

Effect of high sulfate concentration on the corrosivity: a case study from groundwater in Harran Plain, Turkey

Ayşe Dilek Atasoy · Mehmet İrfan Yesilnacar

Received: 18 December 2008 / Accepted: 3 June 2009 / Published online: 25 June 2009
© Springer Science + Business Media B.V. 2009

Abstract Corrosion, which tends to increase the concentrations of certain metals in tap water, is one of the most important water quality problems as it can affect public health and public acceptance of water supply and the cost of providing safe water. In this context, this study aimed at investigating the scale formation tendency or corrosivity of groundwater in the semi-arid Harran Plain. The degree of scale formation tendency/corrosivity of water was determined considering pHs, Langelier Index, and Ryznar Index of groundwater samples. Except for well no.4, which is close to a local hot spring, all the wells had corrosive characteristics. The amount of CO₂ from the soil zone respiration and high sulfate concentration in the wells are important factors affecting corrosiveness. Results showed that precipitation, excessive irrigation, and change in groundwater level caused seasonal variation in corrosive characteristics.

Keywords Corrosion · Sulfate · Scaling · Langelier Index · Groundwater

Introduction

As in other semi-arid and arid parts of the world, water is a valuable resource in Harran Plain in the southeastern region of Turkey. Groundwater is an important resource in the plain. The quality of groundwater is as important as its quantity, owing to the suitability of water for various purposes.

Corrosion is one of the most important water quality parameters. It can affect public health, public acceptance of a water supply, and the cost of providing safe water. Corrosion tends to increase the concentrations of certain metals in tap water, like toxic metals, lead, cadmium, nickel, copper, iron, and zinc, that cause staining of fixtures or metallic taste, or both (Melidis et al. 2007). Water causes corrosion of pipelines and heat-exchange surfaces. Through many years of water use, scientists and technologists have researched numerous ways of fighting corrosion (Prisyazhniuk 2007). Contamination of potable water by outside materials raises the probability of bacterial infection and can lead to epidemic diseases. Further, the accumulation of corrosion products inside the pipes can cause plugging and can lead to operational difficulties. Other aspects of the corrosion problem are the high costs of repair, replacement, and water loss (El Din 2009).

Water's corrosive or scaling tendency depends on its physical and chemical characteristics. Scale formation tendency is the other important water

A. D. Atasoy · M. I. Yesilnacar (✉)
Department of Environmental Engineering,
Harran University, Osmanbey Campus,
63190, Şanlıurfa, Turkey
e-mail: iyasilnacar@yahoo.com, mirfan@harran.edu.tr



Fig. 1 Location map of the study area

quality parameter. The formation of scale on heat-transfer surfaces reduces the heat transfer (Al-Rawajfeh et al. 2005) and offers a resistance to the flow of heat. Scale deposits can accumulate in pipelines, orifices, and other flow passages to the extent that the flow of process fluids is seriously impeded (El Dahan and Hegazy 2000).

The Harran Plain covers the important residential areas like Sanliurfa City center, Harran, and Akcakale districts (Fig. 1). The requirement of drinking, usage, and partially irrigation water is provided from groundwater in 1,500 km² of plain area. As designating the scale formation or corrosivity of groundwater is a very important issue, this study aimed at determining the corrosivity or scale formation potential of the groundwater in Harran Plain using Langelier and Ryznar Indices. For this purpose, 288 samples from 24 observation wells were analyzed monthly for 1 year for the parameters of temperature, pH, electrical conductivity (EC), calcium, sulfate, alkalinity, and total organic carbon (TOC). Also, the paper discusses the seasonal variations of corrosivity and the effect of high sulfate concentration on it.

Materials and methods

Study area

The Harran Plain is located in the south central part of the Sanliurfa–Harran Irrigation District (Fig. 1). The plain is 30 × 50 km and is located in a region of rolling hills and a broad plateau

that extends south into Syria. The plain has 141,500 ha of irrigable land, 3,700 km² of drainage area, and 1,500 km² of plain area. The plain is located approximately between latitudes 36°43′–37°10′ North and longitudes 38°47′–39°10′ East. The plain has a semi-arid climate with almost no precipitation between June and September. The long-term mean annual precipitation is 284.2 mm, the temperature is 18°C, and the evaporation is 1,884 mm (DSI 2003). Because rainfall is rare in this period, irrigation is needed during the growing season to maintain and subsequently enhance crop growth and yield. The temperature in June, July, and August is generally above 40°C and the relative humidity is below 50% (Oktem 2008).

The soils of the plain are mainly clays, and pH values are roughly neutral (pH 7.50–8.00). According to the results of permeability tests on the plain, the minimum permeability value is 0.22 m/day and the maximum is 3.51 m/day (DSI 2003). Soil colors are mostly brown and reddish brown (DSI 1972; Ozer and Demirel 2002).

Geology and hydrogeology

Geological units outcropping in the study area, from the bottom to the top, are comprised of Eocene, Pliocene, and Pleistocene. The Eocene aged unit is composed of karstic, jointed, and fractured limestones, and its thickness is about 300 m. This unit outcrops in the north, west, and east of the study area, and is a deep and confined aquifer. It is overlaid by the Pliocene. The Pliocene is composed of clay containing gypsum locally and its thickness is roughly 200 m. This unit has not formed an aquifer. It forms an impermeable barrier for the Pleistocene aged unit and is overlaid by the Pleistocene. The Pleistocene is composed of clay, sand, and gravel, and its thickness is approximately 60 m. This unit is a shallow/unconfined aquifer. Hundreds of shallow wells on this unit are drilled. For this work, groundwater samples were taken from this unit (DSI 1972; Yesilnacar and Gulluoglu 2008).

The Harran Plain is built up of Eocene limestone, occurring in a graben structure bordered by large N–S-orienting faults. Geological units in the study area and their main geological and

hydrogeological properties are described below. From the bottom to the top, the area is composed of Paleocene, Eocene, Miocene, Pliocene, and Pleistocene aged units (Fig. 2). There are two types of aquifers in the study area. The first is a

deep aquifer, also called a confined aquifer, lower aquifer, or Eocene aquifer. The second is an upper aquifer, also called an unconfined aquifer, shallow aquifer, or Pleistocene aquifer (DSI 1972, 2003; Yesilnacar and Gulluoglu 2008).

