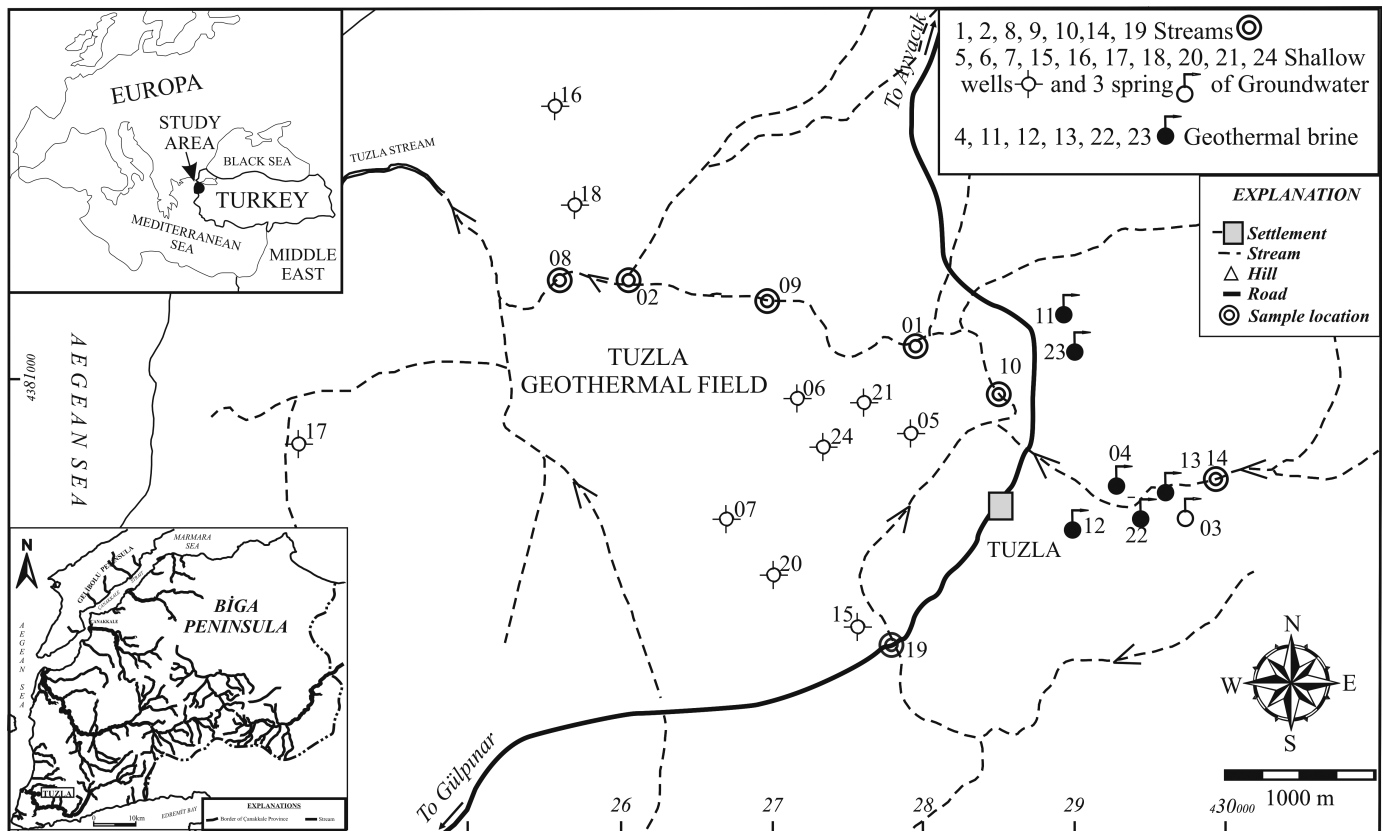


Figure 1. Location of Tuzla Geothermal Field.

evaporates and is formed by chemical alteration (dissolution of halite, dolomitization, reduction of sulphate, precipitation of anhydrite, diagenetic reactions of silicates, Ca and Na ion exchange and reactions with organic matter), which generates the higher mineralization. Alternate models for the origin of the TGF include derivation from relics of evaporated seawater trapped in sediments (Balderer, 1997; Mützenberg, 1997), dissolution of Messinian evaporites (Vengosh et al., 2002) and trapped relict seawater within pore spaces in rocks (Yalcin, 2007).

Table 1. Geothermometry results for Tuzla geothermal brine waters

Name	Measured temperature (°C)	Na/K	K/Mg	Na/K/Ca
Geothermal-13	77	182.4 ^a	185.32 ^a	212.47 ^b
Geothermal-23	60.7	232.59 ^a	209.94 ^a	231.34 ^b
T1*	174	183 ^c		218 ^b
		213 ^d		
T2*	168	239 ^c		254 ^b
		256 ^d		
T1**	171	212 ^a	187 ^a	205 ^b
T1***	174	225		230

^aGigenbach (1988), ^bFournier ve Truesdell (1973), ^cTruesdell (1976), ^dFournier (1979), *Calculated by Tarcan, 2005, **Calculated by Mutlu and Güleç, 1998, ***Calculated by Yalcin, 2007).

Metamorphic rocks and granite intrusion as the basement rocks in the TGF are not exposed in the study area. However, the basement has been identified from drilling as a granite intrusion at 702 m depth (Sener and Gevrek, 2000). The basement rocks are overlain by Tertiary strata comprising pyroclastic rocks, rhyolite tuff, sedimentary units (gravel, sandstone, claystone and marl) and rhyodacite lava (Figure 2). These Tertiary strata are highly altered and covered by Quaternary sediments and alluvium (General Directorate of Mineral Exploration and Research [MTA], 1997; Samilgil, 1983). The currently active thermal regime is associated with Late Miocene volcanism in the TGF (Sener and Gevrek, 2000). Generally, the major geologic structures in the TGF are recognized to be N-S and NW-SE trending fault systems (Figure 2). The N-S trending fault system is situated at the boundary of Neogene sediments and Quaternary alluvium. Along the N-S trending fault system, many geothermal springs have developed. The major faults trending NW-SE along the western and southern slope of Tuzla Tepe Ridge are normal faults.

Three mechanisms threaten the quality of shallow groundwater in the area: 1) upconing of old connate hypersaline geothermal brine; 2) sea-water intrusion from the Aegean Sea; and 3) halite dissolution at the surface and seepage into the shallow aquifer. Most residents of the Tuzla village abstract shallow groundwater from alluvium for irrigation purposes. Therefore, it will be beneficial to understand the effects of the

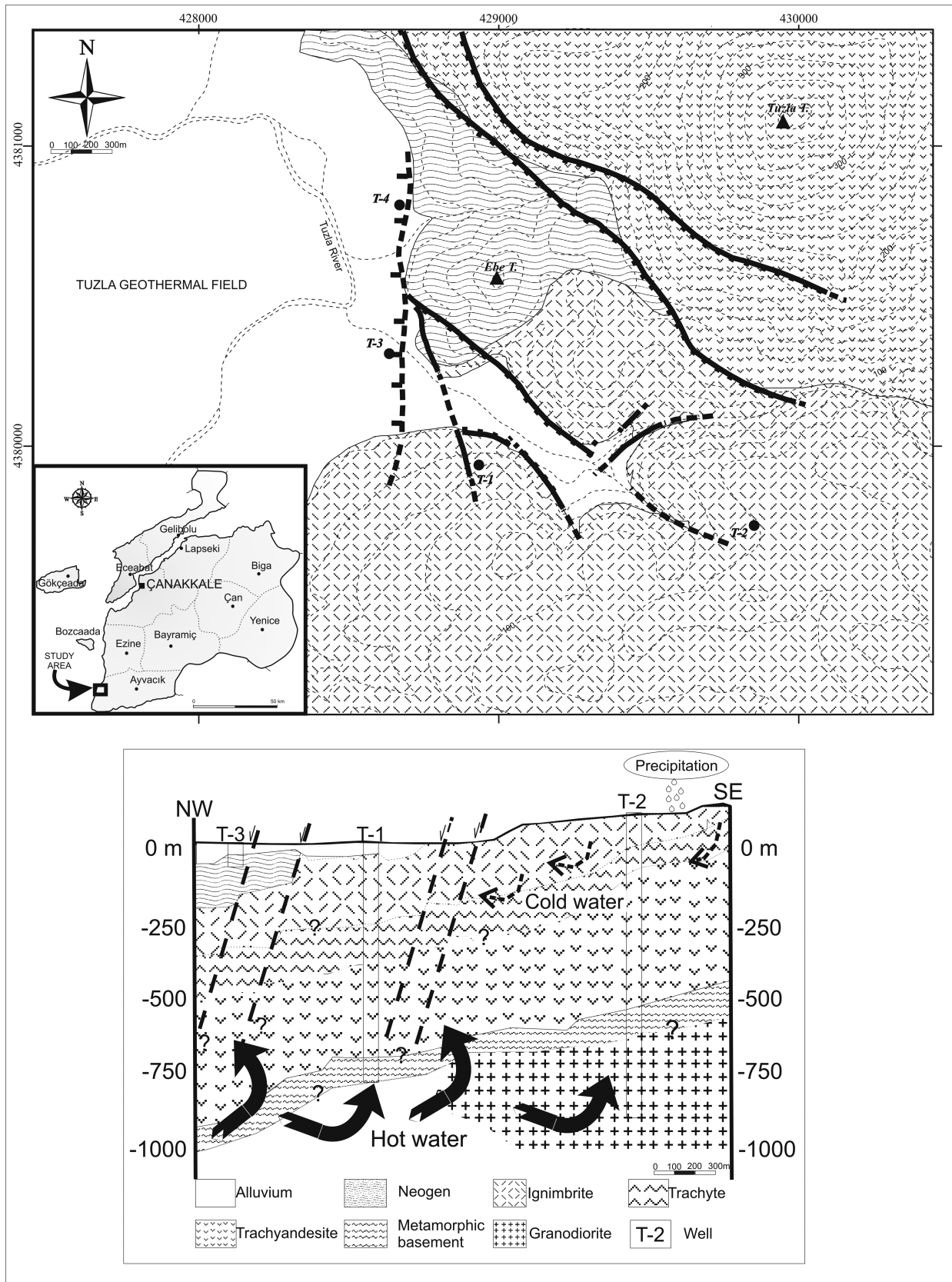


Figure 2. Simplified geological and sampling map of Tuzla Geothermal Field (Modified from Karamandersi, 1986).

