

Groundwater Chemistry in an Area Covered by Lava Flows, Aqool Area, Eastern Al Madinah Al Munawarah City, Saudi Arabia

MAGDY EL MAGHRABY

Geology Department, Faculty of Science
Alexandria University
Egypt

Abstract:

The groundwater of Al Aqool area, 30 km to the east of Al Madina Al Munawarah City, Saudi Arabia is present in alluvium deposits underlying vesicular lava flows. Groundwater occurs under confined, semi-confined and confined conditions in recent alluvial deposits. The groundwater is the main source of water for drinking and agricultural uses in the area of study. The twenty seven collected groundwater samples were chemically analyzed for major ions in order to assess the groundwater quality and to understand the different geochemical processes affecting the quality. The salinity of the groundwater samples of the area of study were ranged between 487–997 mg/l indicating medium salinity. According to the chemical analysis and the constructed diagrams (Piper, Durov, Schoeller) the prevalent chemical facies is Na-Cl water type. The geochemical change of groundwater in the study area was observed where the water types were changed from Ca-HCO₃ of rain water into Na-Cl of groundwater samples. The calculated ionic ratios ((Na+K-Cl)/(Na+K-Cl+Ca), Na/(Na+Cl), Mg/(Ca+Mg), and Ca/(Ca+SO₄)) indicate possible plagioclase weathering, ion exchange, limestone-dolomite weathering and gypsum dissolution; respectively. From chloride mass-balance equation the study area has a recharge (2.54 mm/y) of 4.97 % of precipitation. Major elements analyses and calculated hydrochemical parameters (SAR, RSC, MH) of the groundwater samples from the area of study revealed its suitability for both drinking and irrigation purposes.

Key words: groundwater hydrochemistry, Aqool, Quaternary aquifer, assessment, Saudi Arabia

Introduction

About one-third of the world's population lives in countries suffering from moderate-to-high water stress. Some 80 countries, constituting 40 per cent of the world's population, were suffering from serious water shortages by the mid-1990s. Increasing water demand has been caused by population growth, industrial development and the expansion of irrigated agriculture (UNEP 2002).

Kingdom Saudi Arabia (KSA) is located in the arid zone of south west Asia, where surface water supplies are absent except during the floods which occur after intensive rainfall and thus some intermittent ponds are formed. Groundwater is the primary source of the water for human consumption, as well as for agricultural and industrial uses, which make it an important resource in KSA (Al-Ahmadi 2013a). So, growing population, agricultural expansion and urbanization have placed a heavy demand on water resources, which are among the challenging issues especially in arid and semi-arid regions, where the water resources are limited. The fresh water resources are limited to the groundwater system, where the groundwater in alluvial aquifer, which is dependent on direct recharge from rainfall.

Water quality is important as for its quantity and quality as it moves through the soils and sediments, and hence, its composition is then changed by chemical reactions such as weathering, dissolution, leaching, precipitation, ion exchange, impact of agriculture and urbanization (Al-Ahmadi 2013b). The quality of groundwater has been studied in several basins by many researchers (Magnus et al. 2011; Ramesh and Bhuvana 2012; Cobbina et al. 2012; Emmannoel et al. 2009; El Maghraby et al. 2013; Khashogji and El Maghraby 2013).

The attention to the quality of groundwater of the Al Madinah Al Munawarah region has been increased (Bokhari and Khan 1992; Matsah and Hossain 1993; El Maghraby 2004;

Bayumi, 2008). The hydrogeology and hydrochemistry of groundwater of the western region of the KSA has also been a focus of many researchers such as: Pieke (1985); De Jong et al. (1989); Lloyd and Pirn (1990); Hussain and Sadiq (1991); Bazuhair and Wood (1996); Al-Bassam (1998); Alyamani (2000); Al-Bassam et al. (2003); Subyani (2004); Abderrahman (2006); Al-Sefry and Sen (2006); Al-Shaibani (2008).

This work aims to assess the groundwater quality and to understand the different geochemical processes affecting its quality.

Study area

The study area lies at about 30 km to the east of Al Madinah Al Munawarah City between latitudes $24^{\circ} 21' 45''$ and $24^{\circ} 27' 54''$ N and longitudes $39^{\circ} 45' 54''$ and $39^{\circ} 49' 21''$ E (Fig. 1).

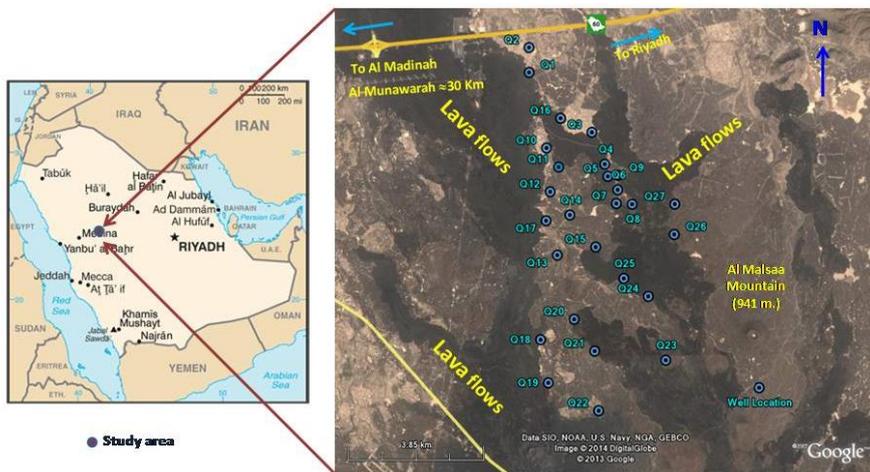


Fig. 1 Location map of the water samples of the study area

The area of study lies within the desert belt which is characterized by very high temperature and semi-arid to extremely arid conditions. The mean temperature range is $25-42^{\circ}\text{C}$ in summer and $10-24^{\circ}\text{C}$ in winter. The maximum rainfall may be up to 85 mm/y . The average annual precipitation is about 49.3 mm/y . Topographic elevations in the study area

range from 783 to 849 m above sea level.

