

Groundwater characterization and quality assessment, and sources of pollution in Madinah, Saudi Arabia

Abdullah O. Bamousa¹ · Magdy El Maghraby^{1,2}

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Abstract Groundwater quality in the Madinah city is increasingly endangered by expanding urbanization, industrial activities, and intensified agricultural land use. In order to investigate the pollution of Madinah groundwater resources, 32 samples have been gathered and examined for major, trace, and nutrient components. Results of groundwater characterization and groundwater quality assessment show that Na^+ and Cl^- are the main anion and cation in the groundwater, respectively. Depletion of HCO_3^- that interacts with water increases salinity. Cluster analysis and principal component analysis were applied in the current study to obtain relationship between parameters and sampling site in order to identify the factors and sources influencing groundwater quality. The CA allowed the formation of three clusters between the sampling wells reflecting differences on water quality at different locations. Four major PCs were extracted, which accounted 86.05 % variance of the original data structure. Forty-four percent of the groundwater samples have high values of NO_3^- , due to human and agricultural activities. Four samples in the southwestern part of the study area show high content of Pb, Cd, Cr, Ni, As, and Al. This may be due to the influence of anthropogenic activities that resulted from the southwestern industrial area of Madinah. The present study illustrates explicitly the stress on groundwater quality and its vulnerability in the aquifer system.

Keywords Madinah · Groundwater · Pollution · Anthropogenic activities · Groundwater quality

Introduction

Groundwater is the main source of water in Madinah, where surface water is rare (Delgado et al. 2010; Li et al. 2013; Hofmann et al. 2015). It is a limited water resource in Saudi Arabia, and it is increasingly threatened by expanding urbanization and intensified land use for agriculture and industrial activities. Besides rare precipitation and overexploitation of groundwater resources, the level of groundwater was declined, and the groundwater was deteriorated. Quality of groundwater is almost influenced by weathering, lithology, nature of geochemical reactions, and evapotranspiration or by various human activities, such as agriculture, sewage, and industrial wastes (Singh and Chandel 2006; Nisi et al. 2008; Jiang and Yan 2010).

In arid and semiarid regions, groundwater salinization results from physical and chemical processes of the groundwater and leads to deterioration in water quality and reduction of usable groundwater (Bernaldez and Benayas 1992; Salama et al. 1999; Wang et al. 2008; Han et al. 2015).

Understanding the hydrogeochemical parameters is necessary to utilize and protect valuable water sources effectively and predict changes in groundwater environments (Guendouz et al. 2003; Edmunds et al. 2006; Bozdağ and Göçmez 2013; Missimer et al. 2014). Little knowledge about the location, extent, and type of groundwater pollution exists in the Madinah. Few hydrogeological and hydrogeochemical studies were performed in the study area (El Maghraby 2004, 2014; Al Harbi et al. 2006; Shraim et al. 2013; El Maghraby et al. 2013; Bob et al. 2015).

✉ Magdy El Maghraby
magdy_elmaghraby@yahoo.com

¹ Present address: Geology Department, Faculty of Science, Taibah University, Medina, Saudi Arabia

² Geology Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Industrial wastewater from southwest of Madinah city is disposed in an unlined site located southwest the study area. This location is considered as the main source of pollution of groundwater that may influence the quality of groundwater by releasing high concentrations of metals (e.g., Pb, Cd, Cr, Ni, As, and Al).

The results of the current work were used to determine the contaminants and the processes governing the groundwater and to assess the quality of groundwater for different uses. The different constituents of groundwater of the Madinah area are of wide ranges of concentrations, which point to the contribution of a number of chemical practices inducing the chemistry of water. Scatter plots between chloride and major ions were constructed to show the extent of correlation among ions.

In the current work, the diagrams of Piper, Durov, and Schoeller were benefited for the purpose groundwater categorization. In order to understand and illustrate the hydrogeochemical processes, concentrations of different major elements and their interrelationship ionic ratios were studied.

Cluster analysis (CA) and principal component analysis (PCA) were applied in the current work. These techniques were used to obtain the relationship between parameters and sampling site and to identify the factors and sources influencing groundwater quality (Usman et al. 2014). CA was employed to examine the spatial groupings of the sampling wells. It is a common method to classify variables into cluster (Massart and Kaufman 1983). CA and PCA are usually referred to as pattern recognition techniques (Adams 1998). The application of different pattern recognition techniques to reduce the complexity of large data set has proven to give a better interpretation and understanding of water quality data (Brown et al. 1980).

Weathering of silicate was studied as an important source for elevated concentrations of sodium besides calcium in groundwater. In the current work, to define the chemical balance between minerals and water, saturation indices (SI) of certain minerals were estimated.