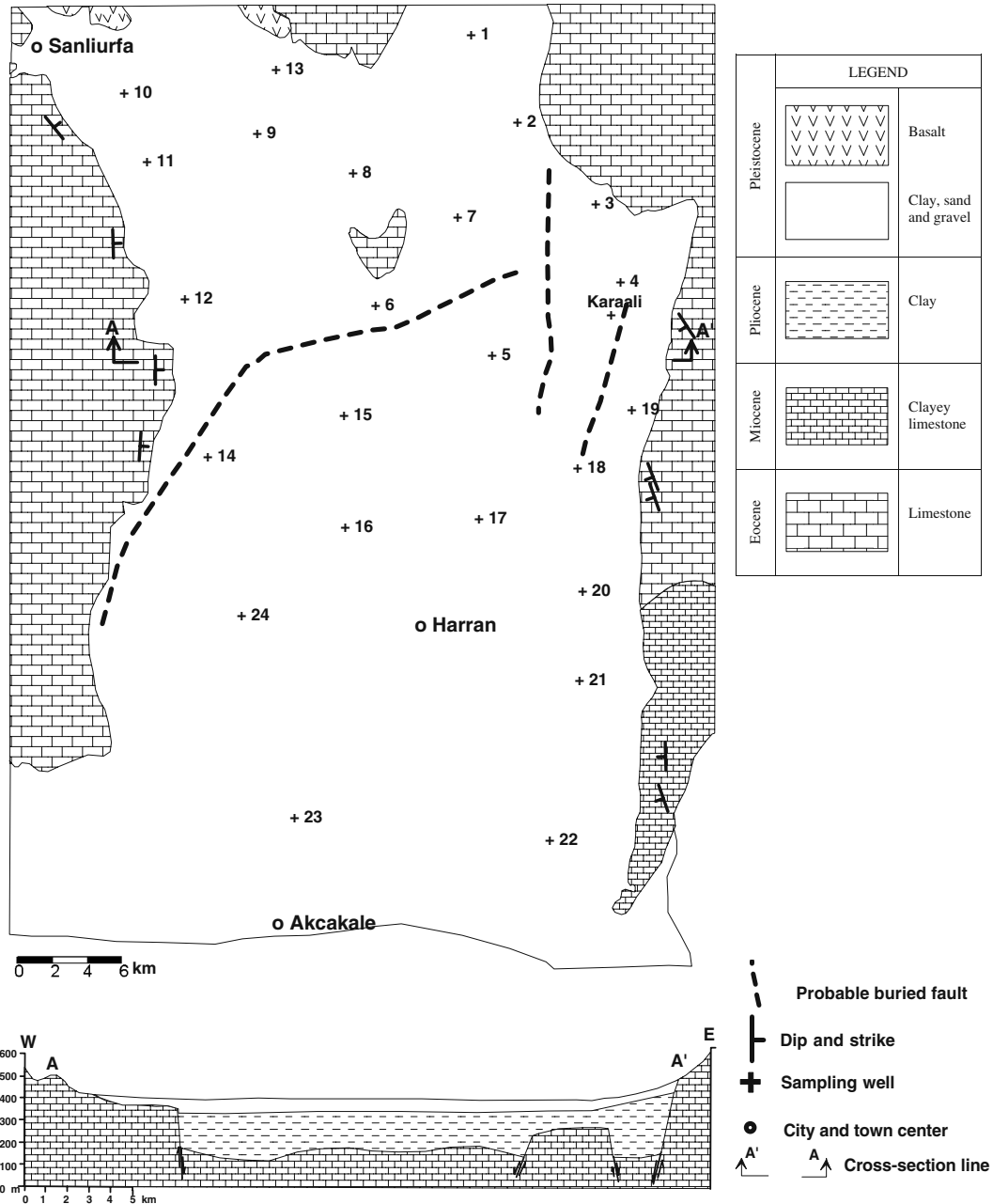


Fig. 2 Geological map and cross-section of the study area (adapted from DSI 2003)

Sampling and analytical methods

A total of 288 groundwater samples were collected monthly from 24 representative observation wells (Fig. 3), which were drilled on the Pleistocene aged unit during the 2006 water year used in Turkey and in the entire northern hemisphere, which starts on 1 October of a year and ends on 30 September of the next year, and takes the name of the latter year. Except for well no. 4, the depths of the sampled wells range from 20 to 60 m. EC, temperature, and pH were measured with YSI 6600 sonde, SevenGo pro-SG7 electrical conductivity meter, a portable pH meter, and an electric contact meter immediately after sampling in the field. Sampling and measurement procedures were carried out in accordance with:

- D4448-01 Standard Guide for Sampling Groundwater Monitoring Wells (ASTM 2001),
- Water Quality Sampling—Part 2: Guidance on Sampling Techniques (TSE 1997) and
- Groundwater Well Sampling (EPA 1995).

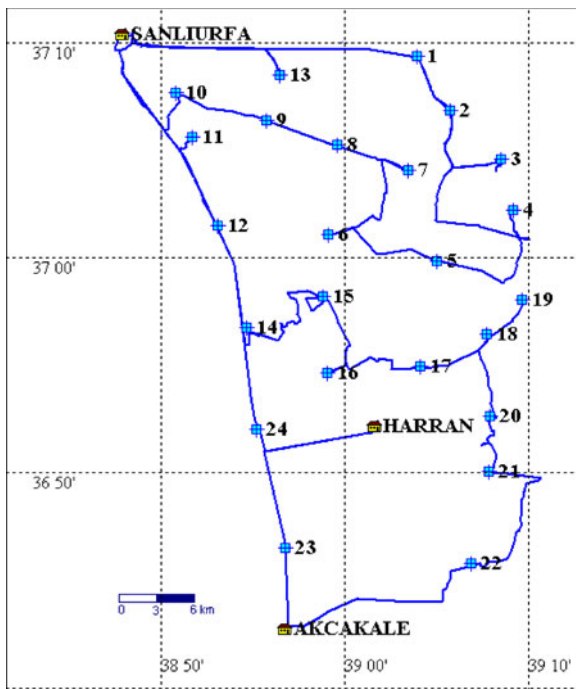


Fig. 3 Study area showing location of the sampling wells

Water samples collected in the field were analyzed for chemical constituents such as calcium (Ca^{+2}), bicarbonate (HCO_3^-), total organic carbon (TOC), and sulfate (SO_4^{-2}). Analyses were conducted in the laboratory according to standard methods (APHA-AWWA-WEF 1999). Concentrations of Ca^{+2} and SO_4^{-2} were determined using Varian flame atomic absorption spectrometer and a Merck Nova 60 photometer, respectively. Concentration of HCO_3^- was analyzed by volumetric titrations. Total organic carbon (TOC) was analyzed by means of a Shimadzu TOC instrument. The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally around 5%.