Hydrogeology of the study area

The study area is located within the Arabian Shield. The area of study is underlain by Proterozoic basement rocks that comprise two major volcanosedimentary groups ranging in age from approximately 800 to 670 Ma. (Pellaton 1981; Johnson 1983; George and Shorbaji 1987). The western part of the Arabian Shield is formed of Precambrian rock that folded, metamorphosed, granitized and intruded during several tectonic phases prior to the Cambrian (Fig. 2). During the Tertiary, olivine basalt flows were extruded in many parts of the Al Madinah Al Munawarah area. This volcanic activity continued into the Quaternary.

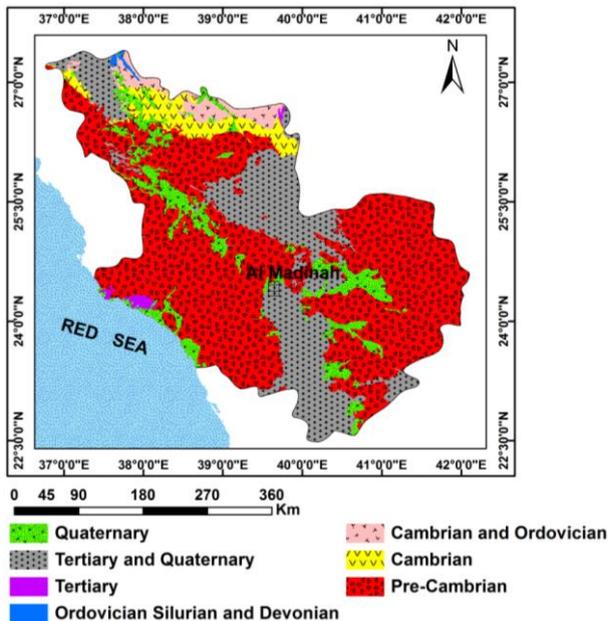


Fig. 2 Geological map of the study area, (Ministry of Petroleum and Mineral Resources KSA 1987)

The area of study is covered by surficial deposits which comprise eluvial deposits, sabkhah and khabra deposits, wadi

deposits and alluvial deposits. Wadi deposits carry water for a few days, but most water is lost through direct infiltration and evaporation.

According to lithologic characteristics and hydraulic behavior, aquifers of the study area are classified into two types; (i) continuous and alluvial, which range from unconfined in the surficial deposits, Paleozoic formations, and weathered Proterozoic bedrock formations, to semiconfined and confined whether these formations are overlain by lava flows or are intercalated with clayey and silty deposits; and (ii) discontinuous bedrock or suballuvial in the fractured Cenozoic lava flows intercalated with volcanic ash or sediment layers, and in the fractured bedrock formations (George and Shorbaji 1987; Bokhari and Khan 1992).

Depth to the water table ranges from 40 to 90 m below ground surface. Rainfall is main source of recharge of the aquifer. Discharge from the aquifer takes place through the controlled pumping and by evaporation.

Recharge Estimation

The recharge amount at the study area was estimated using the chloride mass-balance equation. Wood and Sanford (1995) proposed the equation to estimate the recharge as follows:

$$Q = R \times Cl_{wav} / Cl_{gw}$$

where, Q =recharge flux (LT^{-1}), R =average annual rainfall (LT^{-1}), Cl_{wav} =weighted average chloride concentration in rainfall (ML^{-3}), Cl_{gw} =average chloride concentration in groundwater (ML^{-3}), M = mass unit, L =length unit, and T =time unit.

The average annual rainfall at the study area is 49.3 mm. The regional precipitation-weighted chloride concentration in the study area is 6.5 mg/l. Average chloride concentration in

groundwater from the recharge part of the aquifer of the study area is 126 mg/l. From chloride mass-balance equation the study area has a recharge (2.54 mm/y) of 4.97 % of precipitation.

Sampling and Analytical Procedures

Twenty-seven groundwater samples were collected from drilled wells for hydrochemical investigation (Fig. 1). Sampling was done in accordance with to the US Environmental Protection Agency guidelines (EPA 2004), and strict consideration was given to individual parameter holding time criteria as outlined by the American Public Health Association (APHA 1998). All the samples were analyzed for major and some minor constituents. Results of chemical analyses are presented in Table 1.

Duplicate water samples were taken at each well. One duplicate sample was collected at its natural pH, in polyethylene bottles after rinsing several times with water from the point of collection and preserved (approximately at 4°C) for anion analysis. The second sample was also collected in polyethylene bottles and acidified using HNO₃ to pH < 2 for cation analysis. All the samples for laboratory analyses were filtered through 0.45 µm membrane filters. The cation and anion concentrations in groundwater samples were determined in the laboratories of Chemistry Department, Faculty of Science, Taibah University, Al Madinah Al Munawarah, Saudi Arabia.

Hydrogen ion concentration (pH), Electrical conductivity (EC) and Total Dissolved Solids (TDS) were measured at the wellhead using portable HI 991300 Hanna Instruments.