Nutrients, which include nitrate, nitrite, ammonia, phosphate, fluoride, and boron in groundwater, were analyzed to investigate the anthropogenic effects and the pollution extent in the study area. Trace constituents of the area of study were studied as a possible source of pollution of groundwater.

Studying the different constituents of the groundwater of the study area showed that the Madinah groundwater is unsafe for purpose of drinking, whereas it is moderately appropriate for activities of irrigation work.

Thus, a hydrogeochemical investigation was conducted to identify the pollution sources at the groundwater system of Madinah. The present work also includes groundwater characteristics and a groundwater quality assessment.

Study area

Madinah lies between latitudes 24° 15' 54" and 24° 36' 54" N and longitudes 39° 29' 06" and 39° 50' 15" E (Fig. 1). It forms a shallow basin. Uhud Mountain is located to the north and Ayre and Jammah Mountains to the west. Lava plateaus surround Madinah from south to east. Its altitude ranges between 600 and 610 m. Arid conditions, low rainfall rate, and high temperatures characterize it. Rain takes place usually as uneven gales in November, December, March, and April. In Madinah area, the mean rainfall is nearly 40.1 mm/year. The calculated rate of infiltration varies between 0.13 and 1.01 cm/min. The mean daily temperatures ranged between 27 and 43 °C in July and August and 10–25 °C in December and January (PME 2012).

Madinah city lies within a shallow basin in the central part of the Al Madinah Province (Fig. 2). The mountainous parts that bound the city are geologically part of the Arabian Shield, which is a Neoproterozoic 900 to 540 Mya in age and subjected to several tectonic events (e.g., Stoeser and Camp 1985; Stoeser and Stacey 1988; Stern 1994; Johnson and Kattan 2001, 2008; Nehlig et al. 2001, 2002; Genna et al. 2002; Volesky et al. 2003; Meert and Lieberman 2008; Stern and Johnson 2010; Bamoussa 2013). Tertiary to Quaternary flood basalts of Harrat Rahat bound the city from eastern and western parts. Several eruptions formed a large basaltic plateau and extending 310 km from Wadi Fatimah adjacent to Makkah city to Medina city, with a mean width of 60 km and an area covering about 18,100 km² (Brown et al. 1963; Brown 1972; Blank and Sadek 1983; Coleman et al. 1983; Camp and Roobol 1989; Walker 1993; Mirza 2008). The fractured Harrat basalts contain aquifer zones and traps groundwater (Coleman et al. 1983; Blank and Sadek 1983; Al-Shaibani et al. 2007; Vincent 2008; Wagner 2011).

Wadi Qana and Wadi Aqiq are large wadis run in the Madinah area. The Wadi Aqiq runs northward joining Wadi Qana in the eastern part of Madinah area. They form the outlet of the Madinah basin, then they flow together further due north as one major valley, known as Wadi Al Hamd.

Groundwater resources of Madinah occur in two zones: high permeable Harrat Rahat zone in east and south and alluvial deposits zone to the west including the central part of Madinah city. The deposits belong to Quaternary, consisting of clay, sand, and gravel that resulted from weathering of Precambrian rocks with parts of basalts of late Tertiary and Quaternary. The groundwater wells are drilled randomly (Fig. 1). For this reason, a decrease in the level of groundwater is observed, which ranges between 535 and 594 m level. The water table depth ranges between 28 and 93 m.

Buried wadis were found beneath Harrat Rahat's volcanic area with more than 50-m thickness of alluvial deposits (Italconsult 1989). The hydraulic parameters