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geothermal brine on the shallow groundwater, especially the relationship between dissolution of the surficial salt crust and injection of hypersaline geothermal fluid from the deep source. In this respect, the aim of this paper is to clarify the hydrogeochemistry of the TGF and to determine its environmental effects.

Methods

Four sampling campaigns were carried out in August and December 2003 and March and June 2004. Sixty-nine water samples were taken from geothermal springs, and groundwaters from shallow wells and surface waters. The surface water samples were collected from various points where they mixed with geothermal brine. The sampling locations are shown in Figure 1. The concentrations of major ions (Na, Ca, Mg, HCO₃, Cl, and SO₄), trace elements (As, Sr, Fe and Mn), and environmental isotopes (oxygen-18, deuterium, and tritium) were determined on water samples taken from seven surface water samples (1, 2, 8, 9, 10, 14 and 19), eleven shallow groundwater samples (3, 5, 6, 7, 15, 16, 17, 18, 20, 21 and 24) and six geothermal spring samples (4, 11, 12, 13, 22 and 23) in the study area. Only one sample, collected in June 2004, was analyzed from location 23 as this spring has only recently been identified.

For major ions and for trace metal analyses, 1-L plastic bottles were used. To prevent the complex formation of trace elements with oxygen, samples were filtered by 0.45- μ m filter paper and acidified to pH \leq 2 condition by adding 0.5 N HNO₃. The trace metal analyses were measured by ICP-AES. Electrical Conductivity (EC), temperature ($^{\circ}$ C) and pH values were measured in-situ with a multi-parameter instrument. Chemical analyses were carried out using the ICP-AES for Na, K, Ca, and Mg while Cl and HCO₃ values were determined by titration method at the laboratories of Canakkale Onsekiz Mart University (COMU) (Canakkale, Turkey). The concentration of deuterium (D) and oxygen-18 isotopes (¹⁸O) in the samples were determined in the laboratories of the Technical Research and Quality Control Department of the State Hydraulic Works (DSI) in Ankara. For this purpose, mass spectrometry was used with an overall precision of 1‰ and 0.1‰ for deuterium and oxygen-18, respectively. These values are expressed conventionally in delta notation as per mil deviation from the V-SMOW (Vienna Standard Mean Ocean Water) (Verhagen et al., 1991). Tritium was analyzed in the laboratory of Karst Research and Application Centre at Hacettepe University with a liquid scintillation counter (LSC) after electrolytic enrichment of the water samples with an error of \pm 0.8 Tritium Units (TU).

Results and Discussion

Hydrogeochemical Evaluation

Analytical results for the geothermal brine waters, shallow groundwaters, and surface waters of Tuzla area are given in

Tables 2a, 2b, and 2c, respectively. Results from the sampling campaign of March 2004 have not been considered because these samples have elevated electro neutrality (Apello and Postma, 1992) and a reaction error of $>$ 5% (Freeze and Cherry, 1979). Thus, instead of 69 water samples, 47 water samples were evaluated.

Sodium and chloride are the dominant ions in the geothermal brine waters of the Tuzla region (Table 2a) while calcium and bicarbonate are the dominant ions in the shallow groundwater. Surface waters in the region are characterized by sodium and chloride ions, remarkably high during dry periods. Thus, the chemical composition of surface waters is mainly controlled by the discharge of hyper-saline geothermal brine.

Geothermal brine

The emergence of geothermal brine can be the result of an extensional tectonic regime where the lithosphere is thinner and uplift has occurred due to isostasy (Keisuke, 1978). Active seismicity in the region allows liquid at depth to rise more easily. The ascending brine is to some extent cooled and diluted by mixing with groundwater.

Analytical results for the geothermal brine samples indicate contrasting compositions during wet and dry periods. During dry periods, geothermal brine contains relatively elevated concentrations of Cl and Na compared with wet periods. This may result from Ca/Na ion exchange by albitization of plagioclase and formation of Na-rich clays in the geothermal aquifer (Kloppmann et al., 2001). The higher NaCl concentration seen in dry periods is possibly due to either subsurface evaporation of geothermal brine or to no dilution effect from surface water. Furthermore, an increase in CO₂ during the dry period may cause the pH to decrease and an enrichment of Cl (Kaszuba et al., 2003; 2005). The outflowing of NaCl rich thermal brine is an indication of present hydrothermal activity (Mützenberg, 1997). During the dry period, the Ca content of the geothermal brine decreases since part of the CO₂ is released from the geothermal brine and CaHCO₃ is precipitated. In another regard, the low Mg content in geothermal brine slightly increases during wet periods, possibly due to its mixing with surface waters by rapid recharge to depth.

The solubility of Na slightly decreases while Cl solubility is maintained during dry periods, because concentrations of Na and Cl increase subsequently until saturation with halite occurs, then the Cl content continues to increase with increasing evaporation (Apello and Postma, 1992), which takes place in the subsurface. For this reason, Na concentrations may not increase while Cl does increase in the dry period geothermal brine of the Tuzla area. Moreover, Na is not conservative in water-rock reactions as is chloride. Plots of Na versus B and Cl versus B (Figure 3a and 3b) indicate that the geothermal brine waters (samples 4, 11, 12, 13, 23) can readily be distinguished with their much higher Na, Cl and B values from shallow groundwaters (samples 5, 16, 18). In addition, the arsenic content of Tuzla geothermal brine is elevated probably due to water-rock interactions at depth under the influence of solution from an arsenopyrite

Table 2a. Chemical and isotopic analysis results of Tuzla Geothermal Waters (*SI* = saturation index, *t*: temperature, *T*: tritium, δD : deuterium, *B*: boron)

Sample No	Sampling Date	pH	EC ($\mu S/cm$)	Cations (meq/l)				Anions (meq/l)			E:N (%)	B (ppm)	$\delta^{18}O$ (δD)	Tritium (TU)	t ($^{\circ}C$)	LogP _{CO2}	SI gypsum	SI calcite	SI dolomite	As	Fe	Mn	Sr	HCO ₃ /Cl	Na/Cl	
				(ppm)				SO ₄ ²⁻																		
				Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻																
4	2003																									
	August	7.1	85756	630.7	30.4	88.4	1.5	1.7	849.7	7.6	6.7				2.02		-4.81	-11.80	0.032	0.006	1.319	42.468	0.002	0.74		
	December	6.4	78400	574.2	51.2	147.7	6.7	2.1	818.1	8.0	3.0			79	2.02		-4.41	-10.72	0.136	0.288	4.877	123.368	0.003	0.70		
	2004																									
	March*	7.3	85600	270.5	57.1	146.1	6.3	2.2	240.3	17.8	29.7			45			-7.15	-7.75	0.123	0.060	5.624	134.633	0.001	0.74		
	June	5.7	75900	596.82	35.8	76.5	2.3	1.1	803.3	5.0	6.5	32.00	-0.76	-24.39	2.98	4.69	-0.91	-7.15	0.058	0.010	5.125	130.502	0.001	0.74		
11	2003																									
	August	6.1	78029	750.3	45.0	80.7	2.2	1.7	785.1	2.3	5.4			72	2.02		-4.67	-11.481	0.033	0.001	0.758	34.198	0.002	0.956		
	December	5.4	65000	663.2	43.4	118.7	9.4	3.9	881.2	13.5	3.7			32	2.02		-4.50	-10.686	0.051	0.589	3.902	110.765	0.004	0.753		
	2004																									
	March*	6.4	75900	243.5	43.1	118.8	9.1	2.2	922.7	2.6	38.2			54.9	4.99		-6.94	-7.41	0.104	0.098	3.236	100.484	0.003	0.95		
	June	5.6	71400	737.5	17.3	62.5	3.4	2.2	775.2	6.5	2.3	11.10	-0.19	-11.63	0.00	2.02		-4.86	-11.47	0.070	<0.001	2.364	51.785	0.004	0.889	
12	2003																									
	December	5.5	33400	752.5	18.7	51.4	3.6	3.6	847.1	3.4	1.7			50	2.02		-4.86	-11.47	0.070	<0.001	2.364	51.785	0.004	0.889		
	2004																									
	March*	5.8	32700	144.2	17.8	50.3	3.5	3.3	350.5	4.2	24.8			47			-7.08	-7.59	0.044	<0.001	2.282	49.053	0.003	0.72		
	June	5.4	32100	609.8	9.8	33.7	1.7	2.8	847.3	1.8	13.1	24.7	-3.86	-36.31	0.22	5.10	-1.69	-7.08	0.044	<0.001	2.126	50.126	0.003	0.72		
	2003																									
13	August	6.3	85955	715.8	50.6	137.2	1.5	1.7	834.5	4.1	3.7			73	2.02		-4.44	-11.42	0.032	<0.001	1.306	41.525	0.002	0.86		
	December	6.1	70900	615.5	50.8	126.1	5.9	2.5	804.0	11.5	1.2			87	2.02		-4.47	-10.86	0.006	1.300	4.939	122.328	0.003	0.77		
	2004																									
	March*	6.5	80300	256.3	50.6	131.5	6.2	2.2	642.3	0.7	18.4			87			-7.23	-7.83	0.089	0.136	5.073	122.128	0.001	0.90		
	June	6.3	74400	695.3	19.6	63.2	1.9	1.1	775.0	5.5	0.1	20.11	-0.88	-21.37	0.00	4.69	-0.96	-7.23	0.070	0.095	3.156	129.508	0.001	0.90		
	2003																									
22	December	6.8	692	3.8	0.3	0.2	0.1	1.4	1.7	1.0	3.2			34	2.03		-7.42	-15.67	<0.001	0.040	0.003	0.101	0.817	2.24		
	March*	7.2	758	2.8	0.4	0.2	0.1	1.7	17.7	1.5	71.8			35			0.015	0.016	0.015	0.016	<0.001	0.127				
	2004																									
	June	7.2	580	4.7	0.3	0.3	0.1	1.7	2.8	0.4	5.0	25.95	-5.75	-43.12	0.00	5.04	-3.16	-8.66	0.016	0.045	<0.001	0.111	0.595	1.67		
	2004																									
	June	5.7	74400	728.5	43.0	61.9	3.1	2.2	775.2	6.4	3.3	13.63	-0.35	-17.03	0.77	60.8	-0.92	-6.94	0.087	0.009	0.059	0.089	0.003	0.94		