Analysis of major ions (Ca, Mg, Na, K, HCO₃, SO₄, and Cl) and some trace constituents (NO₃, NO₂, Fe, Mn, Cd, Cr, Cu, Pb) were performed in the groundwater samples using the standard methods (APHA, 1998). The values were observed to

be within a standard limit of $\pm 5\%$ (Domenico and Schwartz 1998).

Bicarbonate concentration was determined using titration against HCl. Chloride was estimated by titration against standard solution of AgNO_3 . Sulfate, nitrate and nitrite, concentrations were determined using DR4000 HACH Spectrophotometer. Calcium and Mg concentrations were determined using titration against EDTA. Sodium and K were determined using by PFP7 Flame Photometer. Whereas, Induced Coupled Plasma Mass Spectrometry (ICP/MS) was used to measure iron, manganese, cadmium, chromium, copper and lead. The concentrations of Mn, Cd, Cr, Cu and Pb were below detection limit.

The geochemical computer program PHREEQC (Parkhurst and Appelo 1999) was used to calculate saturation indices in the groundwater.

Results and discussion

Results of chemical analysis of the groundwater samples of al Aqool area are presented in Table 1. The chemical composition of the groundwater varies over a wide range of salinity and ionic composition.

Sample #	pH	TDS ^a	EC ^b	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	Fe	NO ₃	NO ₂
Q1	7.67	706.90	1104.53	195.00	2.00	35.80	12.40	268.00	88.70	105.00	0.02	16.28	0.0132
Q2	7.40	997.00	1557.81	255.00	3.00	48.40	18.60	335.00	192.00	145.00	0.06	16.72	0.0066
Q3	7.80	676.20	1056.56	180.00	2.00	32.00	11.20	210.00	141.00	100.00	0.47	15.40	0.0132
Q4	7.94	549.44	858.50	134.00	2.00	29.00	10.90	182.00	91.54	100.00	0.64	16.30	0.1254
Q5	7.87	537.61	840.02	132.00	2.00	27.00	11.10	180.00	90.51	95.00	0.36	16.72	0.0132
Q6	7.90	542.85	848.20	130.00	2.00	28.00	11.40	178.00	98.45	95.00	0.05	15.40	0.0132
Q7	7.93	734.75	1148.05	202.00	3.00	34.00	13.00	270.00	112.75	100.00	0.03	15.84	0.033
Q8	7.91	486.89	760.77	118.00	2.00	25.40	10.05	130.00	121.44	80.00	0.23	19.36	0.4488
Q9	7.84	511.00	798.44	121.00	2.00	26.00	11.00	126.00	130.00	95.00	0.04	18.92	0.0099
Q10	7.93	755.90	1181.09	200.00	3.00	33.40	12.50	260.00	147.00	100.00	0.01	18.92	0.0066
Q11	7.66	775.00	1210.94	200.00	3.00	35.00	13.00	265.00	164.00	95.00	0.46	15.28	0.0085
Q12	7.41	815.11	1273.61	198.00	3.00	40.00	14.00	272.00	193.11	95.00	0.06	16.21	0.0123
Q13	7.83	643.60	1005.63	168.00	2.00	31.00	10.60	225.00	112.00	95.00	0.07	16.52	0.0057
Q14	7.91	717.00	1120.31	198.00	3.00	29.00	11.00	248.00	128.00	100.00	0.35	15.34	0.0122
Q15	7.87	668.20	1044.06	178.00	2.00	30.00	12.20	216.00	135.00	95.00	0.58	16.11	0.1214
Q16	7.89	635.00	992.19	168.00	2.00	31.00	11.00	200.00	128.00	95.00	0.33	16.61	0.0131
Q17	7.91	739.00	1154.69	192.00	3.00	37.00	13.00	258.00	141.00	95.00	0.08	15.34	0.0133
Q18	7.66	713.00	1114.06	195.00	3.00	33.00	12.00	261.00	114.00	95.00	0.04	15.88	0.0328
Q19	7.42	655.80	1024.69	175.00	2.00	28.00	10.80	204.00	136.00	100.00	0.21	19.55	0.4405
Q20	7.85	676.10	1056.41	182.00	2.00	32.00	11.10	244.00	110.00	95.00	0.06	19.22	0.0096

Q21	7.95	669.00	1045.31	178.00	2.00	30.00	11.00	231.00	122.00	95.00	0.02	18.12	0.0061
Q22	7.77	532.90	832.66	137.00	2.00	27.00	10.90	178.00	88.00	90.00	0.05	17.57	0.0084
Q23	7.88	670.00	1046.88	182.00	2.00	29.00	12.00	229.00	116.00	100.00	0.06	16.05	0.0127
Q24	7.92	623.00	973.44	169.00	2.00	27.00	11.00	193.00	126.00	95.00	0.08	16.71	0.0059
Q25	7.89	650.00	1015.63	172.00	2.00	29.00	12.00	197.00	138.00	100.00	0.51	17.92	0.0121
Q26	7.81	539.00	842.19	128.00	2.00	26.00	11.00	156.00	121.00	95.00	0.62	16.53	0.1141
Q27	7.94	563.50	880.47	137.00	2.00	27.00	10.50	164.00	128.00	95.00	0.35	16.68	0.0142
^c RW	7.10	35.64	55.69	4.10	1.02	3.77	1.20	6.50	14.65	4.40			

^aTDS: Total Dissolved Solids in (mg/L)

^bEC : in $\mu\text{mohs/cm}$ at 25°C

^cRW : Rain Water

Table 1. Results of chemical analysis of major constituents in the study area (concentrations are in mg/l)

Major constituents

The pH values of the groundwater were varied between 7.4 and 7.95, which indicates that alkalinity is predominately in the form of HCO_3 (Adams et al. 2001). The EC values vary from 760.77 (Q8) to 1557.81 $\mu\text{S/cm}$ (Q2). TDS of groundwater were ranged between 486.89 mg/l (Q8) and 997 mg/l (Q2) indicating fresh water type. Little variations in the salinity of the study area could be attributed to the same hydrochemical processes affecting the chemistry of groundwater (silicate weathering (TDS<500 mg/l; one sample Q8), or carbonate weathering (TDS>500 mg/l; the rest of samples) (Hounslow, 1995)).