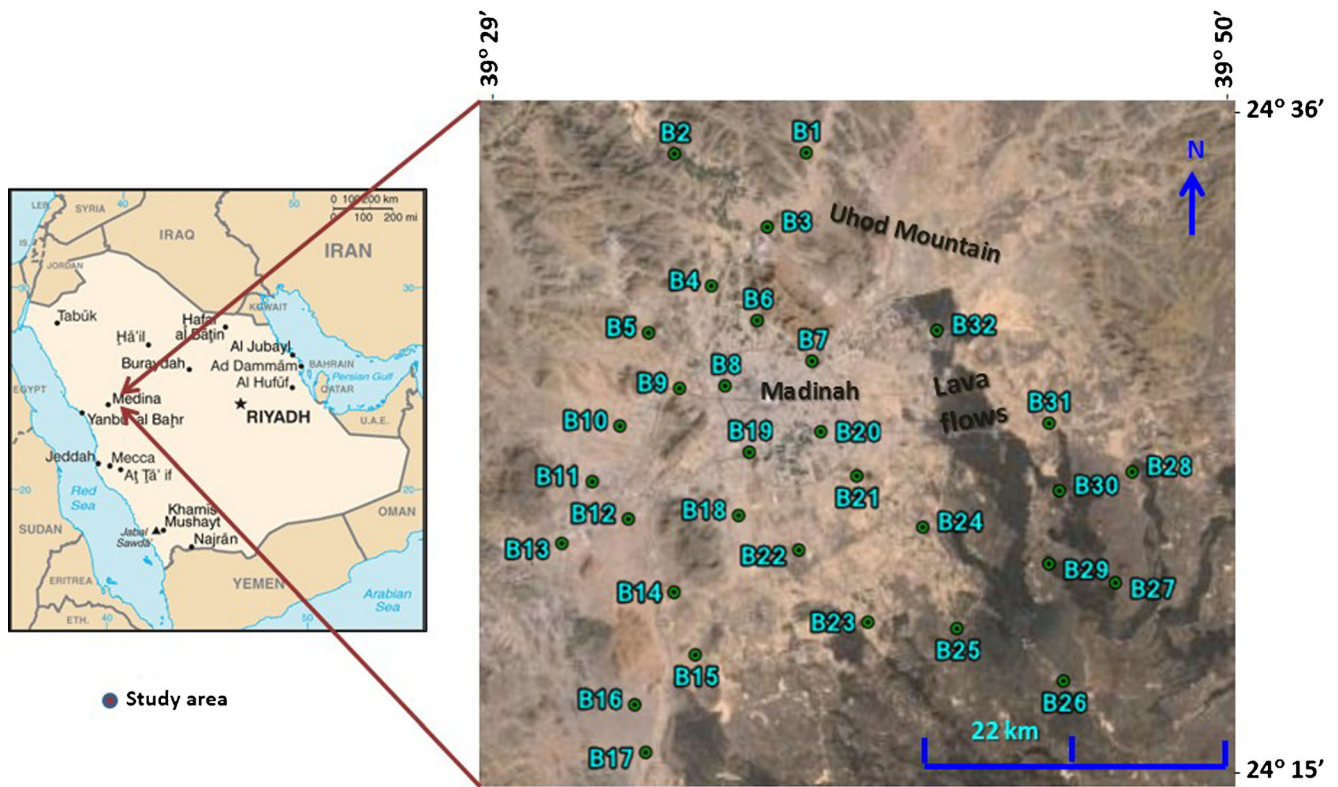
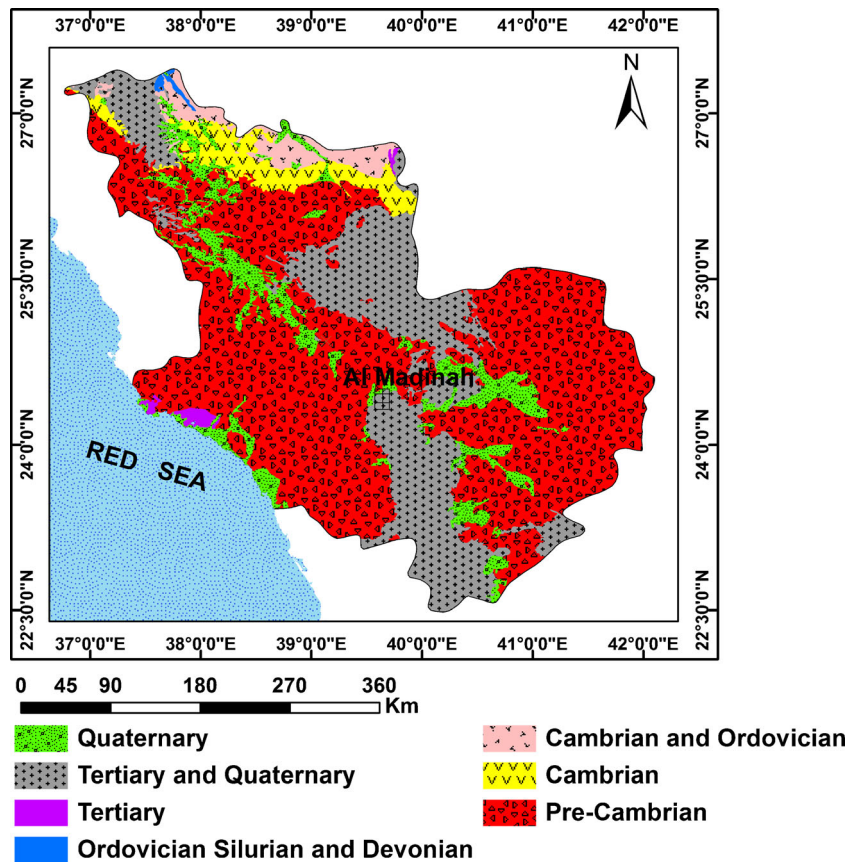


Fig. 1 Map of the study area with location of the groundwater samples

Fig. 2 Geological map of the Al Madinah Province including Madinah city (MPMR, SA, 1987)



of the aquifer in the area of study are shown in Table 1 (Bazuhair et al. 2002).