Table 2c. Chemical and isotopic analysis results of Tuzla Surface (Stream) Waters (SI = saturation index, t: temperature, T: tritium, δD : deuterium, B: boron)

Sample No	Sampling Date	pH	EC ($\mu S/cm$)	Cations (meq/l)			Anions (meq/l)			E.N (%)	B (ppm)	$\delta^{18}O$	δD	Tritium (TU)	t ($^{\circ}C$)	Log P_{CO_2}	SI gypsum	SI calcite	SI dolomite	As	Fe	Mn	Sr	HCO_3/Cl	Na/Cl	
				Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻																	SO ₄ ²⁻
				(ppm)																						
1	2003																									
	August	8.1	83133	848.2	9.0	14.6	0.9	6.1	987.3	3.3	6.6				2.02					0.076	0.132	0.693	10.510	0.006	0.86	
	December	8.2	2200	13.4	1.0	4.0	1.5	3.4	13.8	4.1	3.4		5		2.03					0.001	0.026	0.068	2.245	0.249	0.97	
	2004																									
	March*	8.2	2900	7.6	1.3	5.2	1.3	4.4	23.6	4.3	35.5	-6.08	-47.48	3.55	16					0.009	0.029	0.007	3.222		0.71	
	June	7.5	97200	645.1	52.7	142.6	5.2	1.7	912.6	3.1	4.1	83.0	-3.14	-23.90	0.55	31.2	4.86	-1.34	-7.16	-7.50	0.084	0.030	0.009	3.129	0.002	0.71
2	2003																									
	August	8.0	64043	794.7	7.6	11.4	1.3	9.4	912.6	3.0	6.3				2.02					0.018	0.080	0.611	12.403	0.010	0.87	
	December	8.2	2060	15.0	0.8	3.7	1.1	3.3	14.8	3.1	1.5			5		2.03				0.007	0.025	0.081	2.087	0.223	1.01	
	2004																									
	March*	8.2	3730	8.6	1.6	6.1	1.4	3.9	27.3	4.8	34.0			16						0.006	0.048	0.019	3.816			
8	2003																									
	August	8.2	63772	830.8	9.1	11.0	1.5	7.2	905.5	7.6	3.8				2.02					<0.001	0.026	0.661	12.360	0.008	0.92	
	December	8.3	2500	20.9	0.7	3.7	1.1	3.3	17.2	3.6	4.5			5		2.03				0.013	0.017	0.090	2.064	0.192	1.21	
	2004																									
	March*	8.2	3610	8.3	1.4	5.7	1.3	5.5	28.0	2.2	36.3	-6.05	-45.99	4.17	15					0.009	0.041	0.006	3.628		0.79	
	June	7.3	39300	554.9	12.2	44.0	3.0	2.8	705.0	3.2	7.3	0.78	-3.15	-24.16	4.04	27.5	5.10	-1.31	-6.96	-7.39	0.024	0.026	0.026	6.024	0.004	0.79
9	2003																									
	August	8.1	65803	804.7	11.8	49.5	1.5	11.0	859.0	2.1	0.3				2.02					0.021	0.010	1.066	21.231	0.013	0.94	
	2004																									
	March*	8.1	3300	8.1	1.4	5.8	1.3	5.5	27.6	4.4	38.5			14						0.005	0.043	0.005	3.572		0.69	
	June	6.9	45000	484.7	39.1	96.9	2.7	3.3	704.1	3.5	6.6			27.6						0.037	0.056	0.012	4.562	0.005	0.69	
10	2003																									
	August	7.9	158720	865.6	65.2	122.3	2.3	1.7	1097.3	2.3	2.1				2.02					0.073	<0.001	<0.001	116.815	0.002	0.79	
	December	7.9	71500	522.0	1.3	8.9	1.9	3.3	592.4	1.1	5.6			6		2.02				0.112	<0.001	0.406	10.643	0.006	0.88	
	2004																									
	March*	8.7	5810	10.8	2.4	7.3	1.3	4.4	48.1	0.1	41.2			17						0.010	0.333	0.071	5.453			
14	2003																									
	August	7.7	99400	837.3	12.9	20.7	0.8	0.6	998.6	0.8	6.9			25		2.02				0.021	0.006	0.866	12.566	0.001	0.84	
	December	7.5	51100	369.7	33.3	86.3	3.7	0.8	506.4	13.1	2.7			3		2.02				0.059	<0.001	3.386	85.200	0.002	0.73	
	2004																									
	March*	8.5	25200	105.2	11.8	40.7	6.1	2.8	400.6	3.2	42.5			18						0.019	0.141	0.823	34.913		0.73	
	June	7.5	84500	346.2	18.4	59.4	1.9	1.1	473.3	9.1	6.4	0.21	-0.78	-11.85	1.65	27	4.72	-0.60	-7.17	-7.77	0.052	0.090	0.926	47.601	0.002	0.73
	2004																									
	March*	8.9	471	0.7	0.1	2.6	1.3	3.9	0.8	7.6	44.3			17						0.003	0.010	<0.001	0.362			
	June	8.5	507	1.5	0.0	2.9	1.2	2.2	1.3	1.6	4.8	<0.01	-5.60	-35.73	0.77	24	5.16	-1.67	-7.59	-7.69	<0.001	0.009	<0.001	0.201	1.654	1.14

and pyrite rock assemblage. Consequently, considerable arsenic enrichment in saline Na-Cl type geothermal brine takes place in Tuzla geothermal brine. On the other hand, slight arsenic content can also be traced in the shallow groundwaters while arsenic in geothermal brine is adsorbed onto iron-hydroxides, and then it can easily decline in the shallow groundwater environment by oxidation.

According to the Piper diagram in Figure 4a, the geothermal brine (except for sample 22) is in NaCl facies (in the same facies as seawater) in both dry and wet periods. Sample 22 is of the Na Cl, HCO_3 water type due to steam-heated groundwater because it contains comparatively more bicarbonate than other geothermal brine waters while having a higher temperature than other shallow groundwaters. Accordingly, sample 22 contains a considerably lower total ion concentration (cations and anions), very low Na-Cl, and the lowest "As" content of geothermal brine.

Surface waters

As the Tuzla Stream crosses the area with thermal (brine) spring occurrences, it is clear that its water presents a mixture of shallow surface water, shallow cold groundwater and the water of the upwelling thermal brine. Therefore, according to the chemical constituents, its composition will change according to the mixing proportions depending on whether it is the dry or wet season (base-flow influence).

Except for sample 19, the salinity effect of hyper-saline geothermal brine on the stream clearly plots with the NaCl facies of a traditional Piper diagram (Figure 4b), particularly in dry periods. However, stream water sample 19 plots on the mixed water type with CaHCO_3 dominant due to abundant replenishment from shallow groundwater (Baba et al., 2007) and its position being distant from the geothermal springs.

Overall, the Tuzla Stream samples show increased salinity during dry periods due to a greater relative input from geothermal brine waters compared to rainwater and shallow groundwater (Table 2c). The high boron and chloride contents of samples from the Tuzla Stream reflect an abundant source of geothermal brine throughout the dry period.

Shallow groundwaters

Seasonal trends in the composition of shallow groundwater are variable. Shallow groundwaters are generally CaHCO_3 type waters in the wet period while in the dry period, they change into the mixed water type associated with NaCl and CaSO_4 (Figure 4c). Na/Cl ratios are below 1 in some of the brackish shallow groundwater (samples 5, 6, 7, 16). Recent halite (NaCl) precipitation as a surface crust (on top of the soil) formed by discharge of geothermal brine in the dry period causes deterioration of the shallow groundwater quality (Table 2b) by means of washing down into the shallow aquifer units (samples 5, 6, 7, 16, 18, 21, 24).

Groundwater sample 24 (Figure 4c) records an elevated conductivity value that indicates the influence of geothermal brine. Conforming to, the highest total ion concentration, relatively

high arsenic content (the highest is sample 6) (Table 2b), and the lowest (Na+Ca)/Cl value for shallow groundwater is recorded by sample 24 (Figure 5).