Sodium is the dominant cation in all the analyzed groundwater samples, followed by Ca and Mg (Na>Ca>Mg). The concentration of Na in the study area varies from 118.0 (Q8) to 255.0 mg/l (Q2) (Table 1). The high concentrations may be attributed to cation exchange which results in the release of Na into the groundwater. Potassium shows concentrations range from 2.0 to 3.0 mg/l (Table 1).

The country silicate rocks in the region are mainly composed of gabbro, basalt, diorite, andesite and few granitic rocks. Therefore, Na and Ca are expected to be released during weathering reactions of these rocks according to the following reactions:

The possible sources of bicarbonate include presence of organic matter in the groundwater which is oxidized to produce carbon dioxide, which in turn promotes dissolution of minerals. This weathering enriches groundwater in Ca, Mg and bicarbonates. Weathering of silicate minerals may also be accounted as a source for bicarbonate (Gastmans et al. 2010), in addition to cations such as Ca and Mg. The presence of HCO_3 in the groundwater of the study area indicates presence of recharge areas.

The concentrations of bicarbonate in the groundwater samples of the study area ranged from 88 mg/l to 193.11 mg/l (Table 1).

The sources of sulfate in the groundwater samples in the study area may be attributed to the breaking of organic substance from top soil/water, leachable sulfate present in fertilizer, and other human influences (Srinivasamoorthy et al. 2008). The concentrations of sulfate in the groundwater samples of the study area ranged from 80 and 145 mg/l (Table 1).

Hydrochemical facies

One of the most common methods for the hydrochemical data presentation is the Piper (1944) trilinear diagram which can help in hydrochemical classification (Back and Hanshaw 1965). Distribution of groundwater of Aqool area is shown on the Piper diagram (Fig. 3). It is clear that the groundwater samples have the alkali metals ($\text{Na} + \text{K}$) exceeding the alkaline earth elements ($\text{Ca} + \text{Mg}$). These alkali metals are probably derived from the effect of cation exchange on clay exchange sites.

This geochemical change of groundwater of the study area is indicated by the arrow in Fig. 3 from the rain water (Ca-HCO_3 water-type) to the groundwater of the study area (Na-Cl water-type). The water chemistry of the study area is related to dissolution of more acidic silicate minerals found in the

alluvium and their interaction with water which tend to alter the groundwater quality.

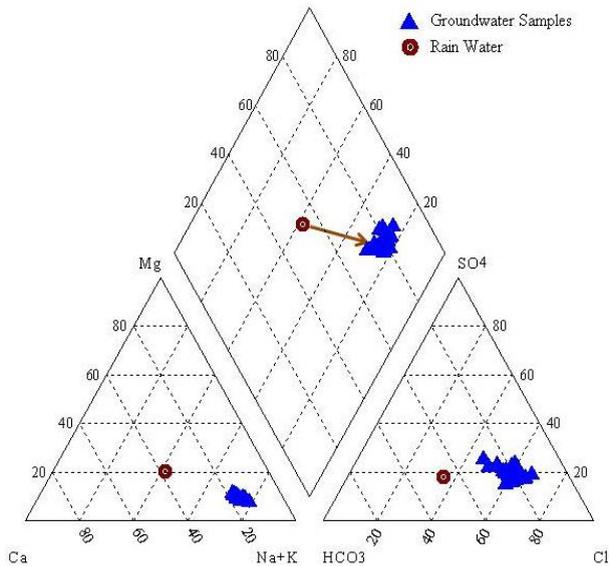


Fig. 3 Piper diagram of the groundwater samples of the study area

All groundwater samples have Cl followed by SO₄ or HCO₃ as the dominant anions. The water samples have the same hydrochemical facies of Na–Cl, which indicates the final stage of the geochemical evolution of groundwater.

In order to facilitate interpretations of the evolutionary spatial trends and hydrochemical processes in the aquifer in relation to the groundwater flow, chemical data of groundwater samples have been plotted on the Durov diagram (Burdon and Mazloum 1958; Lloyd 1965) (Fig. 4). As shown in Fig. 5, all the groundwater samples are plotted in fields 8 and 9 indicating reverse ion-exchange reactions and end point waters.

The arrow on the Durov diagram shows possible geochemical evolution of the groundwater of Aqool area from Ca–HCO₃ recharge water (rain water) to Na-Cl water type. Rain water is subjected to different processes of evaporation and interaction with soils and sediments that infiltrate through them to reach the groundwater. Moreover, as the groundwater

flows through the alluvial aquifer, additional processes of dissolution/precipitation, cation exchange, and mixing with return flow will act to increase the groundwater salinity and change the dominance of ions from Ca to Mg, and finally to Na-rich water. Simultaneously, anion dominance is changed from HCO_3 to SO_4 and finally to Cl, representing end point waters.