Methodology

The 32-groundwater sampling points of Al Madinah area are collected from Al Aqool, Quba, Uhud areas and around the Prophet's Holy Masjid area (Fig. 1). The selection of the groundwater sites was designed to cover the whole city and its surroundings. The wells are selected to be as uniform as possible to study the behavior of groundwater and the extent of pollution. Prior to groundwater sampling, wells were pumped for enough time, until the field parameters are stabilized.

At each water sampling location, two 1-l polyethylene bottles were filled. All sampling bottles were soaked with 1:1 HNO₃ and washed using detergent. These bottles were then rinsed with double-distilled water. At the time of sampling, bottles were thoroughly rinsed 2–3 times by the groundwater.

Duplicate samples of groundwater were collected from all wells. The first sample was acidified using concentrated nitric acid to pH <2 for the cations and minor constituents' analysis. The second sample of groundwater was also gathered at its ordinary pH and well kept (almost at 4 °C) for anions analysis. Groundwater samples were filtered using membrane filters (0.45 µm) for laboratory analyses following the procedures established in standard methods (Clesceri et al. 1999). Results of chemical analyses are presented in Tables 2, 4, and 6.

Beside the well, a probe (portable HI 991300 Hanna Instruments) was used for field determinations of electrical conductivity (EC), hydrogen ion concentration (pH), total dissolved salts (TDS), and temperature (T°C). The groundwater samples were analyzed in the chemical laboratory of Taibah University. Major ions and trace components were analyzed according to instructions of the APHA (1988). The error of ionic balance is below ±5 % (Domenico and Schwartz 1998). The minor components were measured using ICP/MS (7500cx series, Agilent Technologies). SI of specific minerals were measured with the help of PHREEQC software (Parkhurst and Appelo 1999).

Table 1 Hydraulic parameters of the aquifer in the area of study

Hydraulic parameter	Value
Transmissivity of Harrat Rahat's	260 m ² /day
Mean storativity	3 × 10 ⁻³
Annual recharge	7–14.6 mm
Water level from the earth surface	40:80 m

Results and discussion

Hydrogeochemical characteristics

The characteristics of hydrogeochemistry of Madinah groundwater are provided in Table 2. The results were used to determine the contaminants and the processes governing the groundwater and to access the quality of groundwater for different uses. The temperature values generally ranged between 27.4 and 33.4 °C, which may be due to the geothermal phenomena, where all wells were drilled in basement rocks. The elevated temperatures encourage dissolution process resulting in increasing the dissolution of the existed salts.

The values of pH in groundwater of the area of study vary from 7.12 to 7.87, revealing the slight alkaline nature of water. The pH values approaching 8.00 (Appelo and Postma 2005) propose the dissolution of silicates and carbonates. The values of EC in samples varied between 1683.36 and 5185.48 µS/cm at 25 °C. The quality of groundwater varied from brackish water to saline water, where the TDS values were ranged between 1077.35 mg/l in the southern parts of the area of study and 3318.71 mg/l in the northern parts of the Madinah area.

The drawn iso-TDS map (Fig. 3) of the groundwater reveals that lower values of TDS were noticed in the southwestern, southeastern, and southern parts of the Madinah, although, high salinity values are detected in northern part of the area of study. Besides, the salinity increase may also be ascribed to indigenous conditions of the environment (Lloyd and Heathcote 1985), e.g., leaching from cultivated soil zone and the return flow of irrigation activities to the leakage of septic wastewater or to the interaction between water and rock and cycling salting. The elevated salinity values are present in highly agricultural and residential areas.

Distribution of major ions

The constituents of groundwater of the Madinah area are of wide ranges of concentrations, which point to the contribution of a number of chemical practices inducing the chemistry of water (Table 2). The results of groundwater constituents of the Madinah area indicated the following ranges: 255–670 mg/l for Na, 80.45–327.59 mg/l for Ca, 36.42–147.36 mg/l for Mg, 5–9 mg/l for K, 395–1350 mg/l for Cl, 190–655 mg/l for SO₄, and 72.66–186.41 mg/l for HCO₃.

The groundwater of Madinah area showed two ionic dominances: the first is Na > Ca and Cl > SO₄ (24 samples), and the second is Na > Ca > Mg and Cl > SO₄ (8 samples).