Almost all groundwater samples (mainly Na and Cl contents of samples 5, 6, 7, 15, and 16 increased from June or August to December) shifted to mixed water type under influence of geothermal brine during the dry period (Table 2a). For example, sample 3 is characterized as a NaHCO_3 water type during wet periods and as a mixed water type during dry periods, due to the influence of thermal brine with high chloride content (Figure 4c). Sample 3 is representative of shallow groundwater with lower electrical conductivity (EC), temperature, and ion concentrations. It is suggested that the higher chloride values of shallow groundwater samples in dry periods are due to the seepage of NaCl salts accumulated at the surface from geothermal springs in the area. The increase in sodium and chloride values in shallow groundwater would lead to degradation of soil structure and properties with respect to permeability, porosity, and agricultural attributes. The shallow groundwater is utilized by farmers for irrigation purposes and most complain about the deterioration of water quality due to the influence of geothermal brine on both shallow groundwater and the surface water of the Tuzla Stream. Shallow groundwaters are influenced by geothermal brine in ratios between 1.5% and 9% based on their chloride values. However, there is no remarkable negative effect of irrigation return water on the shallow aquifer, since irrigation is not widely performed in the area. The main salinity problem of shallow groundwater derives from the seepage of geothermal brine in the area. In the case of the wells which were drilled by the MTA and some springs, the unsealed evaporation basin probably caused the vertical infiltration of geothermal brine into the shallow plain aquifer. Approximately 50 m below the well, the mineralized water discharges at the surface as a small spring. As a consequence of the high salt content of the geothermal component, evaporation process and low discharge rate of the spring, the surrounding dark-grey to black soil is covered by white salt crust with an aerial extension of ca. 1 km² (Baba et al., 2005). As previously mentioned, the TGF is located near recent volcanic activity areas. The slightly acidic NaCl Tuzla brine flows out of places where the permeability is high (i.e. fault and fracture zones). Eventually, the geothermal brine diffuses into shallower aquifers, which changes its fluid chemistry.

According to the solution indices (SI), all waters are under-saturated with respect to calcite, dolomite, and gypsum (Figure 6). If the geothermal water is in equilibrium with considered minerals at a given temperature, all SI converge to zero at that temperature. If the geothermal waters (brine) mix with water of low salinity (i.e. shallow groundwater), then all SI are shifted downward into the under-saturation field (Marini). As can be seen in Figure 6, waters are relatively saturated with respect to gypsum, compared with calcite and dolomite, and this saturation is partly maintained in the dry period because the dissolution of gypsum occurs more readily than calcite and dolomite since a higher amount of NaCl exists in the water (Apello and Postma,

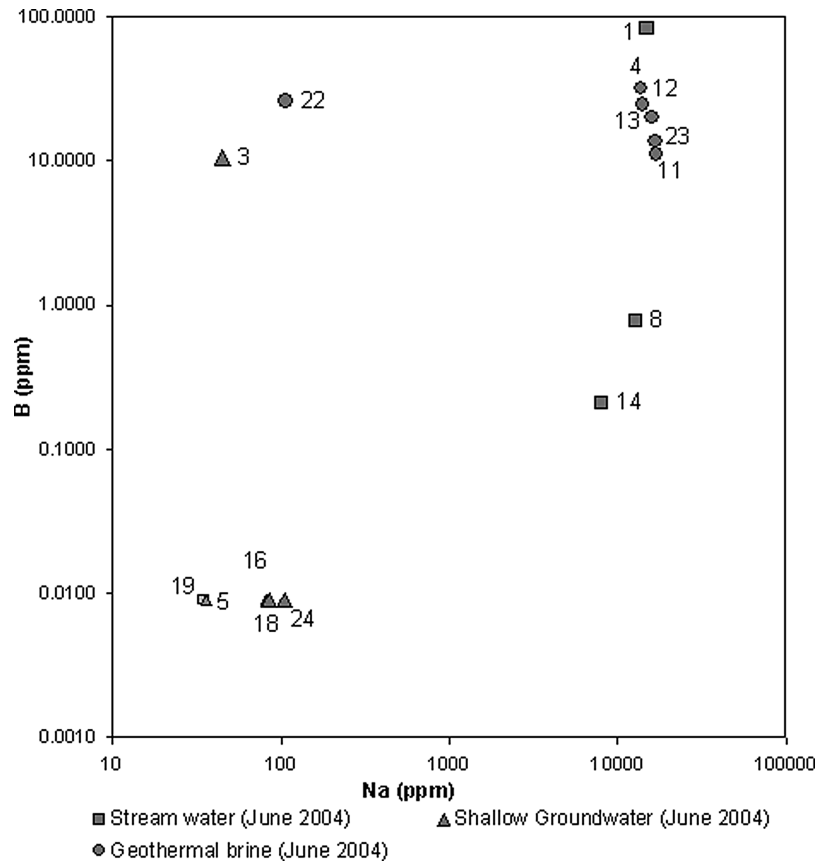


Figure 3a. Na-B diagram.

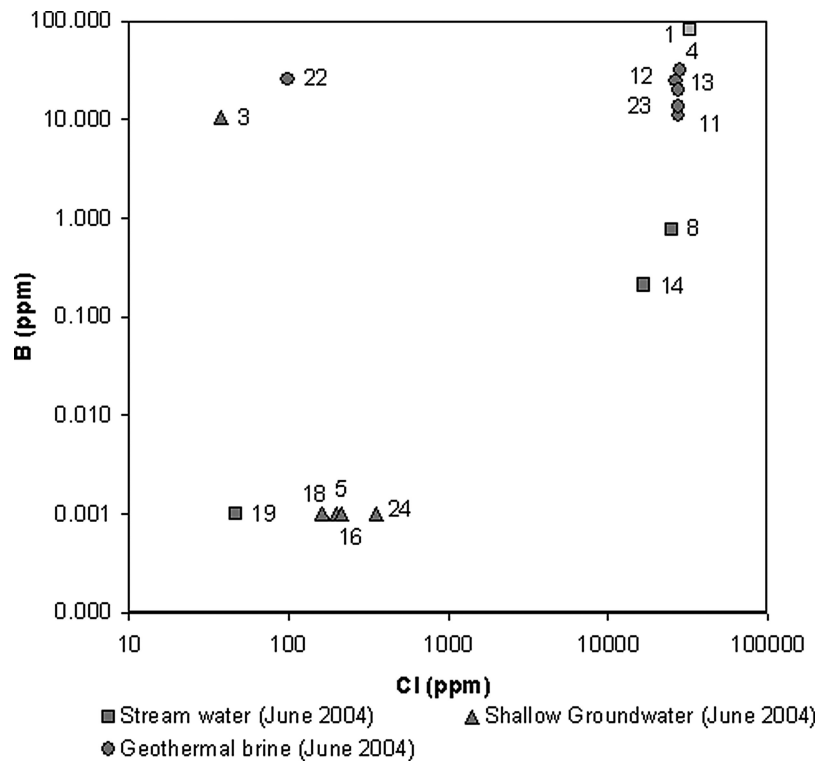


Figure 3b. Cl-B diagram.

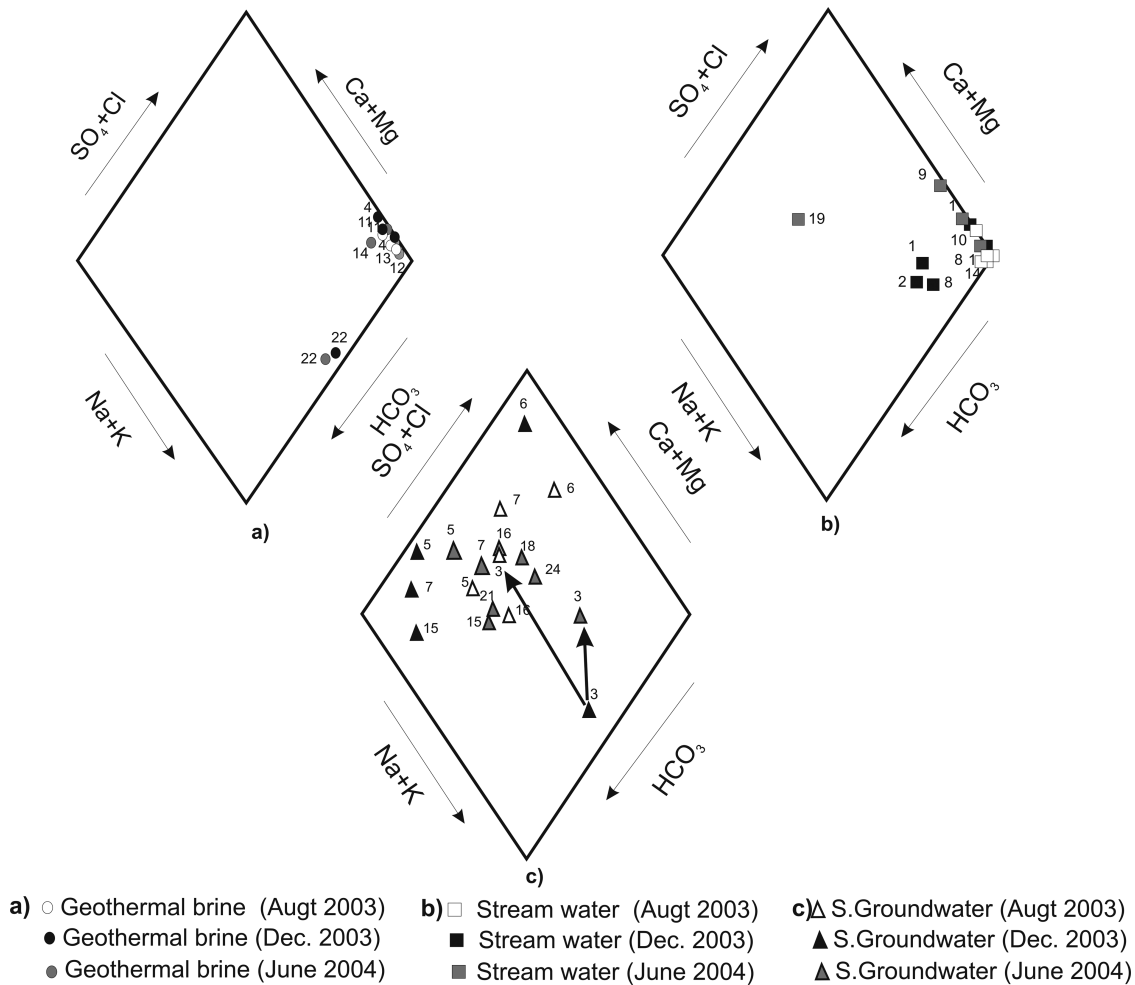


Figure 4. Chemical analysis of water in the study area plotted on Piper diagrams.