Plotting the results of groundwater chemical analysis on Schoeller's diagram (Fig. 5) (1962) revealed that the groundwater samples in the study area had nearly the same trends of increase and decrease with rain water.

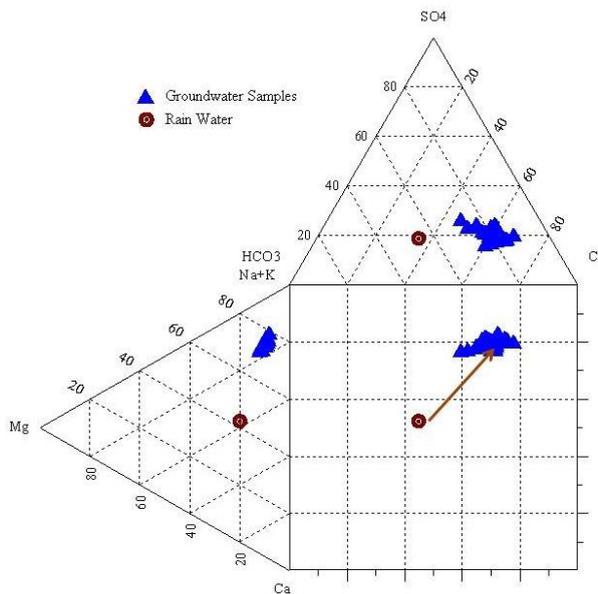


Fig. 4 Durov's diagram of the groundwater samples of the study area

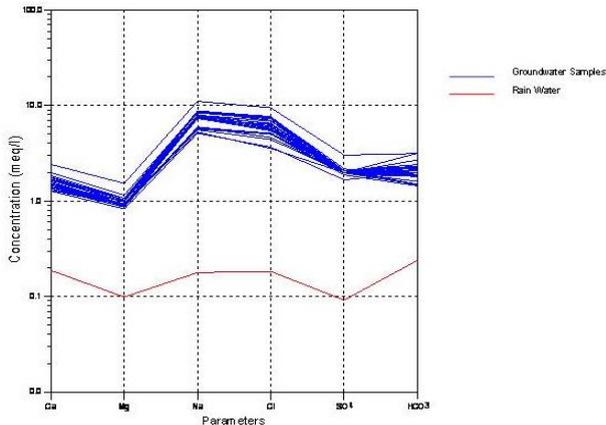


Fig. 5 Schoeller's diagram of the groundwater samples of the study area

Nitrate and nitrite

Nitrate (NO_3) contamination of groundwater is a common occurrence in many parts of the world. The U.S. Environmental Protection Agency has set 10 mg N/l as the Maximum Contaminant Level (MCL) for nitrate in drinking water (Federal Register 2002), as consumption of high-nitrate water can cause methemoglobinemia, a potentially fatal condition in infants (Exner et al. 2010).

The nitrate concentration in the study area lower than the WHO (2011) and Saudi drinking water standards (SASO 1984) of 50 mg/l and the nitrite is lower than 3 mg/l (Table 1) which means that they are within the safety limits for drinking purposes.

Trace elements

The main sources of different trace elements in the groundwater of the study area may be from the leaching processes.

The analyses of Fe, Mn, Cd, Cr, Cu and Pb constituents of groundwater samples of the study area reveal that Mn, Cd,

Cr, Cu and Pb are below detection limit. The Fe shows concentrations ranged between 0.01 and 0.64 mg/l as shown in Table 1. This indicates less effect of leaching process and recent recharge water.

Geochemical modeling

The geochemical interactions lead to changes in water chemistry. The potential for a chemical reaction can be determined by calculating the chemical equilibrium of the water with the minerals phases. The equilibrium state of the water with respect to a mineral phase can be determined by calculating a saturation index (SI) using analytical data. Where, the reactive mineralogy of the subsurface can be predicted by using the saturation index approach from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch 1997). The potential for mineral precipitation or dissolution is assessed using the saturation index (SI), which is based on the relation between analytic activities (the ion activity product, IAP) and the thermodynamic calculation of the solubility product (K_{sp}). The SI of a mineral is calculated based on the following equation (Parkhurst 1995):

$$SI = \log_{10} \frac{IAP}{K_{sp}}$$

If $SI > 0$ the solution is theoretically oversaturated with respect to the mineral and precipitation may be expected. For $SI = 0$, the mineral and solution are in equilibrium and neither dissolution nor precipitation is predicted to occur. If $SI < 0$, the solution is theoretically undersaturated with respect to the mineral, and if present in the system, dissolution might be possible.

The geochemical modeling program PHREEQC (Parkhurst and Appelo 1999); interfaced with Aquachem 2010.1; was used to calculate saturation indices in the

groundwater of the study area. Table 2 shows the results of SI calculations for the groundwater with respect to various specific minerals.

The saturation index of the most common carbonate minerals are undersaturation with respect to these minerals. SI varies from -1.34 to -0.82 for aragonite, from -1.19 to -0.67 for calcite and from -2.49 to -1.47 for dolomite.

It is evident that undersaturation with respect to carbonate minerals is enhanced by high rate of evaporation which leads to concentration and precipitation of these minerals in soil. The formation of white carbonate crust was noticed in some farms after irrigation process, as well as some clogging of narrow irrigation pipes in the area of study.