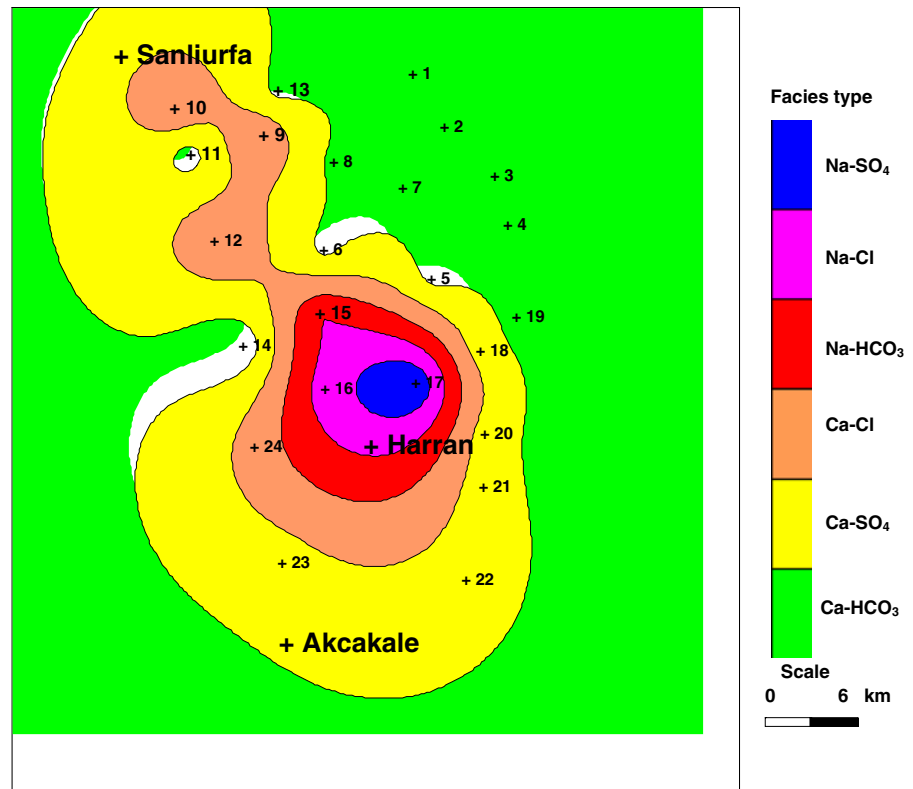
Hydrochemical facies

Yesilnacar and Gulluoglu (2008) determined the hydrochemical facies of 24 wells on the study area. On the basis of chemical analyses of 24 well waters from the shallow aquifer during the 2006–water year, groundwater is divided into six facies. Well nos. 1, 2, 3, 4, 5, 6, 7, 8, 11, 13, 14, and 19 on the eastern side of Şanlıurfa, Harran, and Akcakale, and near to the Eocene aged limestones represent Ca-HCO_3 facies. Well nos. 18, 20, 21, 22, and 23, which reach to the clay containing gypsum aged the Pliocene, in the vicinity of Şanlıurfa, Harran, and Akcakale, represent Ca-SO_4 facies. Well nos. 9, 10, 12, and 24 on the northern side of Harran represent Ca-Cl facies. Well nos. 15, 16, and 17 on the southern part of Harran represent as Na-HCO_3 , Na-Cl , and Na-SO_4 facies, respectively (Fig. 4). Ca-HCO_3 and Ca-SO_4 are the dominant hydrochemical facies in the study area.

Definition of saturation pH and corrosion index

The Langelier Index (LI) is probably the most widely used indicator of water scale potential or of water corrosivity. LI is a thermodynamic parameter that determines the scale formation potential which is related to the precipitating or dissolving of calcium carbonate (Withers 2005).

Fig. 4 Facies map of all wells in the study area



Calcium carbonate dissociates in the water as follows (Hamrouni and Dhahbi 2002):



K_{sp} of calcium carbonate is,

$$K_{\text{sp}} = (\text{M}_{\text{Ca}^{+2}} \cdot \gamma_{\text{Ca}^{+2}}) \cdot (\text{M}_{\text{CO}_3^{-2}} \cdot \gamma_{\text{CO}_3^{-2}}) \quad (2)$$

$$(\text{M}_{\text{CO}_3^{-2}} \cdot \gamma_{\text{CO}_3^{-2}}) = K_{\text{sp}} / (\text{M}_{\text{Ca}^{+2}} \cdot \gamma_{\text{Ca}^{+2}}) \quad (3)$$

M is molarity and γ is activity coefficient in Eq. 2. The relationship between CO_3^{-2} and HCO_3^{-} can be given by the second dissociation constant of the carbonic acid (Hamrouni and Dhahbi 2002);



$$K' = (\text{M}_{\text{CO}_3^{-2}} \cdot \gamma_{\text{CO}_3^{-2}}) \cdot (\text{M}_{\text{H}^{+}} \cdot \gamma_{\text{H}^{+}}) / (\text{M}_{\text{HCO}_3^{-}} \cdot \gamma_{\text{HCO}_3^{-}}) \quad (5)$$

$$(\text{M}_{\text{H}^{+}} \cdot \gamma_{\text{H}^{+}}) = K' \cdot (\text{M}_{\text{HCO}_3^{-}} \cdot \gamma_{\text{HCO}_3^{-}}) / (\text{M}_{\text{CO}_3^{-2}} \cdot \gamma_{\text{CO}_3^{-2}}) \quad (6)$$

$K_s = 5.25 \times 10^{-9}$ and $K' = 5.01 \times 10^{-11}$ at 25°C . K_{sp} and K' are variable with temperature as;

$$\ln K_1 / K_2 = (\Delta H^\circ / R) \cdot (1/T_2 - 1/T_1) \quad (\text{Van't Hoff equation}) \quad (7)$$

$\Delta H_{\text{HCO}_3}^\circ = -165.18$ and $\Delta H_{\text{CaCO}_3}^\circ = -269.78$ and T is accepted in Kelvin. K' and K_{sp} are obtained for the sample temperatures. Equations 3 and 6 are incorporated:

$$(\text{M}_{\text{H}^{+}} \cdot \gamma_{\text{H}^{+}}) = K' \cdot (\text{M}_{\text{HCO}_3^{-}} \cdot \gamma_{\text{HCO}_3^{-}}) \cdot (\text{M}_{\text{Ca}^{+2}} \cdot \gamma_{\text{Ca}^{+2}}) / K_{\text{sp}} \quad (8)$$