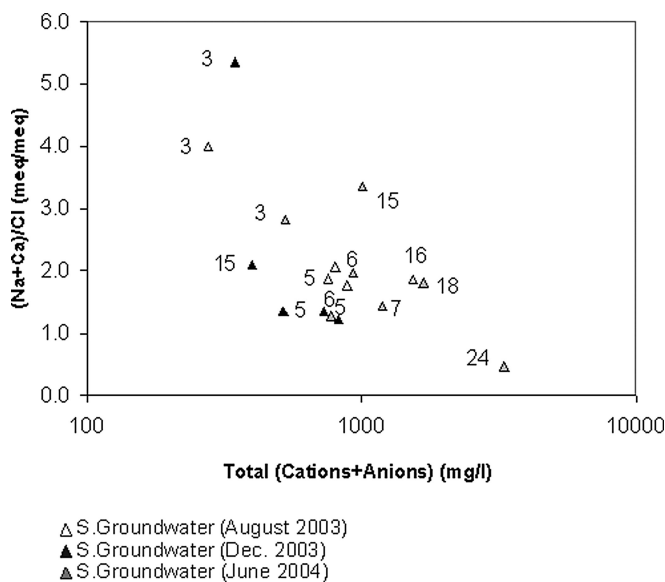


Figure 5. (Na+Ca)/Cl-Total (Cations+Anions) diagram of the shallow groundwaters.

1992). As NaCl increases the ionic strength of the solution, concentrations generally increase (Kehew, 2001), but calcite dissolution rates generally decrease with increasing brine concentration (Gledhill, 2005).

A further evaluation of the cation-anion distribution can be completed using the ternary diagrams of Giggenbach (1988) (Figure 7a, 7b, 7c). The ternary diagram is based on hydrothermal systems where the compositions of deep high-temperature fluids (full equilibrium line) are the result of isochemical recrystallization. Samples from deep geothermal waters generally plot on the full equilibrium curve (mature water) and their temperatures are slightly higher than those physically measured in these waters (Marini). However, most of the shallow groundwaters in Tuzla appear to be mixed waters (Figure 7a), Ca dominated (Figure 7b), and highly immature waters, indicating that these waters have not attained equilibrium (Figure 7c). The surface waters plot on mixed (Figure 7a), Na dominated (7b), and immature waters while geothermal brine falls on the corner of mature waters (7a), Na dominated (7b), and partially equilibrated waters, which indicates attainment of partial equilibrium with respect to chemical composition. The geothermal brine in Tuzla is a

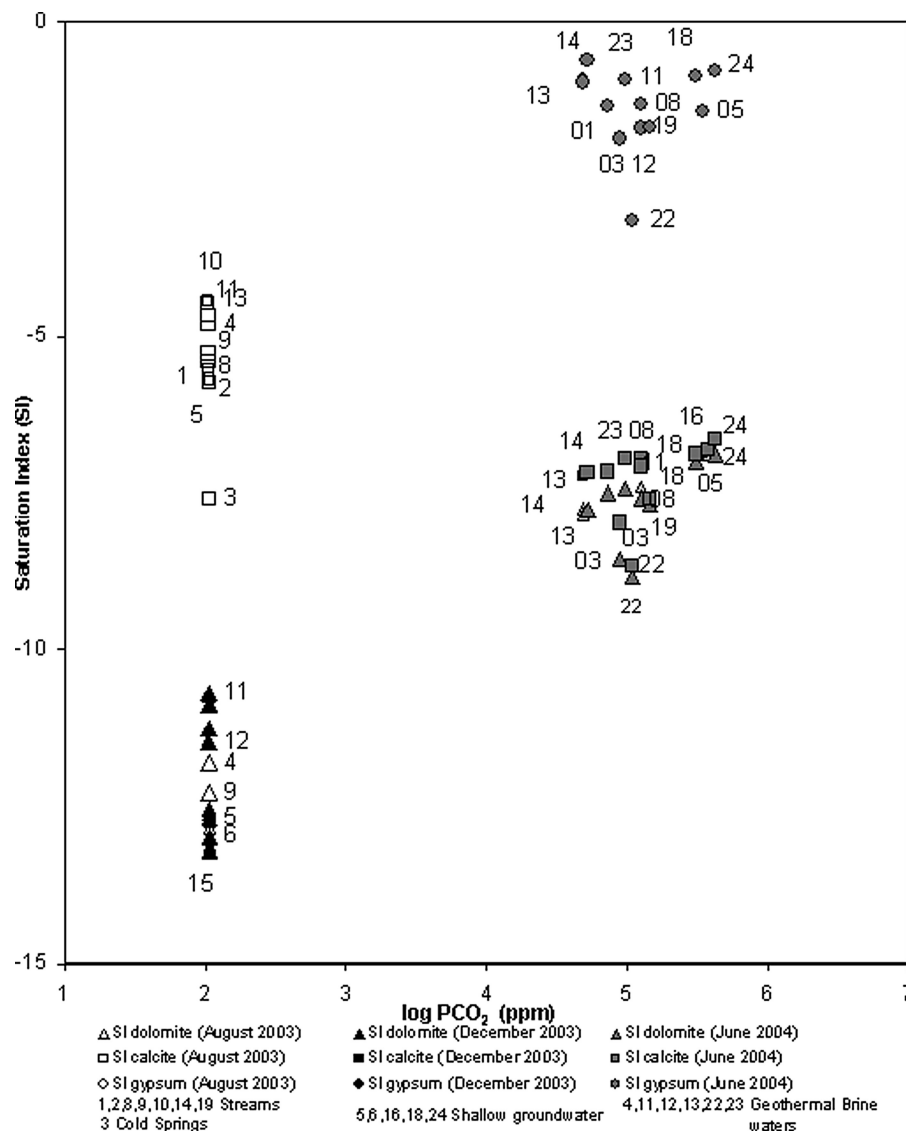


Figure 6. Chemical equilibrium of samples on saturation diagram showing relative mineral saturations.

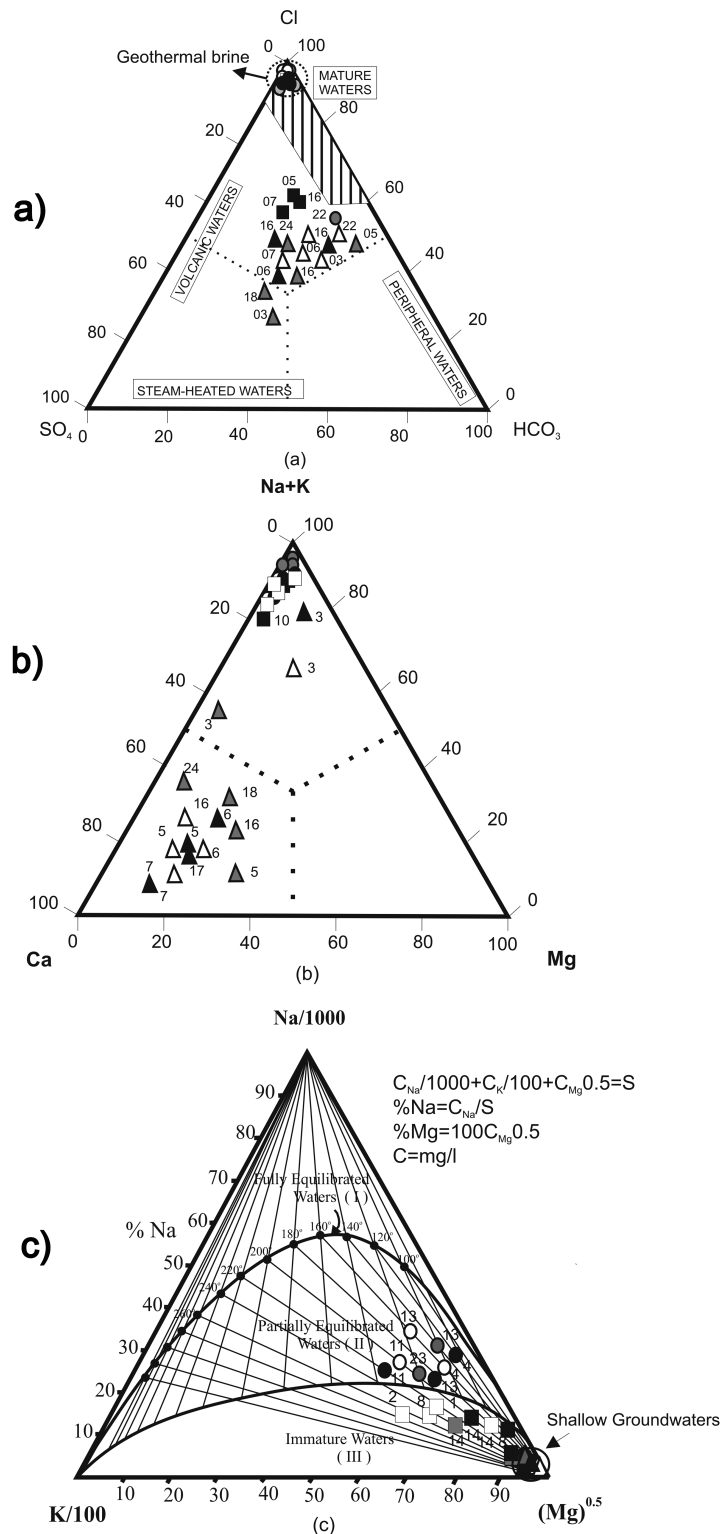
Cl dominated geothermal brine (Figure 7a) (except sample 22) while the shallow groundwaters are in the mixed area (Figure 7a). The HCO_3/Cl ratios of geothermal brine are much lower than those of shallow groundwater, which is expected (Table 2a and 2b). The dilution process by shallow groundwaters in geothermal brine having a short circulation plays an important role that is reflected in the $\text{Na}/1000\text{-K}/100\text{-Mg}^{0.5}$ ternary diagram (Figure 7c). Apart from samples 12 and 22, all other geothermal brine waters plot as partially equilibrated waters, namely 4, 11, 13 and 23. Based on their location on Figure 7c, samples 12 and 22 are presumed to be steam-heated shallow groundwater and mixed water with shallow groundwater, respectively.