Calculations of SI values in the studied groundwater indicate that these waters are moderately undersaturated with respect to sulfate minerals (gypsum and anhydrite) and strongly undersaturated with respect to halite (-2.10 - -1.71 for gypsum, -2.34 - -1.94 for anhydrite, -6.39 - -5.67 for halite).

Figure 6 shows that the groundwater samples are slightly undersaturation with respect to aragonite, calcite, dolomite, gypsum and anhydrite, and highly undersaturated with respect to halite.

Well No.	Aragonite	Calcite	Dolomite	Gypsum	Anhydrite	Halite
1	-1.24	-1.09	-2.36	-1.91	-2.15	-5.87
2	-0.82	-0.67	-1.47	-1.71	-1.95	-5.67
3	-1.08	-0.93	-2.04	-1.96	-2.20	-6.00
4	-1.30	-1.15	-2.44	-1.98	-2.21	-6.19
5	-1.33	-1.18	-2.46	-2.02	-2.26	-6.20
6	-1.28	-1.13	-2.36	-2.01	-2.25	-6.21
7	-1.16	-1.01	-2.16	-1.95	-2.19	-5.85
8	-1.21	-1.07	-2.25	-2.10	-2.34	-6.38
9	-1.18	-1.04	-2.16	-2.03	-2.27	-6.39
10	-1.06	-0.91	-1.96	-1.96	-2.20	-5.87
11	-0.99	-0.83	-1.83	-1.97	-2.21	-5.86
12	-0.86	-0.72	-1.61	-1.92	-2.16	-5.86
13	-1.19	-1.04	-2.27	-1.99	-2.23	-6.00
14	-1.17	-1.02	-2.18	-2.01	-2.25	-5.89
15	-1.13	-0.98	-2.06	-2.01	-2.25	-5.99
16	-1.13	-0.98	-2.13	-1.99	-2.23	-6.05
17	-1.03	-0.88	-1.94	-1.94	-2.18	-5.89
18	-1.16	-1.02	-2.19	-1.98	-2.22	-5.88
19	-1.15	-1.00	-2.14	-2.01	-2.25	-6.03
20	-1.19	-1.04	-2.26	-1.98	-2.22	-5.93
21	-1.17	-1.02	-2.20	-2.01	-2.25	-5.97
22	-1.34	-1.19	-2.49	-2.05	-2.28	-6.19

23	-1.21	-1.06	-2.22	-2.00	-2.24	-5.96
24	-1.20	-1.05	-2.20	-2.04	-2.28	-6.06
25	-1.13	-0.98	-2.07	-2.00	-2.24	-6.05
26	-1.22	-1.07	-2.23	-2.04	-2.28	-6.27
27	-1.18	-1.03	-2.19	-2.03	-2.26	-6.22

Table 2. Values of saturation indices for groundwater samples of the study area with respect to specific minerals

Ionic ratios

Specific ionic ratios were calculated to gain insight into the possible origin of the water sample and to reveal the possible hydrochemical processes that dominated in the area of study (Hounslow, 1995). These ionic ratios are $(Na+K-Cl)/(Na+K-Cl+Ca)$, $Na/(Na+Cl)$, $Mg/(Ca+Mg)$, and $Ca/(Ca+SO_4)$. Their calculated values showed little variations (Table 3). The computed values for $(Na+K-Cl)/(Na+K-Cl+Ca)$ ionic ratio of the groundwater samples are ranged between 0.33 and 0.59 (> 0.2 and < 0.8) indicating possible plagioclase weathering (Hounslow, 1995).

The computed values for $Na/(Na+Cl)$ ionic ratio of the groundwater samples are ranged between 0.53 and 0.60 (>0.5) indicating that the sodium source other than halite - albite, ion exchange (Hounslow, 1995).

The computed values for $Mg/(Ca+Mg)$ ionic ratio of the groundwater samples are ranged between 0.36 and 0.41 (<0.5) indicating limestone-dolomite weathering (Hounslow, 1995). The computed values for $Ca/(Ca+SO_4)$ ionic ratio of the groundwater samples are ranged between 0.40 and 0.50 (≈ 0.5) indicating gypsum dissolution (Hounslow, 1995). The calculated SI for gypsum is ranged between -2.10 - -1.71.