To show the extent of correlation among ions, scatter plots between chloride and major ions were constructed (Fig. 4). The concentrations of Na, Ca, and Mg indicate a direct relationship with chloride. The elevated concentrations of sodium and calcium in the majority of groundwater samples of the

Table 2 The chemical analysis results of major constituents (mg/l) of Madinah

Well no.	T°C	pH	EC	TDS	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl
B1	31.40	7.44	5185.48	3318.71	327.59	128.46	670.00	9.00	178.66	655.00	1350.00
B2	30.90	7.39	5043.47	3227.82	319.44	134.77	625.00	9.00	174.61	645.00	1320.00
B3	32.40	7.51	5042.25	3227.04	324.27	147.36	600.00	9.00	186.41	655.00	1305.00
B4	28.90	7.31	4789.78	3065.46	296.34	128.26	595.00	9.00	181.86	645.00	1210.00
B5	29.80	7.42	4615.75	2954.08	233.34	130.10	609.00	9.00	167.64	615.00	1190.00
B6	28.80	7.56	4671.06	2989.48	284.67	125.67	590.00	9.00	175.14	605.00	1200.00
B7	29.70	7.74	4653.14	2978.01	287.11	117.64	590.00	9.00	164.26	620.00	1190.00
B8	30.30	7.12	4649.20	2975.49	275.63	124.22	605.00	9.00	161.64	630.00	1170.00
B9	30.40	7.19	4507.28	2884.66	291.65	109.64	585.00	9.00	184.37	595.00	1110.00
B10	31.70	7.45	4249.42	2719.63	230.54	106.77	575.00	9.00	148.32	535.00	1115.00
B11	30.00	7.68	4203.94	2690.52	235.67	106.49	555.00	9.00	134.36	545.00	1105.00
B12	29.70	7.66	4083.63	2613.52	221.67	108.47	545.00	9.00	144.38	520.00	1065.00
B13	27.40	7.81	3616.11	2314.31	197.13	67.59	519.00	9.00	110.59	481.00	930.00
B14	31.10	7.24	3420.69	2189.24	198.45	61.24	494.00	9.00	106.55	460.00	860.00
B15	31.00	7.26	3153.75	2018.40	184.28	54.36	464.00	7.00	88.76	440.00	780.00
B16	28.50	7.64	3067.70	1963.33	170.64	57.34	442.00	7.00	81.35	445.00	760.00
B17	27.40	7.26	2944.92	1884.75	161.95	44.14	439.00	7.00	72.66	425.00	735.00
B18	31.20	7.29	3261.42	2087.31	182.46	56.18	487.00	7.00	89.67	455.00	810.00
B19	29.50	7.39	3294.83	2108.69	191.71	55.31	490.00	7.00	91.67	468.00	805.00
B20	33.40	7.35	3316.67	2122.67	188.87	58.41	500.00	7.00	93.39	485.00	790.00
B21	33.40	7.34	3233.30	2069.31	182.61	55.53	485.00	7.00	89.17	470.00	780.00
B22	32.50	7.26	3081.92	1972.43	167.15	57.14	455.00	7.00	86.14	455.00	745.00
B23	30.80	7.24	3041.02	1946.25	159.22	58.69	465.00	7.00	76.34	430.00	750.00
B24	29.60	7.42	2996.75	1917.92	153.66	64.11	415.00	7.00	88.15	545.00	645.00
B25	30.10	7.87	3000.88	1920.56	160.54	61.78	425.00	7.00	91.24	535.00	640.00
B26	32.40	7.75	1683.36	1077.35	80.45	36.42	255.00	5.00	115.48	190.00	395.00
B27	33.10	7.67	1816.27	1162.41	88.27	38.77	274.00	5.00	116.37	205.00	435.00
B28	31.60	7.87	1893.27	1211.69	93.26	44.32	280.00	5.00	124.11	210.00	455.00
B29	31.70	7.67	2001.84	1281.18	99.52	51.19	290.00	5.00	135.47	220.00	480.00
B30	32.40	7.74	2092.09	1338.94	103.45	52.76	305.00	5.00	142.73	225.00	505.00
B31	30.50	7.50	2190.98	1402.23	110.44	55.55	315.00	5.00	151.24	235.00	530.00
B32	31.60	7.77	2318.67	1483.95	112.14	60.03	335.00	5.00	156.78	250.00	565.00
RW ^c		7.10	55.69	35.64	3.77	1.20	4.10	1.02	14.65	4.40	6.50

EC electrical conductivity (in $\mu\text{S}/\text{cm}$ at 25 °C), TDS total dissolved salts (in mg/l), RW rainwater

area of study may be due to the Na-rich and Ca-rich silicates and carbonates dissolution, as well as gypsum and halite. To some extent, Na replaces Ca during its pathway through the effect of the process of cation exchange, in which clay exchangers are common in the soil matrix of the aquifer. The anthropogenic calcium in the study area comes from different sources, e.g., domestic effluents, wastewater, and leather industry (Somasundaram et al. 1993; Reimann and Caritat 1998). The magnesium in the samples might be initiated as a result of the dissolution of dolomite and silicate minerals (Hem 1989). The elevated concentrations of magnesium found in industrial regions may result from the metal industry

(Pitt et al. 1999). K ion comes from wastewater and fertilizers (Trauth and Xanthopoulos 1997).