Briefly, three processes play an important role in the salinization of soil and degradation of shallow groundwater quality in the Tuzla region: 1) albitization (the production of albite as a secondary mineral in the rock) of plagioclase in the deep-

seated geothermal aquifer resulting in an increase in NaCl and CO_2 , and decrease in Ca concentration; 2) a deep geothermal brine influence either into shallow groundwater or discharging to surface water; and 3) halite crystallization.

Trace Elements and Environmental Impact

The black and reddish color of geothermal brine samples (4, 11, 12, 13) with high As, Mn, and Fe content (except for sample 12 because it partially mixes with shallow groundwater that may cause a decrease in Fe concentration due to precipitation by oxidative condition) (Figure 8) is attributed to the dissolution of ferromanganese minerals within Late Miocene sediments. The high trace metal content in the hot-saline waters of the TGF results from rapid evolution of anoxic conditions in brines (Drever, 1997) and reduction of the sulphite (SO_3) formed by reactions with trace elements, followed by release of trace elements during



- Geothermal brine (August 2003)
- Geothermal brine (Dec. 2003)
- Geothermal brine (June 2004)
- Stream water (August 2003)
- Stream water (Dec. 2003)
- Stream water (June 2004)
- △ S.Groundwater (August 2003)
- ▲ S.Groundwater (Dec. 2003)
- ▲ S.Groundwater (June 2004)

Figure 7. Chemical analysis of waters in study area plotted on Ternary-Giggenbach (1988) diagrams. a) Cl-SO₄-HCO₃. b) (Na+K)-Ca-Mg. c) Na/1000-K/100-(Mg)^{0.5}.

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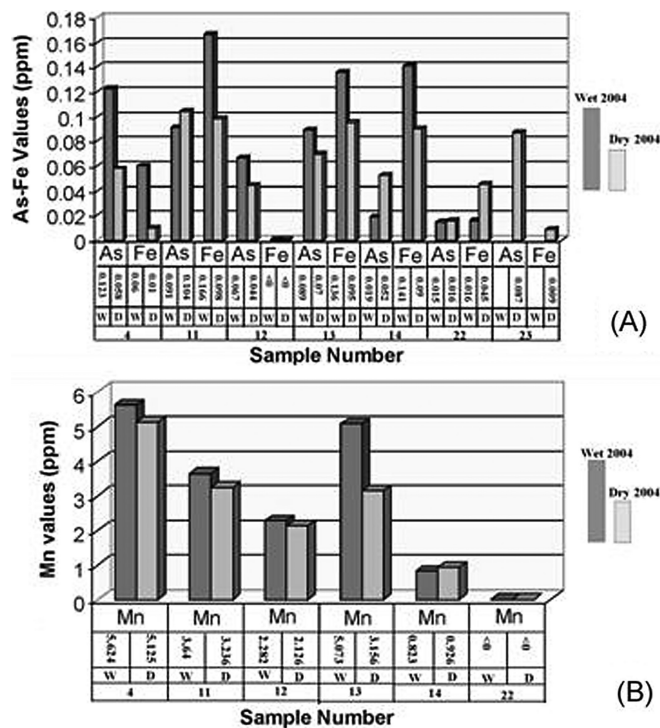


Figure 8. Arsenic, iron, manganese and strontium contents of geothermal brine waters in Tuzla Region.

oxidation of the metal sulfides by bacterial activities. For this reason the concentration of As, Fe, and Mn in the geothermal brine recorded in March 2004 (wet period) is similar and/or slightly higher than in June 2004 (dry period) due to mixing with shallow groundwater (having oxidizing condition) which provides easy dissolution of As in an aquatic environment (Figure 8). The As content may also be elevated due to dissolution of As in rhyolite tuff (Stauffer and Thompson, 1984) that outcrops in the study area.

Sr content of groundwater is a good indicator of seawater intrusion, as evident from the high Sr concentration in shallow well no. 17 (Table 2b), located near the coastline. The high electrical conductivity (EC), chloride, and sodium contents of sample 17 support the seawater encroachment interpretation. It is considered that seawater intrusion is a relatively recent event due to its CaCl_2 composition, because, when seawater influences a coastal fresh water aquifer, sodium in seawater is occupied by soil, and calcium is released by the fresh water aquifer. The water quality then changes from NaCl (coming from seawater) to CaCl_2 (Apello and Postma, 1992). Accordingly, sample 17 from shallow groundwater, originally CaHCO_3 , shifted to CaCl_2 composition as a result of seawater encroachment.

The EC, sodium, chloride, and temperature values of the waters of Tuzla Stream (samples 1, 2, 8, 10) (Table 2c) increase during the dry period (August 2003) due to discharge of geothermal fluid into the Tuzla Stream. It is thought that salts, including trace metal salts, precipitate during the dry period and that surface water with higher mineralization due

to leaching of the superficial salt crusts infiltrate the shallow groundwater.

Geothermometers

Chemical analyses of geothermal fluids can be used to estimate subsurface reservoir temperature. Chemical geothermometers depend on the water-mineral equilibrium and give the last equilibration temperature for the reservoir (Nicholson, 1993). Several geothermometry techniques have been developed to predict reservoir temperatures in geothermal systems (Fournier and Truesdell, 1973; Fournier, 1979; Fournier and Potter, 1982; Arnórsson et al., 1983; Giggenbach et al., 1983; Giggenbach, 1988). All of these techniques are based on the assumption that temperature dependent water-mineral equilibrium is attained in the reservoir. Solute geothermometry techniques were applied to the hot waters from springs in the Tuzla geothermal field. The cation geothermometers applied to water samples 13 and 23 for June 2004 include Na-K, K-Mg (Giggenbach, 1988) and Na-K-Ca (Fournier and Truesdell, 1973). The results of geothermometer applications (Table 1) indicate some estimations for subsurface reservoir temperature that range from 182.4°C to 232.59°C. These results also are consistent with previous results calculated by Mutlu and Gulec, 1998; Tarcan, 2005, and Yalcin, 2007. Temperatures of up to 145°C were observed at 50-m depth in some of wells in the TGF. According to MTA drilling (well T1 at 814 m depth, Fig. 2), the reservoir depth is in the range of 333–553 m in volcanic rock with a temperature of 173°C.

Isotope Analyses Results and Discussion

The $\delta^{18}\text{O}$ values of the geothermal brine (Table 2a) vary between -0.19 and -3.86‰ (except sample 22 because it is steam-heated groundwater) versus Standard Mean Ocean Water (SMOW) (Verhagen et al., 1991) and the δD values vary between -11.63 and -36.31‰ (except sample 22) versus SMOW. The $\delta^{18}\text{O}$ content of geothermal brine is enriched up to -0.19 , while δD is depleted to -21.37 indicating a high $\delta^{18}\text{O}$ shift, which is due to rock-water interaction at higher temperatures. The $\delta^{18}\text{O}$ values of the shallow groundwaters (Table 2b) vary between -5.20 and -6.50‰ and the δD values vary between -33.95 and -45.32‰ . Hence, the most saline geothermal brine is enriched in respect to the shallow groundwater by as much as 6.31‰ in $\delta^{18}\text{O}$ and 41.46‰ in δD . Tritium values ranged from 0 to 2.98 TU for geothermal brine, and from 3.25 to 5.96 TU for shallow groundwaters. The three samples between the circles of dry period and brine (12, 01 and 08) are the result of mixing of shallow groundwater and brine.

Detailed information about geothermal brine, shallow groundwaters, and surface waters is given in Tables 2a, 2b, and 2c. The high tritium (T) and low deuterium (δD) values at T- δD plotted in Figure 9 represent rapid circulation in the shallow groundwater system while geothermal brine having higher δD and lower T values implies a longer and deeper circulation of

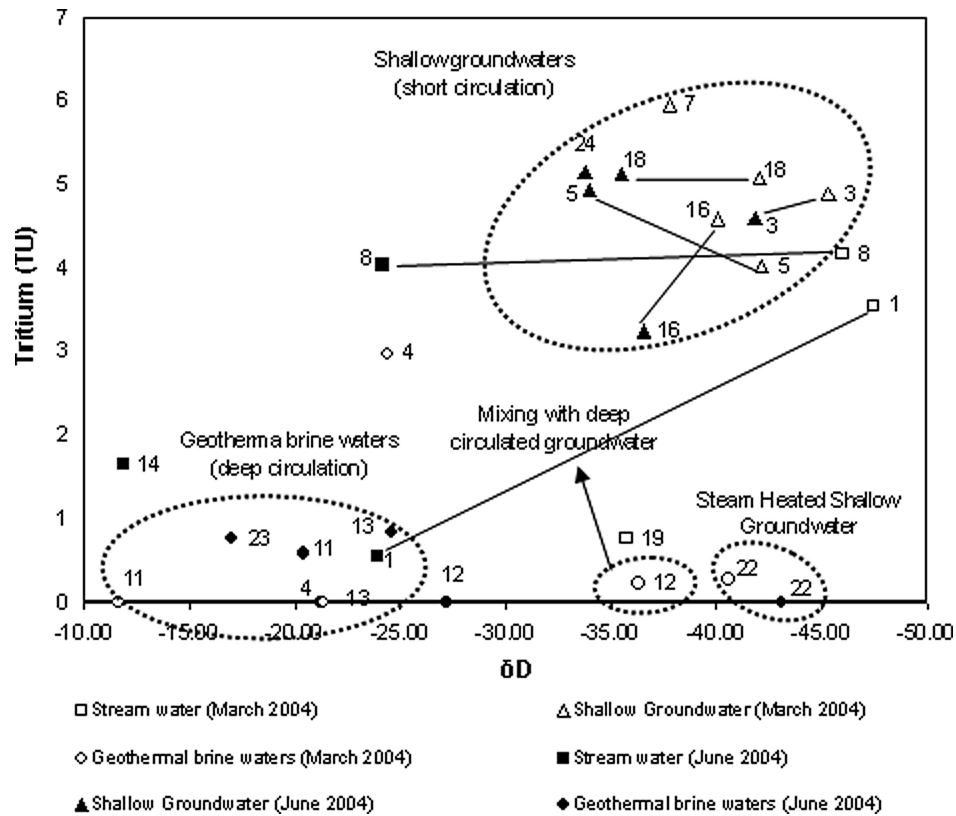


Figure 9. Deuterium (δD)-Tritium (TU) diagram (open symbols represent March 2004 samples, closed symbols represent June 2004 samples).