γ activity coefficients are obtained by ‘‘Guntelberg correlation’’ as;

$$\log \gamma = -0.5 \cdot Z_i^2 \cdot \mu^{1/2} / (1 + \mu^{1/2}) \quad (9)$$

$$\mu = 2.50 \cdot 10^{-5} \cdot \text{TDS} \quad (10)$$

$\text{pH}_{\text{saturation}}$ (pH_s) is calculated as follows;

$$\text{pH}_s = -\log [\text{H}] \text{ and } [\text{H}] = (\text{M}_{\text{H}^+} \cdot \gamma_{\text{H}^+})$$

and \log (Eq. 7) is the pH_s ;

$$\text{pH}_s = -\log (K' \cdot (\text{M}_{\text{HCO}_3^-} \cdot \gamma_{\text{HCO}_3^-}) \cdot (\text{M}_{\text{Ca}^{+2}} \cdot \gamma_{\text{Ca}^{+2}}) / K_{\text{sp}}) \quad (11)$$

Eventually, Langelier Index (LI) is found as;

$$\text{LI} = \text{pH}_{\text{sample}} - \text{pH}_s \quad (12)$$

And Ryznar Index (RI) is found as;

$$\text{RI} = 2 \cdot \text{pH}_s - \text{pH}_{\text{sample}} \quad (13)$$

If a water has a negative LI value ($\text{pH} < \text{pH}_s$), it is undersaturated with respect to calcium carbonate and is potentially corrosive. Conversely, for waters with a positive LI ($\text{pH} > \text{pH}_s$), the water is supersaturated with CaCO_3 and the water has the potential to form scale. Saturated water has a LI of zero ($\text{pH} = \text{pH}_s$) (Al-Rawajfeh et al. 2005). The Langelier Index shows the direction of the driving force but does not indicate if the supersaturation is high enough to initiate crystallization. Ryznar, therefore, suggested an index which attempts to quantify the relationship between CaCO_3 saturation state and scale formation. The evaluation of the Ryznar Index (RI) is given in Table 1.

Statistical analyses of data

Statistical analyses of Langelier Index, Ryznar Index, and sulfate concentration were performed by the Minitab (Release 13.20) computer program.

Table 1 Definition of the Ryznar Index (Ludwig and Hetschel 1990)

RSI value	Indication
4.0–5.0	Severe scaling
5.0–6.0	Moderate to slight scaling
6.0–7.0	Stable water, slight tendency for dissolving of scale
7.0–7.5	Dissolving of scale, corrosive
7.5–9.0	Intense dissolving of scale and corrosion
>9.0	Very intense dissolving of scale and corrosion

Pearson product moment correlation coefficients and significant levels of data were calculated to define the correlation between the Langelier Index, Ryznar Index, and sulfate concentrations. The correlation coefficient shows the linear correlation between the two parameters and ranges between -1 and $+1$. If the linear correlation between two parameters is negative, then the coefficient is -1 . The correlation coefficient is $+1$ for the positive linear variations. The statistical significant of correlation is determined by the comparison of selected (generally $\alpha = 0.05$) and calculated significant levels (p). If $p < \alpha = 0.05$, then the correlation is statistically significant (MINITAB 2000).

Results and discussions

Certain characteristics of groundwater

Range, mean, and standard deviation of temperature, pH, electrical conductivity (EC), calcium, sulfate, alkalinity, and total organic carbon (TOC) of the groundwater samples are summarized in Table 2. There was no significant seasonal variation in the groundwater temperature during the sampling period. The annual mean temperature was approximately 20°C and the average pH of the groundwater (7.0–7.8) is within the limits accepted by the TSE standard (266), the WHO guidelines, and the EU directive. The EC has been used a criterion in classification of drinking and irrigation waters. The average EC values (1,317–2,935 $\mu\text{S}/\text{cm}$) are fairly above the TSE standard (266) (guide level = 650 $\mu\text{S}/\text{cm}$) and the WHO (maximum admissible concentration = 250 $\mu\text{S}/\text{cm}$) guidelines (the TDS values are calculated as 65% of the EC and variations of the TDS values in 2006 year are as the same as of the EC). The average pH values of groundwater range from 7.0 to 7.5. The values were found to be between the guide levels of 6.5 and 9.5 designated by the TSE, (266) standard, the WHO guidelines, and the EU directive. The annual mean of the calcium is between the range of 41–495 mg/l. The highest calcium concentrations are in the well nos. 22, 21, 12, and 24, respectively.

Table 2 Mean values of some physical and chemical parameters of groundwater in the sampling wells (Concentrations are expressed in mg/l, temperature in °C, EC in µS/cm)

Well no.	pH	Temperature	EC	SO ₄ ⁻²	HCO ₃ ⁻	TOC	Ca ⁺²
S1	7.0	16.5	908	32.2	380.8	3.7	108.2
S2	7.5	19.8	790	29.0	267.9	2.8	45.1
S3	7.3	20.9	738	38.0	209.4	1.6	75.8
S4	7.4	29.7	905	105.9	243.9	1.9	81.5
S5	7.4	20.3	1,384	83.4	190.0	3.7	95.6
S6	7.4	20.5	604	18.7	171.2	2.7	95.6
S7	7.4	20.6	716	32.3	149.8	3.3	53.0
S8	7.4	20.2	757	18.4	103.6	2.3	55.1
S9	7.0	20.6	2,270	16.5	78.6	3.6	195.7
S10	7.2	19.5	1,155	21.0	179.4	3.3	114.3
S11	7.2	19.0	985	33.2	220.8	3.2	86.4
S12	6.9	20.2	3,442	198.8	206.5	1.7	314.8
S13	7.6	20.5	469	5.0	128.8	2.6	40.9
S14	7.3	18.9	796	26.8	168.2	3.8	47.3
S15	7.4	19.4	1,048	143.1	183.3	4.7	55.3
S16	7.5	20.4	2,542	217.2	309.9	3.7	59.2
S17	7.3	21.5	4,848	870.5	19.9	3.1	271.7
S18	7.1	20.6	2,151	461.3	59.2	1.0	191.0
S19	7.5	21.1	779	52.8	94.2	2.9	63.9
S20	7.4	20.2	1,358	212.2	76.6	5.0	96.5
S21	7.4	20.9	3,410	1,218.7	6.3	2.9	413.2
S22	7.3	19.8	4,584	1,901.7	6.4	2.4	495.3
S23	7.4	21.6	1,519	262.2	86.3	4.2	109.8
S24	7.2	20.8	2,828	153.8	80.3	2.3	290.3

Except for well nos. 22, 21, 17, 18, and 23, the average sulfate concentrations were found to be below the maximum admissible concentration (MAC) of 250 mg/l designated by the TSE (266) standard, the WHO guidelines, and the EU directive. Higher sulfate concentrations result from thin gypsiferous layers within the Pliocene aged deposits. In particular, gypsum and anhydrite appear in evaporite deposits in the center of Anatolia and in the Southeast Anatolia (Erguvanli and Yuzer 1987). Devadas et al. (2007) specified Sarada River basin, India as a center for agriculture like the Harran Plain, Turkey. Agricultural practice is intensive and long-term without any control of using chemical fertilizers for higher crop yields in both study areas. Fertilizers used contain sulfate with other ions. Hence, high sulfate concentration in some wells in Harran Plain can be explained also by the intensive agricultural activities.