Chloride is an effective pollution indicator. Chloride is likely to be enriched in groundwater. The high concentration of Cl mainly originated from cyclic salting in agricultural areas along the path of groundwater flow starting from southwestern parts toward northeastern parts, as well as from sewage and fertilizers. HCO₃ displays weak correlation with chloride indicating varied sources of HCO₃ (Fig. 4). Elevated concentration of HCO₃ resulted from CO₂ gas dissolution, which originated by the organic biodegradation, which may come from the leakage of domestic and industrial manure (Canter

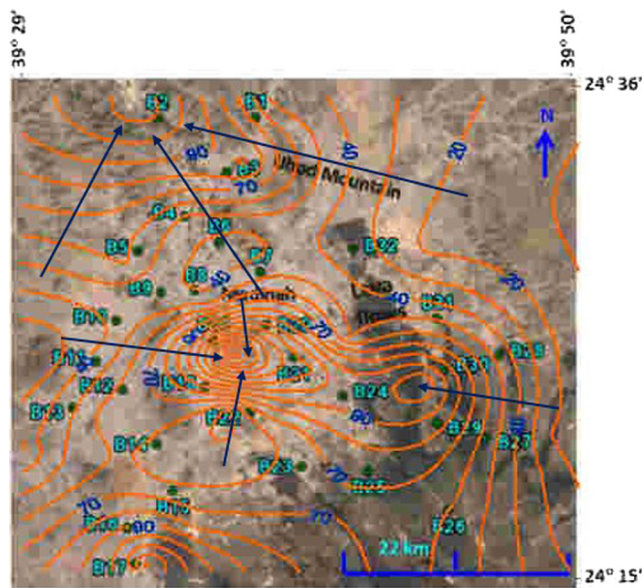


Fig. 3 TDS distribution in the Madinah area

1997; Jeong 2001; Zilberbrand et al. 2001). Sulfates display direct relationship with chloride (Fig. 4). SO_4 may be originated from gypsum dissolution from the matrix of aquifer or from phosphate fertilizers and industrialized wastes (Subbarao et al. 1996; Pitt et al. 1999; Cortecci et al. 2002).

Groundwater classification

Hydrochemical diagrams show the relative concentrations of the major ions, which can summarize the main contrasts in hydrochemical composition among different water sources (Soulsby et al. 1998). In the current work, the diagrams of Piper (1944), Durov (1948), and Schoeller (1962) were benefited for the purpose groundwater categorization (Figs. 5, 6, and 7).

Classification of groundwater of the area of study is illustrated in the diagram of Piper (Fig. 5). From the Piper diagram, it is obvious that the Madinah samples have high alkali metals (Na + K). They are possibly resulting from cation exchange process.

The arrow in Fig. 5 shows the direction of geochemical evolution of the Madinah groundwater, where it changes from the composition of rainwater (Ca-HCO_3) to the current composition of the groundwater in Madinah (Na-Cl). The geochemical composition of the groundwater of the area of study is affected by the silicate mineral dissolutions and their reaction with the groundwater, which tend to change the quality of groundwater.

Chloride ion is the prevailing anion in the groundwater. The groundwater samples are characterized by Na-Cl facies, which point to final phase of the groundwater evolution.

With the purpose of simplifying clarifications of the evolutionary trends and hydrogeochemical reactions in the

groundwater system, the results of analysis of samples were presented on the diagram of Durov (Burdon and Mazloum 1958; Lloyd 1965). From Fig. 6, the groundwater samples are located in the ninth field representing reactions of reverse ion exchange and waters of end point facies.

The arrow on the diagram of Durov displays probable evolution of the Madinah groundwater from Ca- HCO_3 facies (rainwater) to Na-Cl facies. Rainwater was exposed to many processes such as evaporation and interaction with soils and deposits that penetrate them to reach the groundwater. Furthermore, as the groundwater runs through the alluvial aquifer, extra practices of dissolution/precipitation, cation exchange, and mixing with return flow will act to raise the salinity of groundwater and alter the prevalence of ions from Ca to Mg and lastly to Na-rich water. Concurrently, anion prevalence is altered from HCO_3 to SO_4 and lastly to Cl, signifying end point waters.