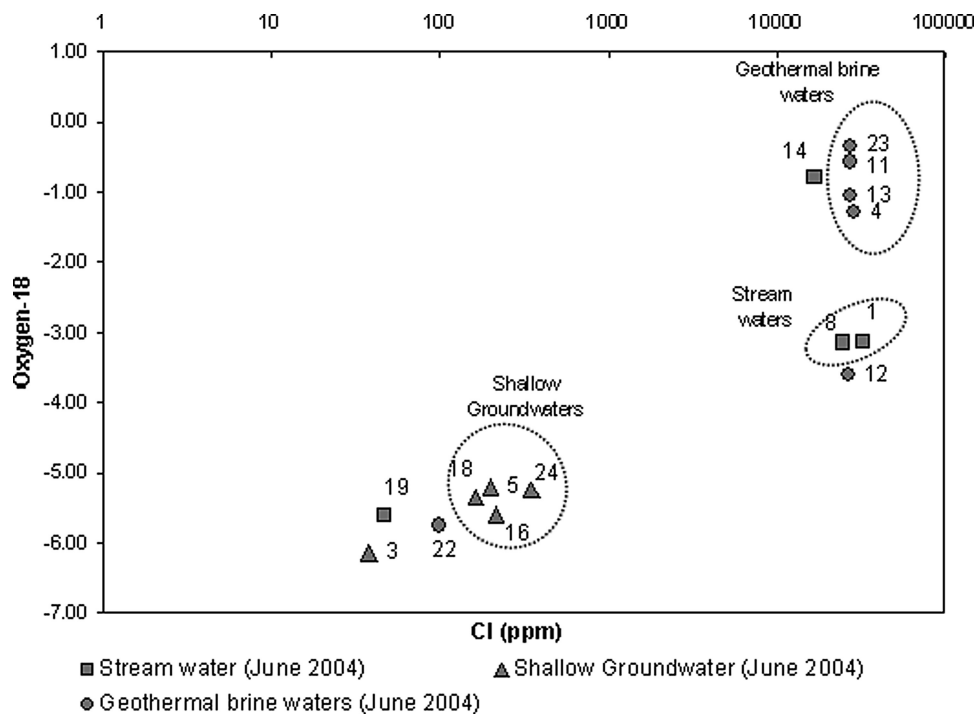


Figure 10. Chloride- $\delta^{18}O$ diagram.

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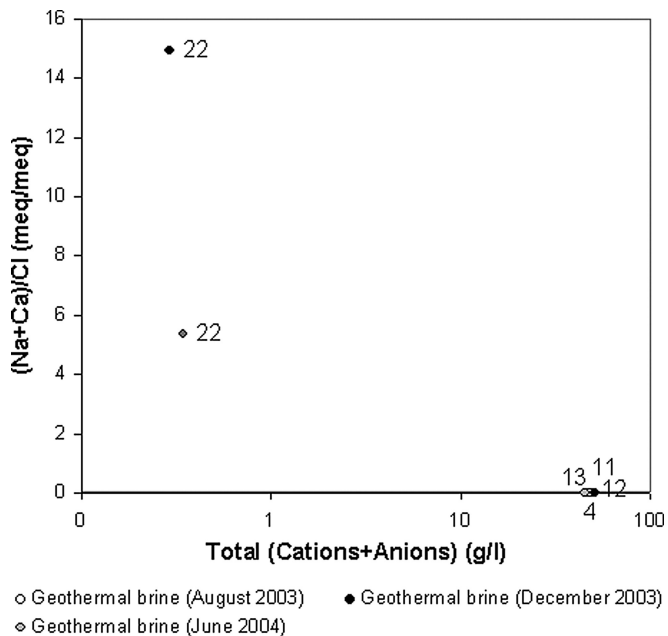


Figure 11. (Na+Ca)/Cl-Total (Cations+Anions) diagram of geothermal brine waters.

groundwater. Geothermal spring no. 12 is mixing with geothermal brine and deep circulated groundwaters with lower tritium and relatively depleted oxygen-18 and deuterium values. Samples 4 and 12 were able to maintain their original properties in the dry period with lower tritium and more positive deuterium values, i.e. they arise from a deep-seated geothermal aquifer and groundwater sources, respectively.

Sample 22, with low temperature and conductivity, represents steam heated shallow groundwater having relatively depleted stable isotope values compared with other geothermal brine waters (Figure 9 and Figure 10). As shown in Figure 10, the concentration of cations and anions shows large differences between the rainy and dry seasons and the $\delta^{18}\text{O}$ -Cl relationship can be employed to distinguish seawater and halite-dissolved solution (Ma et al., 2007). The relatively higher HCO_3/Cl ratio (Table 2a) and the elevated (Na+Ca)/Cl ratios with the lowest total ions (Figure 11) of sample 22 also support this idea. The lower tritium value of sample 22 indicates older groundwater age. The chloride and stable isotope values of stream waters (1, 8, 14) are increased by overflowing of geothermal brine, especially in the dry period (Figure 10 and Figure 12). This increase can be traced in major ion contents. Geothermal sample-22 plots

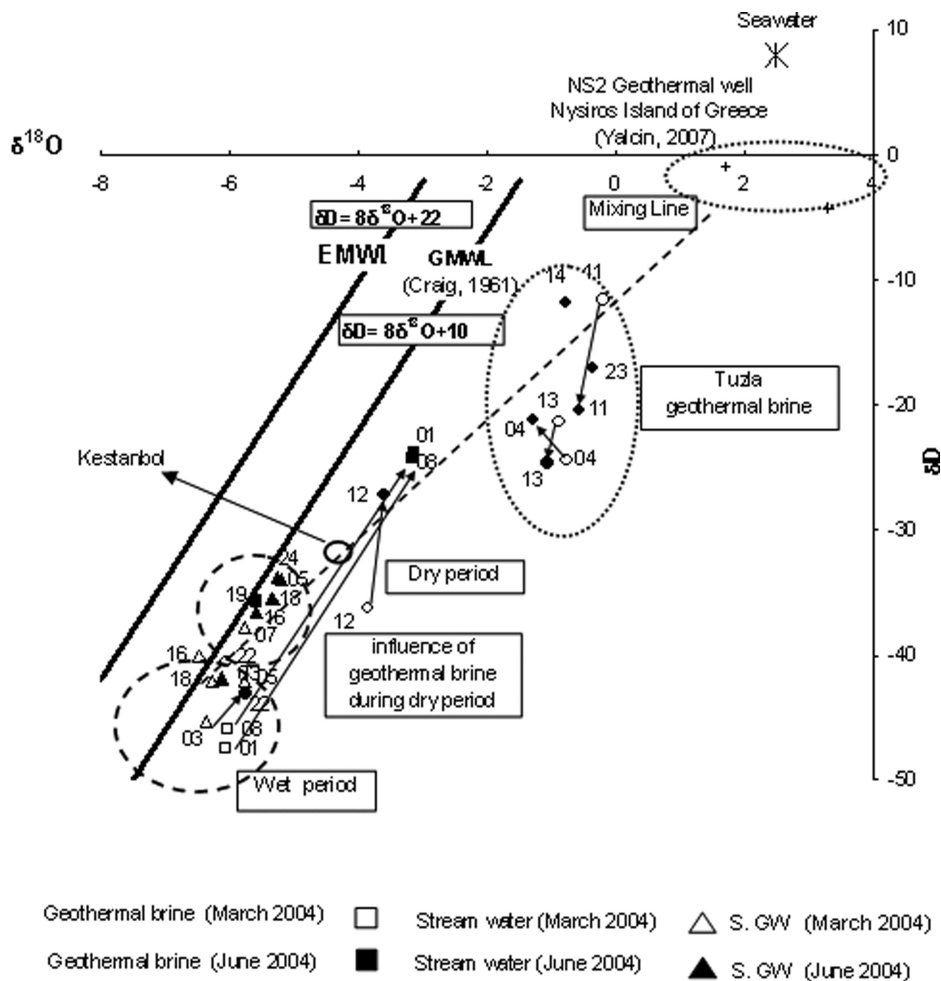


Figure 12. Oxygen-18 ($\delta^{18}\text{O}$)-Deuterium (δD) diagram (EMWL: Eastern Mediterranean Water Line, GMWL: Global Meteoric Water Line).

with shallow groundwaters, indicating either shallow circulation or mixing with shallow aquifer waters. There seems to be no effect of enrichment due to evaporation in the oxygen-18 and deuterium plot (Figure 12). The Tuzla Stream waters (samples 1 and 8) are surface waters recharged by precipitations at high altitudes of the study area in the wet period. When these locations are influenced by discharging of geothermal brine, they become of a similar salinity to geothermal brine with higher oxygen-18 and deuterium values. For this reason, waters taken from the Tuzla stream show abrupt change due to the effect of geothermal brine discharging during the dry period (Arrow shows change due to geothermal influence during dry and wet periods in Figure 12). The $\delta^{18}\text{O}$ values of geothermal brine water 4, 11, and 13 show no remarkable seasonal changes except for their δD values, probably due to exchange with clays or hydrocarbons (International Atomic Energy Agency [IAEA], 1981). In fact, the low tritium and high $\delta^{18}\text{O}$ and δD values of these geothermal brine waters (samples 4, 11, 13) show that they have a long residence time and are deep-originated geothermal brine.