The annual mean of alkalinity values in the wells are in the range of 6.3 and 381 mg/l. Well no. 1 has the highest and well no. 21 has the lowest HCO₃⁻ alkalinity. The average total organic car-

bon (TOC) values vary between 1.0 mg/l in well no. S18 and 5.0 mg/l in well no. S20.

Scaling or corrosion tendency of groundwater in Harran Plain

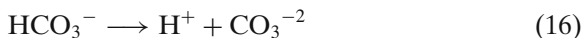
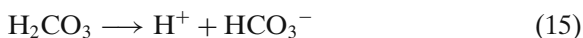
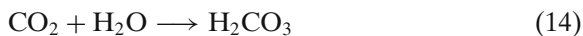
The annual mean of pHs, Langelier Index (LI), and Ryznar Index (RI) of groundwater samples are presented in Table 3. The graphs of Langelier and Ryznar Indices of representing wells are shown in Figs. 5 and 6, respectively. Negative LI represents corrosion (Withers 2005) and positive value predicts scale formation of water. On the other hand, water is considered to be corrosive when the RI exceeds 6.0 and scale forming when this index is less than 6.0 (Pátzay et al. 1998). LI values are negative except for well no. S4 and ranged from -0.07 in well no. S6 to -1.22 in well no. S22. Well no. S4 has positive LI (0.03). Therefore, it has a scale formation tendency. RI values ranged from 7.26 in well no. S1 to 9.69 in well no. S22. RI is higher than 6.0 and the LI is negative (except for S4) for all representing wells. Well no. 4 is closer to Karaali Hot Springs

Table 3 The annual mean of pHs LI and RI of representing wells

Well no.	pHs	Langelier Index (LSI)	Ryznar Index (RI)
S1	7.12	-0.15	7.26
S2	7.61	-0.08	7.69
S3	7.48	-0.18	7.66
S4	7.35	0.03	7.33
S5	7.50	-0.09	7.60
S6	7.45	-0.07	7.52
S7	7.78	-0.39	8.17
S8	7.93	-0.49	8.42
S9	7.65	-0.68	8.33
S10	7.43	-0.28	7.71
S11	7.45	-0.22	7.67
S12	7.10	-0.22	7.32
S13	7.92	-0.29	8.20
S14	7.80	-0.49	8.29
S15	7.73	-0.36	8.08
S16	7.60	-0.13	7.72
S17	8.24	-0.95	9.20
S18	7.78	-0.65	8.42
S19	7.91	-0.38	8.28
S20	7.89	-0.50	8.39
S21	8.49	-1.07	9.56
S22	8.47	-1.22	9.69
S23	7.79	-0.42	8.21
S24	7.51	-0.33	7.84

(see Fig. 1), which is located 32 km southeast of Sanliurfa province, and has a temperature of between 41.5 and 49.0°C and a depth of between 138 and 198 m (Dogdu and Kirmizitas 2006).

The groundwater samples are expected to have the corrosion tendency because of the high CO₂ concentration (Al-Rawajfeh et al. 2005).

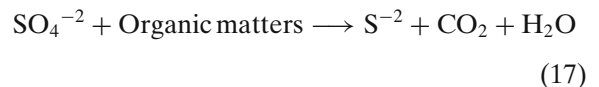


Dissociation of CO₂ in the water reduces the pH of water (annual mean of the pH is 7.3) according to the above equations and causes to increase the corrosion tendency. Therefore, both LI (except for S4) and RI values indicate corrosion conditions for all representing wells. Al-Rawajfeh and

Al-Shamaileh (2007) indicated a similar case in the tap water resources in Tafila Province, South Jordan. They determined negative LI values for the water samples (ranged from -0.39 to -1.55) and corrosivity was explained with CO₂ effect on the pH.

Effects of sulfate concentration on the corrosivity

The sulfate concentrations in the groundwater samples are presented in Fig. 7. The wells which have the high sulfate concentrations also have the low Langelier or high Ryznar Index. Well nos. S22, S21, S17, and S18, respectively, are more corrosive samples and also have higher sulfate concentrations. Alkalinity, pH, chloride, and sulfate are primary water quality parameters affecting metal corrosion (Tang et al. 2006). The presence of sulfates does pose a major risk for metallic materials in the sense that sulfates can be converted to highly corrosive sulfides by anaerobic sulfate-reducing bacteria (Ismail and El-Shamy 2009). As the sulfide-producing bacterial population increases, hydrogen sulfide gas produces by the sulfide-producing bacteria and sulfate-reducing bacteria (SRB) reacts with metal surfaces (Kaur et al. 2009). Sulfate can be reduced to sulfide by sulfate-reducing bacteria in the presence of organic compounds, which are used as electron donor and carbon source. The activity of sulfate-reducing bacteria produces CO₂, which impact the corrosivity of water (Eq. 17) (Sahinkaya et al. 2007).



Organic carbon values range from 1 to 6.2 mg/l in the groundwater samples (Table 2). CO₂ production from sulfate reduction in the presence of organic compound tends to increase CO₂ concentration. Therefore, Langelier and Ryznar Index values of the wells containing high sulfate concentration indicated a corrosion tendency.

The LI values of the wells in Ca-SO₄ facies are lower than others during a year in Harran Plain. Ca-HCO₃, Ca-SO₄, and Ca-Cl facies have the