Representing the Madinah groundwater results on the diagram of Schoeller (1962) revealed that the Madinah samples had almost similar trends of increase and decrease with rainwater (Fig. 7). Evidently, the groundwater is affected by evaporation, ion exchange, anthropogenic pollution, and water-rock interaction. The groundwater samples of the area of study show prevalence of Na, Ca, Cl, and SO_4 over Mg, K, and HCO_3 .

Multivariate statistical techniques

The results of hydrochemical data were analyzed using multivariate statistical techniques, such as Cluster Analysis (CA) and Principal Component Analysis (PCA), to identify the sources of pollution that presently affects the groundwater. The water quality data was monitored at 32 different wells, using 23 water quality parameters.

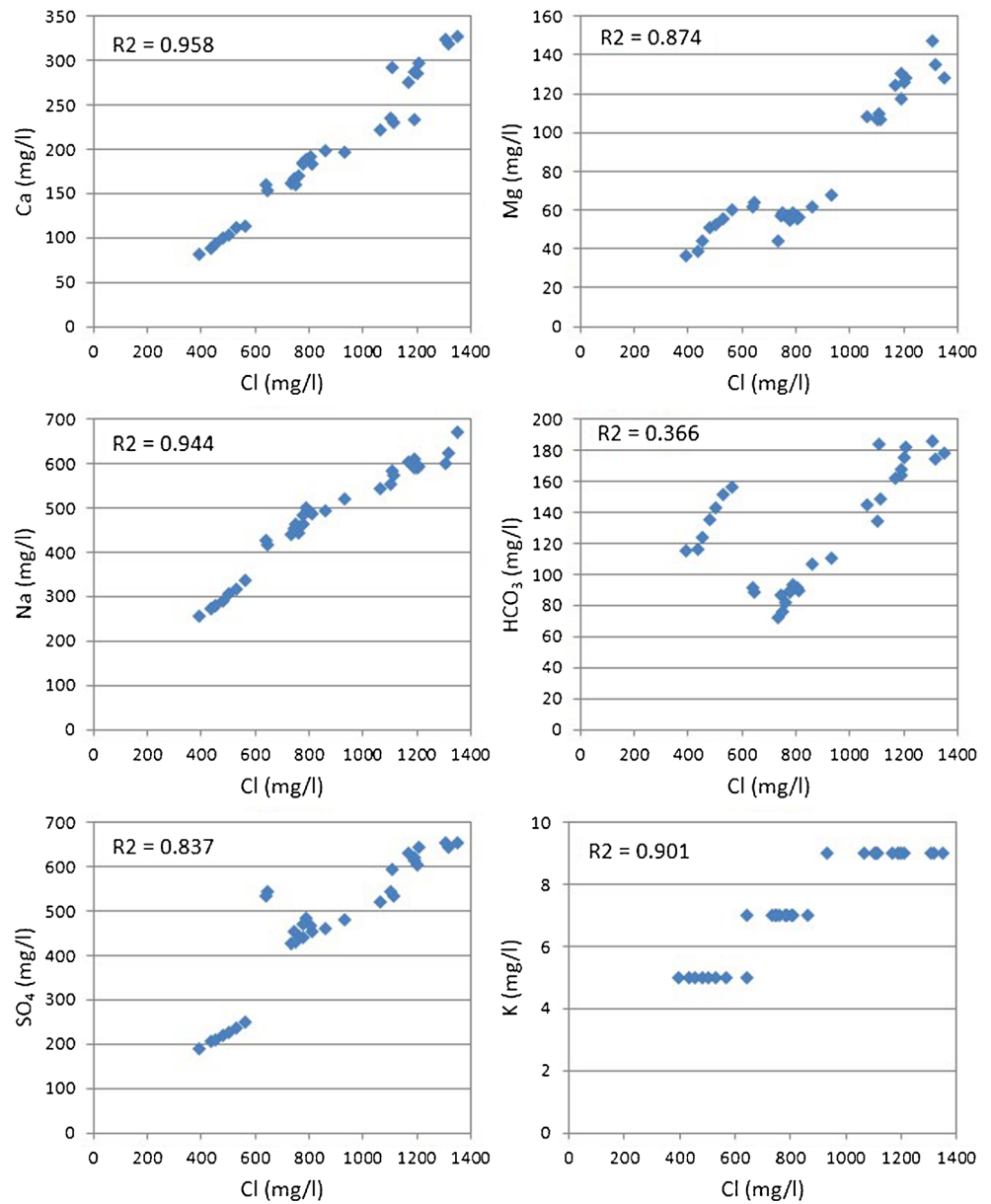
Cluster analysis

This is a group of multivariate techniques, which primarily classify (Massart and Kaufman 1983) samples into cluster with high homogeneity level within the class and high heterogeneity level between classes.