In Figure 12, most of the shallow groundwaters in the wet season fall below GMWL (Craig, 1961). This setting can be explained by mixing with geothermal brine, which has caused a shift in the isotopic composition of shallow groundwater samples that were originally on GMWL or another local meteoric water line. The higher electrical conductivity (EC) values of shallow groundwater also support this idea. Stable isotope values of shallow groundwaters in the dry period are relatively more positive than those of the wet period due to a decrease in the contribution of winter precipitation into the shallow aquifer. According to Figure 12, geothermal brine is enriched in $\delta^{18}\text{O}$ because water-rock interaction takes place when the temperature is $>150^\circ\text{C}$ in the aquifer system (Hoefs, 1987).

Geothermal brine waters are situated in a completely different cluster (Figure 12) from the shallow groundwater, which have lower δD and elevated T values varying from 4 TU to 6 TU compared with the geothermal waters with higher δD and lower tritium. The isotopic values of Kestanol (10 km north of Tuzla) and Tuzla have similar salinity values to Nysiros brine shown in Figure 12. Yalcin (2007) gives the most probable explanation for the origin of discharging brine in Tuzla and Kestanol areas as deep-seated hot fossil seawater resulting from dilution and cooling during uprising by infiltrating meteoric water. Accordingly, the Br/Cl ratio of the Tuzla brine is rather lower than that of the recent seawater (Mützenberget al., 1992). Furthermore, Yalcin (2007) points out that Tuzla geothermal brine is stretched to the values of Nysiros brine by dilution of deep-seated hot brine. This explanation is shown in Figure 12 by the dashed line. Thus, the origin of Tuzla geothermal brine is deep brine water entrapped in pore spaces of the rocks. The present day isotopic composition of Mediterranean Sea Water is $\delta^{18}\text{O} = +2.5$, $\delta^2\text{H} = +8$ and the origin of Nysiros brine is a mixture of deep thermal fluid and shallow cold groundwater. The addition of groundwater input is less in Nysiros.

As the geothermal brine moves to the surface, it is probably cooled by either mixing with surface water or conductive

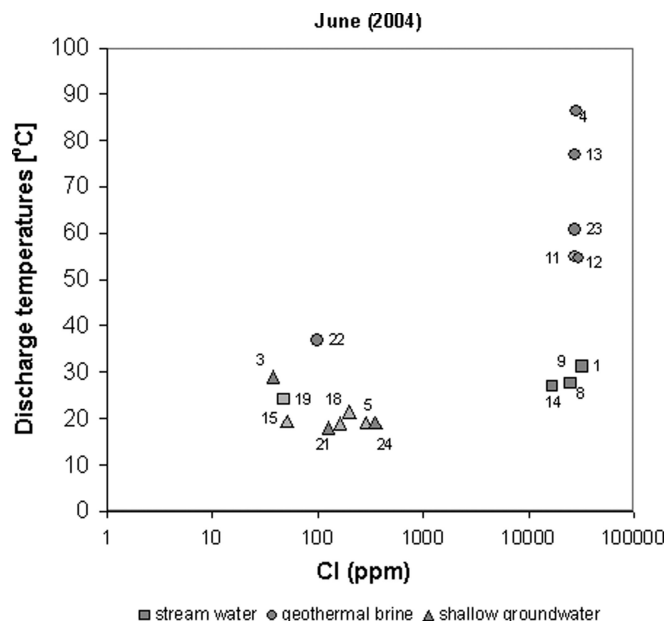


Figure 13. Relationship between discharge temperatures and chloride contents.

cooling (i.e. during ascent of liquid water with conductive heat loss). The hydrogen composition is not changed, as there is no other hydrogen-containing mineral available (Figure 13). All geothermal brine waters in the TGF (except sample 22, steam-heated water) have similar Cl-contents against the descending discharge temperatures.

The d-excess ($=\delta\text{D}-8\delta^{18}\text{O}$) of the shallow groundwaters varies between 5–10‰, reflecting no substantial post-precipitation change of isotope composition (Figure 14). The shallow groundwater with d-excess $>5\text{‰}$ and lower $\delta^{18}\text{O} < -5\text{‰}$ are representative of low evaporation and higher permeability (Gupta et al., 2005; Istvan et al., 2006). The higher tritium values are also in good consistence with this setting. Thus, the lower d-excess and higher $\delta^{18}\text{O}$ values imply high evaporation and low permeability or a long residence time.

The stable isotope data indicate that the infiltration of evaporated return irrigation water is somewhat responsible for the occurrence of subsurface salinity in the shallow groundwater. Since the Tuzla plain has a topographically flat area where salt accumulation is easily formed due to flowing out from the geothermal brine springs and salts are leached to the subsurface during significant recharge periods. However, these salts can reach the shallow groundwater in a few months. This is confirmed by the elevated salt contents of the samples taken during the dry season. Although there is no clear evidence to identify the main source of the salinization in the shallow groundwater, as either upward movement of geothermal brine or surficial leakage into the shallow aquifer, the low temperature of shallow groundwater supports the second alternative.

The tritium contents of shallow groundwaters are between 4.02 TU and 5.96 TU in the wet period and between 3.25 TU and 5.15 TU in the dry period. These tritium values are in the

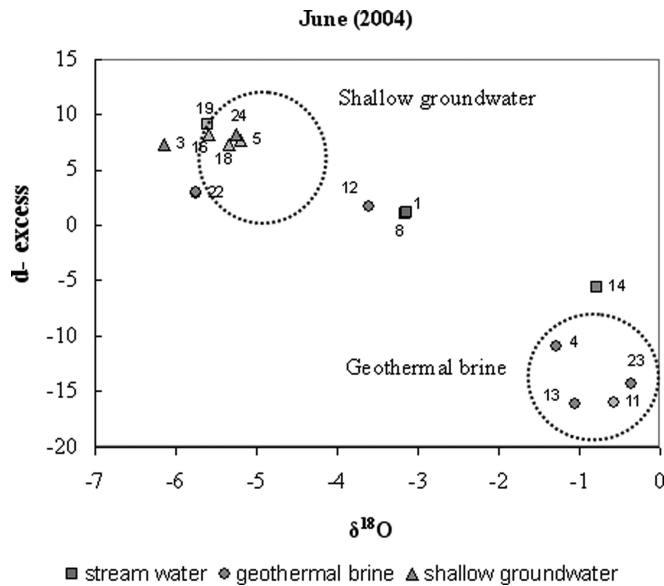


Figure 14. d-excess vs. $\delta^{18}\text{O}$ plot showing relationship between evaporation and permeability features of waters.

range of annual mean values of precipitation (Global Network of Isotopes in Precipitation [GNIP]/IAEA Network). The residence times of shallow groundwater generally vary from several months to years (Mützenberg, 1997). In Tuzla Stream water, sample 1, the tritium value decreases from 3.55–0.55 TU due to the contributions of geothermal brine free of tritium in the dry period. The tritium value of the cold-water spring (sample 3) near the geothermal brine manifestations is the same as that of the groundwater. Tritium data show a relative age of geothermal brine to be more than 50 years. Thus, the Tuzla hot brine seems to have a longer time of residence within the crystalline rocks. This result is consistent with the conclusions of Balderer and Synal (1996; 1997) who calculated the mean residence time of the Tuzla brine as 430 000 years by $^{36}\text{Cl}/\text{Cl}$ ratio. In addition, the residence time of the Tuzla brine was also calculated to be as long as 1 million years by Mützenberg (1997). This confirms the hydrogeological conceptual model of Tuzla brine as coming from fossil pore-water, previously suggested by the studies (Balderer, 1997; Mützenberg, 1997).

Conclusions

The Tuzla geothermal brine, which has NaCl composition, discharges into the Tuzla Stream and spreads to the downstream area, consequently deteriorates the quality of shallow groundwater. The worsening in freshwater quality was investigated by chemical and isotopic tracers ($\delta^{18}\text{O}$, δD , and tritium) in the area. Since the residence time of the shallow groundwater is relatively short (i.e. permeability of unsaturated zone is high enough for rapid infiltration) surficial salt accumulation can readily penetrate into the shallow aquifer in a short time. This observation is in good agreement with the findings of Mützenberg (1997). Thus, excessive enrichment of sodium in shallow groundwater

leads to a decrease of soil permeability and drainage condition, eventually causing a salinity hazard.

The obtained results show that mainly two mechanisms may be hold responsible for the deterioration of shallow groundwater quality: 1) seasonal influx of salts and trace elements coming from the geothermal brine, which have accumulated at the surface; 2) direct mixing of geothermal brine with shallow groundwater via vertical faults and cracks. Due to these mechanisms, the stable isotope values of shallow groundwater are more positive than expected. However, the first mechanism seems to be more dominant due to the low temperature of shallow groundwater. Thus, the chemistry and isotope characteristics of the shallow groundwater are mainly controlled by the geothermal brine influence and halite dissolution on the surface of the soil that modifies surface water and groundwater quality. Therefore, the uncontrolled discharge from geothermal springs should be monitored and controlled to reduce its adverse effects.

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