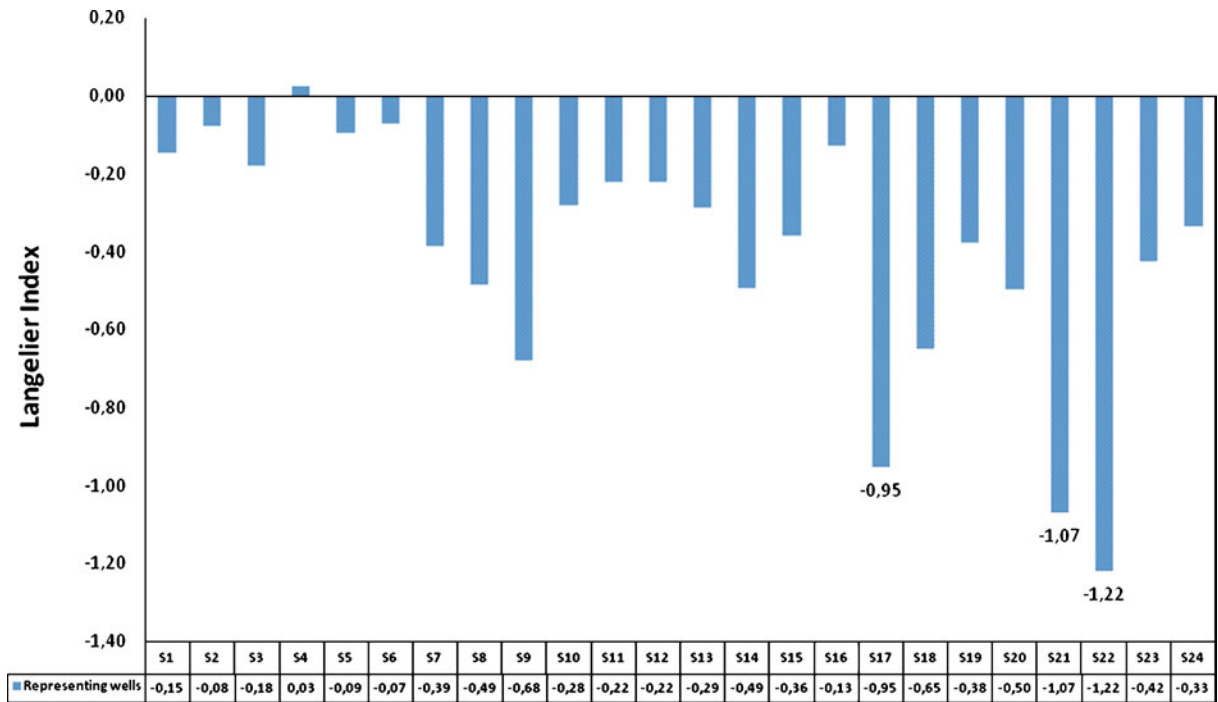


Fig. 5 Langelier Index graph of representing wells

corrosive groundwater but the wells in Ca–SO₄ facies are the most corrosive ones (Fig. 8). High sulfate concentrations resulted from thin gypsiferous layers within the Pliocene aged deposits reduced the pH and the Langelier Index of the groundwater. Natural geochemical processes play an important role in groundwater quality (Coetsiers and Walraevens 2006). Devadas et al. (2007) reported that the hydrogeochemical characteristics affected the groundwater quality for the Sarada river basin. The study of geochemistry of groundwater is an important aspect for drinking, irrigation and industrial purposes. Each groundwater system has a unique chemistry due to chemical alteration of meteoric water, recharging the aquifer system (Drever 1988; Hem 1991). Hence, geochemistry of the area should be considered when evaluating the corrosivity of the groundwater.

Statistical analyses of corrosivity and sulfate concentration

Pearson product moment correlation coefficients and significant levels between Langelier Index,

Ryznar Index, and sulfate concentration are tabulated in Table 4, indicating that both of the Langelier and the Ryznar Indices are significantly correlated with the sulfate concentration and the Langelier Index is significantly correlated with the Ryznar Index ($p = 0$). The correlation coefficient between Langelier Index and sulfate concentration is negative as between the Langelier and Ryznar Index. Conversely, the correlation coefficient between Ryznar Index and sulfate concentration is positive for two variables.

Seasonal variation of Langelier Index values

Monthly variation of the Langelier Index is presented in Fig. 8. The variation of Langelier Index of the all wells in different facies resemble to each other between October and March. December is the time for the beginning of the first hard rains in the region. Precipitations go on up to March or April. Dry period begins generally after April and goes on till November (Bulut et al. 1996). Langelier Index values of the wells in three facies reduce between December and February that is a