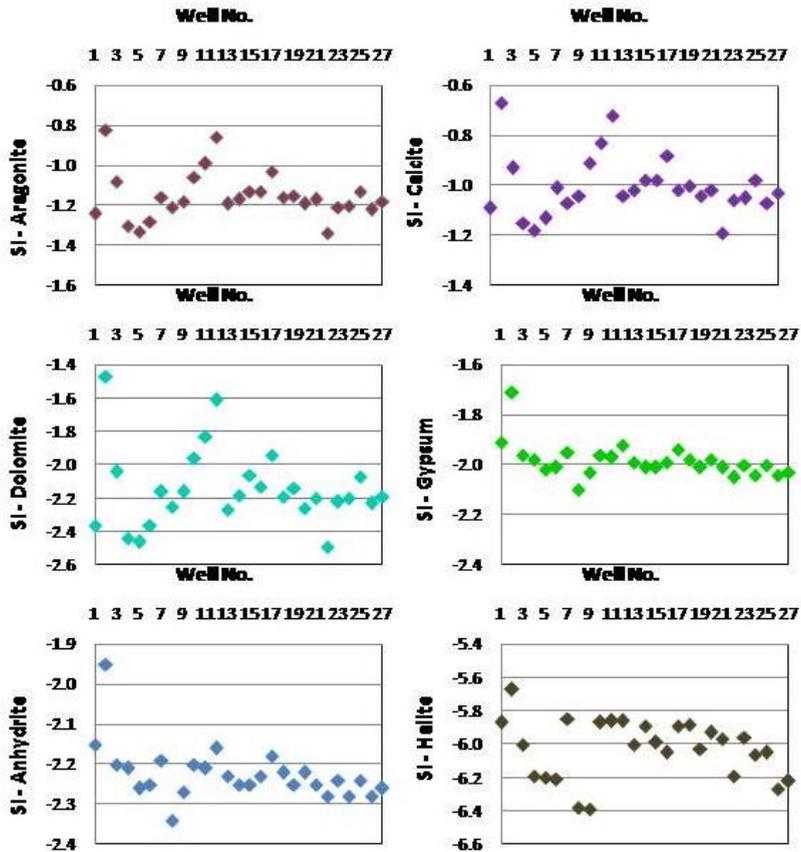


Fig. 6 Saturation indices (SI) of aragonite, calcite, dolomite, gypsum, anhydrite and halite

Groundwater quality assessment

Drinking purposes

World Health Organization (WHO 2011) guidelines for drinking water were used to evaluate the groundwater samples at Aqool area for drinking purposes. According to the WHO (2011), no standards have been established for TDS, chloride, sodium, potassium, bicarbonate, calcium, magnesium, and sulfate and their effects on health. The only standards that have been established are based on taste. The nitrate and nitrite standards, however, are based on health effects. The natural

concentrations of trace constituents present in groundwater used for drinking are not of health concern.

The palatability of water with a total dissolved solids (TDS) level of less than about 600 mg/l is generally considered to be good; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/l (WHO 2011). The presence of high levels of TDS may also be objectionable to consumers, owing to excessive scaling in water pipes, heaters, boilers and household appliances. No health-based guideline value for TDS has been proposed

However, all the groundwater samples of the study area have TDS values less than 1000 mg/l, NO₃ values less than 50 mg/l and NO₂ values less than 3 mg/l which are considered below the safe limits for drinking purposes. Consequently, groundwater of Aqool area can be used safely for drinking.

Sample #	(Na+K-Cl)/ (Na+K-Cl+Ca)	Na/ (Na+Cl)	Mg/ (Ca+Mg)	Ca/ (Ca+SO ₄)	SAR ^a	RSC ^b	MH ^c
Q1	0.35	0.53	0.36	0.45	7.16	-1.35	36.35
Q2	0.42	0.54	0.39	0.44	7.90	-0.80	38.79
Q3	0.55	0.57	0.37	0.43	6.98	-0.21	35.59
Q4	0.34	0.53	0.38	0.41	5.38	-0.84	38.26
Q5	0.35	0.53	0.40	0.41	5.40	-0.78	40.40
Q6	0.33	0.53	0.40	0.41	5.23	-0.72	40.17
Q7	0.42	0.54	0.39	0.45	7.47	-0.92	38.67
Q8	0.54	0.58	0.39	0.43	5.02	-0.10	39.48
Q9	0.58	0.60	0.41	0.40	5.02	-0.07	41.09
Q10	0.46	0.54	0.38	0.44	7.49	-0.29	38.16
Q11	0.43	0.54	0.38	0.47	7.33	-0.13	37.98
Q12	0.34	0.53	0.37	0.50	6.86	0.02	36.59
Q13	0.40	0.54	0.36	0.44	6.64	-0.58	36.05
Q14	0.54	0.55	0.38	0.41	7.94	-0.25	38.48
Q15	0.53	0.56	0.40	0.43	6.92	-0.29	40.14
Q16	0.53	0.56	0.37	0.44	6.60	-0.35	36.91
Q17	0.38	0.53	0.37	0.48	6.92	-0.61	36.68
Q18	0.42	0.54	0.37	0.45	7.39	-0.77	37.49
Q19	0.58	0.57	0.39	0.40	7.12	-0.06	38.88
Q20	0.40	0.53	0.36	0.45	7.07	-0.71	36.39
Q21	0.46	0.54	0.38	0.43	7.06	-0.40	37.68
Q22	0.42	0.54	0.40	0.42	5.63	-0.80	39.96
Q23	0.51	0.55	0.41	0.41	7.18	-0.53	40.56
Q24	0.59	0.57	0.40	0.41	6.93	-0.19	40.18
Q25	0.58	0.57	0.41	0.41	6.78	-0.17	40.56
Q26	0.48	0.56	0.41	0.40	5.31	-0.22	41.09
Q27	0.51	0.56	0.39	0.41	5.67	-0.11	39.07

^aSAR : Sodium Adsorption Ratio

^bRSC: Residual Sodium Carbonate

^cMH: Magnesium Hazard

Table 3. Ionic ratios, SAR, RSC and MH of the groundwater of Al

Aqool area

Irrigation purposes

The suitability of groundwater for irrigation depends on the effects of mineral content of the water on plant as well as soil. The salts can harm the plants through growth stage by limiting the uptake of water through modification of osmotic processes. In addition, the damage can be chemical through the toxic constituents. On the other hand, the effects of salts can be on soils by changing the soil structure and permeability, which directly affect plant growth (Todd 1980).

The assessment of groundwater for irrigation purposes depends upon irrigation quality parameters, including total dissolved solids, sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and magnesium hazard (MH).

A better measure of the sodium hazard for irrigation is the SAR, which is used to express reactions with the soil (Fetter 1994). SAR is computed as:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

in which Na, Ca and Mg are in meq/l.