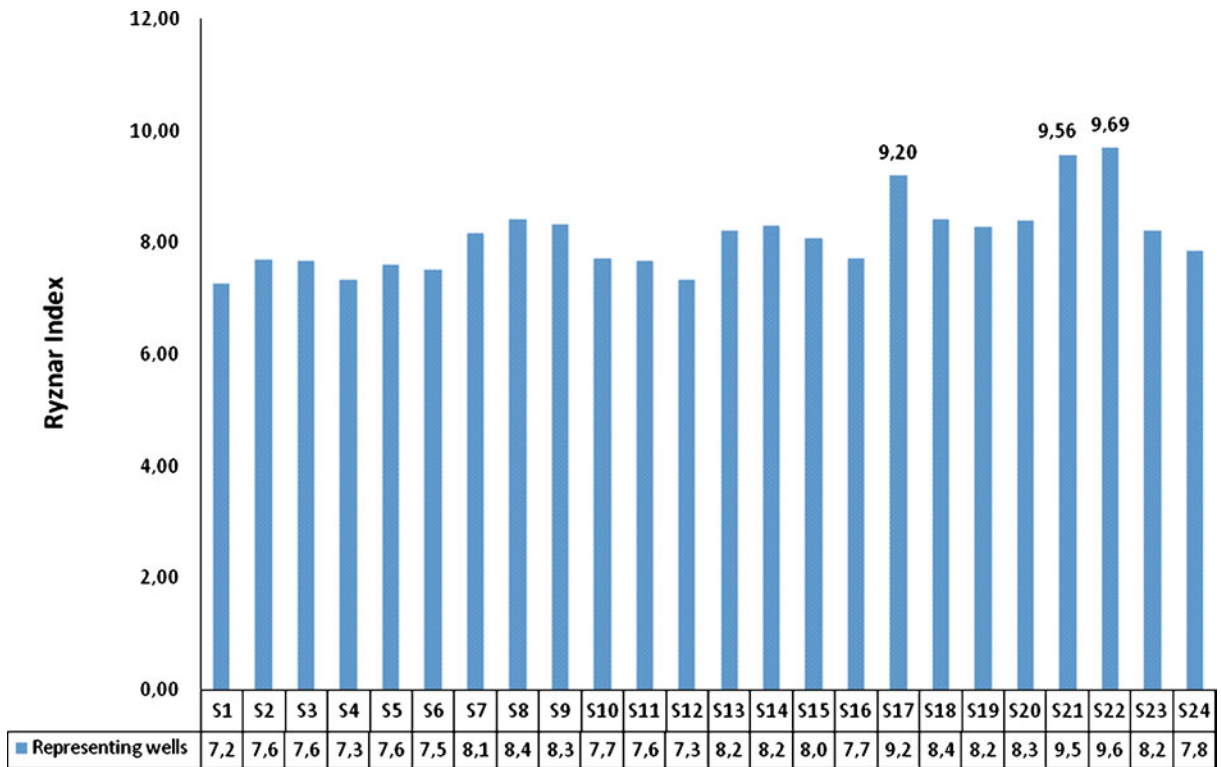


Fig. 6 Ryznar Index graph of representing wells

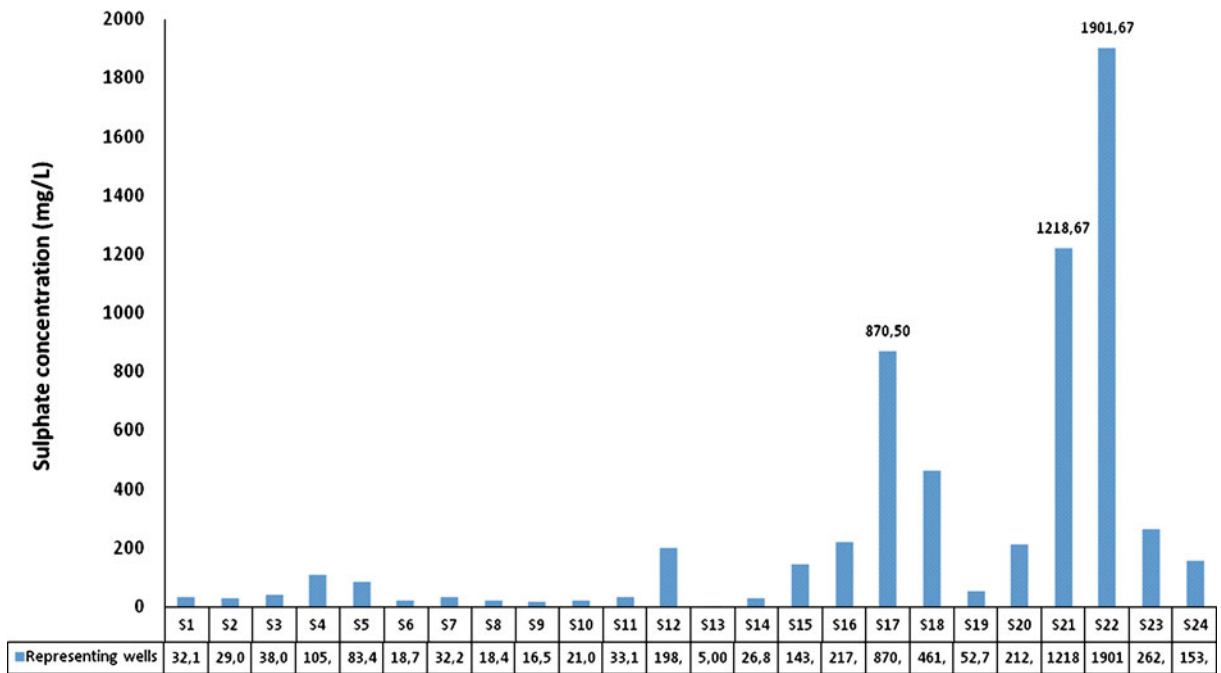
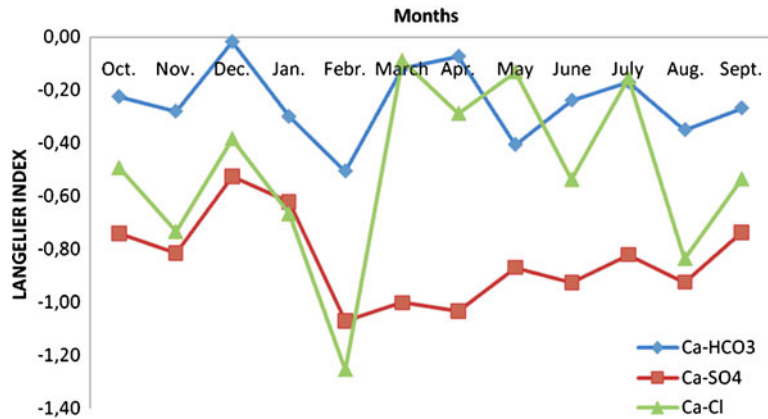


Fig. 7 Annual mean of sulfate concentration in the wells

Fig. 8 Monthly variation of Langelier Index of the wells that were classified in different facies



rainy period. Groundwater level rises in the wells with the continuing precipitation in this rainy period and the amount of dissolved CO₂ increases inducing the corrosivity as shown in Fig. 8. Similar investigations were made by Singh et al. (2000) and Subba (2006) for Agra city and Guntur district (Andhra Pradesh), respectively. Especially precipitation and evaporation were the important factors in the seasonal variation of the groundwater corrosivity for Harran Plain. The corrosive tendency (LI value) of the groundwater samples between March and September is not stable because of the excessive irrigation for the cotton in Harran Plain. The groundwater level rises with irrigation but high temperature causes excessive evaporation. Therefore, monthly variation of groundwater level and also the corrosive tendency is changeable in this period (between March and September). Similarly, Devadas et al. (2007) reported that excessive irrigation can detrimentally affect the groundwater quality.

Conclusions

The groundwater of Harran Plain have intense corrosion tendency. High sulfate concentration contributed the corrosivity of groundwater. The activity of sulfate-reducing bacteria produces CO₂ in the presence of organic compounds. When the sulfate ions are converted to sulfide ions, hydrogen sulfide gas is produced by the sulfide-producing bacteria. Sulfate-reducing bacteria (SRB) which reacts with metal surfaces and CO₂ gas produced from SRB are the sources of corrosivity in the groundwater. Langelier and Ryznar Index values of the wells containing high sulfate concentration indicated a corrosion tendency. LI values of the wells in the Ca–SO₄ facies were lower than the wells in Ca–HCO₃ and Ca–Cl facies. Therefore, the groundwater samples from the Ca–SO₄ facies are more corrosive than the others. Natural geochemistry of the area affects the groundwater corrosivity. Well no. 4, which is closer to Karaali hot springs, has positive LI (0.03) and a scale formation tendency as it contains a high amount of dissolved ions contributing to scaling.

Precipitation also influences the LI values of groundwater. Because rising or falling down of the groundwater level affects the amount of dissolved CO₂ and also the corrosivity of water. Besides, the irrigation of cotton fields causes the rising of groundwater level in the summer months. The high temperature induces the contrast effect.

Table 4 Correlation coefficients and significant levels of LI, RI and sulfate concentration

	LI	RI
RI	-0.959 0.000*	
Sulfate concentration	-0.827 0.000*	0.807 0.000*

**p* ≤ 0.05

Therefore, LI values are not stable in this period. The corrosion will create the important problems in the pipe lines, well equipment, and water tanks in the region. The water quality will be negatively affected by the corrosion. Stabilization or aeration of water can be a solution for the problem.