The SAR is an important parameter because high Na content in irrigation water may increase soil hardness and reduce its permeability. The SAR values of the groundwater samples of the study area (Table 3) range between 5.02 and 7.94 (i.e. <10), indicating excellent water for irrigation (USSL 1954).

Wilcox classification diagram (1955) was used to identify the suitability of groundwater for irrigation purposes (Fig. 7).

Wilcox graph classifies groundwater for irrigation purposes based on SAR and EC. The use of saline waters in permeable rocks may also increase the salinity of groundwaters. The plots of groundwater samples of the study area in Wilcox diagram (Fig. 7) show that the groundwater

samples of the study area are grouped within two fields: C3S1, and C3S2; which indicate high salinity hazard and low to medium sodium hazard.

The groundwater of the study area can be used safely for irrigation on almost all soils; though it may be sensible to keep control on salinity by suitable management and also by selecting plants which have good salt tolerance.

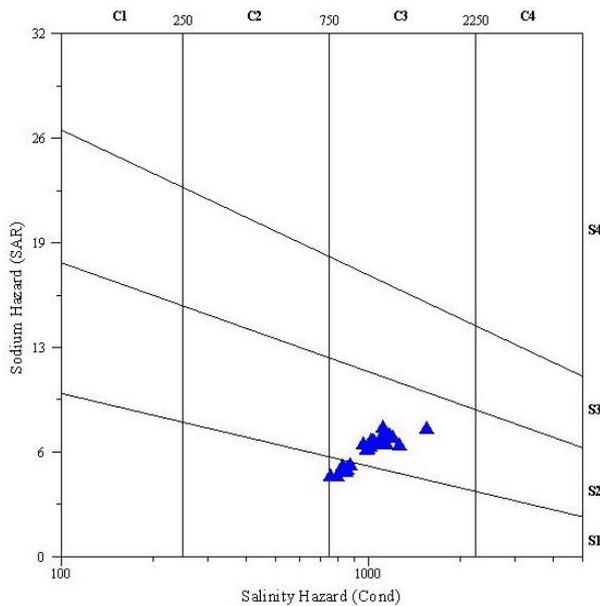


Fig. 7 Wilcox diagram of salinity and sodium adsorption ratio (SAR) hazards for all groundwater samples in the study area

The excesses of carbonate and bicarbonate values in groundwater samples over those of calcium and magnesium affect the suitability of groundwater for irrigation. This is expressed as RSC, which is widely used to indicate the suitability of groundwater for irrigation purposes and it can be calculated as follows (Eaton 1950, McLean et al. 2000):

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

where all ions are expressed in meq/l. The calculated RSC

values of groundwater samples in the study area are found to range from to -0.35 to 0.02 (Table 3). The classification of groundwater for irrigation purposes according to RSC values indicates that all the groundwater samples are <1.25 and hence it is a good category (USSL 1954).

Szabolcs and Darab (1964) proposed magnesium hazard (MH) value for irrigation water as given below:

$$MH = Mg^{+2}/(Ca^{2+} + Mg^{2+}) \times 100$$

where all ions are expressed in meq/l. If $MH > 50$, the water is considered harmful and unsuitable for irrigation use. The calculated values of MH of the groundwater samples in the Aqool area are ranged between 36.05 and 41.09 (Table 3); which mean they are within the acceptable limits for irrigation.

Refereeing to the TDS values (Table 1) and the calculated SAR, RSC and MH (Table 3) for the groundwater samples of Aqool area, it is concluded that these waters are suitable for irrigation purposes.

Conclusions

The results of chemical analyses of twenty seven groundwater samples from Aqool area 30 km to the east of Al Madinah Al Munawarah were used to assess the groundwater quality and to understand the different geochemical processes affecting its quality.

The estimated recharge rate of the aquifer of the study area was 4.97 % of the annual precipitation using the chloride mass-balance method. Different hydrochemical processes such as cation-exchange and leaching had been influenced the water quality of groundwater of the study area. The geochemical change of groundwater in the study area was observed where the water types were changed from Ca-HCO₃ of rain water into Na-Cl of groundwater samples.

The drawn Piper and Durov diagrams showed almost all the samples fall in one zone indicating similar chemical signature. The constructed Schoeller's diagram revealed that the groundwater samples in the study area had nearly the same trends of increase and decrease with rain water.

The saturation index (SI) of the most common carbonate minerals are undersaturation with respect to aragonite, calcite and dolomite. It is evident that undersaturation with respect to carbonate minerals is enhanced by high rate of evaporation which leads to concentration and precipitation of these minerals in soil. Calculations of SI values in the studied groundwater indicate that these waters are moderately undersaturated with respect to sulfate minerals (gypsum and anhydrite) and strongly undersaturated with respect to halite. The calculated specific ionic ratios $(Na+K-Cl)/(Na+K-Cl+Ca)$, $Na/(Na+Cl)$, $Mg/(Ca+Mg)$, and $Ca/(Ca+SO_4)$ indicate possible plagioclase weathering, ion exchange limestone-dolomite weathering, and gypsum dissolution; respectively.

Groundwater of Aqool area showed lower concentrations for TDS, NO_3 and NO_2 , consequently, it can be used safely for drinking purposes.

The TDS values, and the calculated SAR, RSC and MH parameters of the groundwater samples of Aqool area indicated excellent water for irrigation.

It is recommended that drip irrigation method must be applied in this area to prevent aquifer depletion which results due to over pumping. On the other hand, monitoring the groundwater quality including the possibility of leaching soils of the agricultural land which causes an increase in salinity of the water in this area.

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