Acknowledgements This study was funded by the Scientific & Technological Research Council of Turkey (TÜBİTAK project no. 104Y188) and the Scientific Research Projects Committee of Harran University (HÜBAK project no. 603). The authors would like to thank Muhsin Naz, Yasemin Bayindir, Özlem Demir, Atiye Atgüden, and Nuray Gök for their continuous help in the field and laboratory studies as well as to Dr. Erkan Şahinkaya for many fruitful discussions and suggestions.

References

- Al-Rawajfeh, A. E., & Al-Shamaileh, E. M. (2007). Assessment of tap water resources quality and its potential of scale formation and corrosivity in Tafila Province, South Jordan. *Desalination*, 206, 322–332.
- Al-Rawajfeh, A. E., Glade, H., & Ulrich, J. (2005). Scaling in multiple-effect distillers: The role of CO₂ release. *Desalination*, 182, 209–219.
- APHA-AWWA-WEF (1999). *Standard methods for the examination of water and wastewater* (20th ed.). American Public Health Association, 1325.
- ASTM (The American Society for Testing and Materials) (2001). *Standard guide for sampling groundwater monitoring wells*. D4448-01, 17.
- Bulut, H., Senocak, M. I., & Karasu, H. (1996). Sanliurfa climate and meteorology file. In *GAP 1. Engineering conference* (pp. 151–159). Sanliurfa—Turkey.
- Coetsiers, M., & Walraevens, K. (2006). Chemical characterization of the neogene aquifer, Belgium. *Hydrogeology Journal*, 14, 1556–1568.
- Devadas, D. J., Rao, N. S., Rao, B. T., Rao, K. V. S., & Subrahmanyam, A. (2007). Hydrogeochemistry of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India. *Environmental Geology*, 52(7), 1331–1342.
- Drever, J. I. (1988). *The geochemistry of natural waters*. Englewood Cliffs: Prentice-Hall.
- Dogdu, M. S., & Kirmizitas, H. (2006). Occurring and reservoir temperature estimation of Karaali (Şanlıurfa–Yardımcı) hot water. *Geological Engineering Journal*, 30/1, 1–16 (in Turkish).
- DSI (The General Directorate of State Hydraulic Works) (1972). *Harran Ovası Hidrojeolojik Etüt Raporu, DSI Genel Müdürlüğü Matbaası* (p. 49). Ankara, Turkey (in Turkish).
- DSI (2003). *Problems of drainage and salinity in the Harran plain* (p. 10). Summary Report, The 15th District Directorate of the State Hydraulic Works, Sanliurfa, Turkey (in Turkish).
- El Dahan, H. A., & Hegazy, H. S. (2000). Gypsum scale control by phosphate ester. *Desalination*, 127, 111–118.
- El Din, A. M. S. (2009). Three strategies for combating the corrosion of steel pipes carrying desalinated potable water. *Desalination*, 238, 166–173.
- EPA (U.S. Environmental Protection Agency) (1995). *Groundwater well sampling*. SOP#:2007, USA. 26 January 1995.
- Erguvanli, K., & Yuzer, E. (1987). *Groundwater geology (hydrogeology)* (p. 339). İstanbul: İTÜ Maden Fakültesi (in Turkish).
- Hamrouni, B., & Dhahbi, M. (2002). Calco-carbonic equilibrium calculation. *Desalination*, 152, 167–174.
- Hem, J. D. (1991). *Study and interpretation of the chemical characteristics of natural water*. US Geological Survey Water Supply Paper 2254, Scientific Publishers, India.
- Ismail, A. I. M., & El-Shamy, A. M. (2009). Engineering behavior of soil materials on the corrosion of mild steel. *Applied Clay Science*, 42, 356–362.
- Kaur, G., Mandal, A. K., Nihlani, M. C., & Lal, B. (2009). Control of sulfidogenic bacteria in produced water from the Kathloni oilfield in northeast India. *International Biodeterioration & Biodegradation*, 63, 151–155.
- Ludwig, H., & Hetschel, M. (1990). Treatment of distillates and permeates from sea water desalination plants to make potable water. In H. G. Heitmann (Ed.), *Saline water processing*. Weinheim: VCH Verlagsgesellschaft.
- Melidis, P., Sanozidou, M., Mandusa, A., & Ouzounis, K. (2007). Corrosion control by using indirect methods. *Desalination*, 213, 152–158.
- MINITAB (2000). *Minitab statistical software*. Help Document, 13.2 Version.
- Oktem, A. (2008). Effect of water shortage on yield, and protein and mineral compositions of drip-irrigated sweet corn in sustainable agricultural systems. *Agricultural Water Management*, 95, 1003–1010.
- Ozer, N., & Demirel, A. F. (2002). *Groundwater and soil salinity problems in operation stage in Sanliurfa–Harran plain* (pp. 332–333). International Conference on Sustainable Land Use and Management, Çanakkale—Turkey.
- Pátzay, G., Stáhl, G., Kármán, H., & Kálmán, E. (1998). Modeling of scale formation and corrosion from geothermal water. *Electrochimica Acta*, 43(1–2), 137–147.
- Prisyazhniuk, V. A. (2007). Prognosticating scale-forming properties of water. *Applied Thermal Engineering*, 27, 1637–164.
- Sahinkaya, E., Ozkaya, B., Kaksonen, A. H., & Puhakka, J. A. (2007). Sulfidogenic fluidized-bed treatment of metal-containing wastewater at 8 and 65°C temperatures is limited by acetate oxidation. *Water Research*, 41, 2706–2714.
- Singh, R. P., Chauhan, B. S., Swaroop, D., & Yadav, Y. S. (2000). Seasonal variation in groundwater quality of Agra City. *Indian Journal of Environmental Health*, 42, 59–69.

- Subba, R. N. (2006). Seasonal variation of groundwater quality in a part of Guntur District, Andhra Pradesh, India. *Hydrological Sciences Journal*, *45*, 835–847.
- Tang, Z., Hong, S., Xiao, W., & Taylor, J. (2006). Characteristics of iron corrosion scales established under blending of ground, surface, and saline waters and their impacts on iron release in the pipe distribution system. *Corrosion Science*, *48*, 322–342.
- TSE (Turkish Standards Institution) (1997). *Water quality-sampling—part 2: Guidance on sampling techniques* (15 pp.). TS 5090 EN 25667-2, Ankara, Turkey (in Turkish).
- Withers, A. (2005). Options for recarbonation, remineralisation and disinfection for desalination plants. *Desalination*, *179*(1–3), 11–24.
- Yesilnacar, M. I., & Gulluoglu, M. S. (2008). Hydrochemical characteristics and the effects of irrigation on groundwater quality in Harran plain, GAP Project, Turkey. *Environmental Geology*, *54*/1, 183–196.