The spatial variability of groundwater was determined by CA. CA was first performed to group all sample site in order to classify them into cluster to minimized their number. CA was used to link sample site in the configuration of a tree with different branches (dendrogram), which provide visual summary of the clustering process, giving a picture of the cluster and their closeness. Branches that have relation closer to each other show a stronger relationship between samples.

In present study, CA was applied for the grouping of 32 different wells using ward's linkage method (Ward 1963). A classification scheme using Euclidean distance (straight-line distance between two points in C-dimensional space define by

Fig. 4 Scatter plots between chloride and major ions of the Madinah groundwater



C variable) for similarity measurement together with Ward’s method for linkage produces the most distinctive groups, where each member within groups is more similar to its fellow member than to any member outside the group (Guler et al. 2002).

CA was carried out on the results of chemical analysis of groundwater samples to evaluate the spatial variability among the studied wells. This analysis resulted in the grouping of the studied wells into three clusters between the sampling wells, reflecting differences on water quality at different sites as shown in Fig. 8.

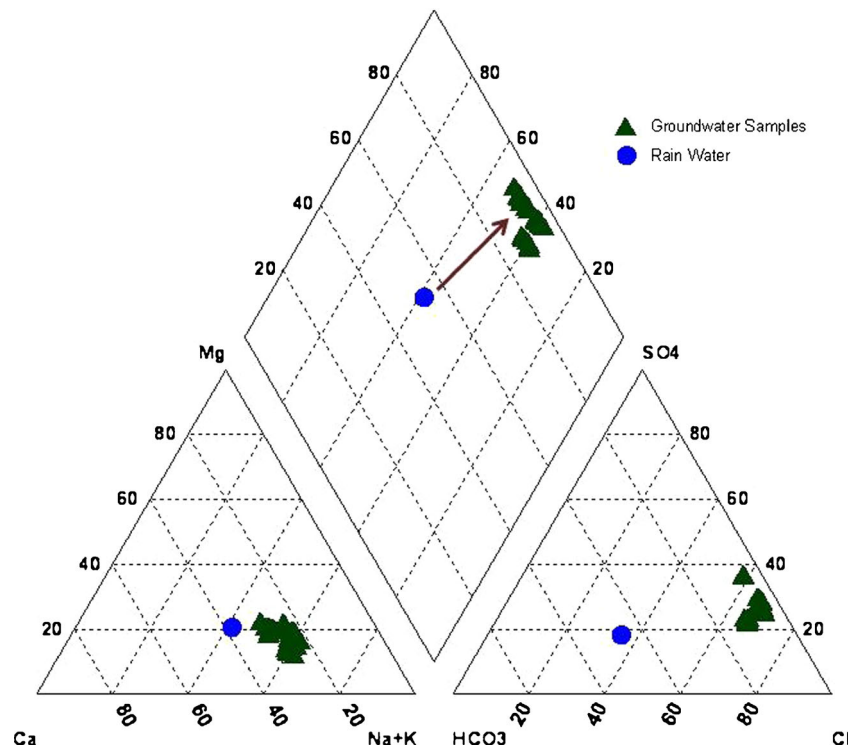
Cluster 1 includes 12 wells located at the northwestern part; cluster 2 includes 7 wells located in southeastern part; and cluster 3 contained 13 wells located at the center, southern, and southwestern parts (Fig. 9).

The clustering of wells indicates that water quality of groundwater varies, and such variation is likely due to different hydrochemical processes, anthropogenic pollution, and water–rock interaction in the Madinah area.

Principal component analysis

PCA analysis was used as a technique of factor extraction. For this work, it needs a previous estimation of the amount of variation in each groundwater quality parameter elucidated by the factors. Eigenvalues are the amount of variance elucidated by each factor; each parameter had a variance of 1 with a total variance of 23 for the whole data set. Factors with eigenvalue >1 elucidated more total variation in the data than individual groundwater quality parameters, and factors with

Fig. 5 Trilinear diagram of Piper for the Madinah groundwater



eigenvalue <1 clarify less total variation than individual variable. Therefore, only the factors with eigenvalue >1 were taken for the explanation, while retained factors were subjected to varimax rotation (Vega et al. 1998).

The coefficients having correlation greater than 0.75 are considered as strong and indicate that high

proportion of its variance explained by the factor, between 0.50 and 0.75 is considered as moderate loading, while coefficients having 0.30–0.50 correlation are considered as weak significant factor loading, indicating that much of that attribute’s variance remains unexplained and it is less important (Reghunath, et al. 2002).

Fig. 6 Diagram of Durov showing the geochemical evolution of the Madinah groundwater

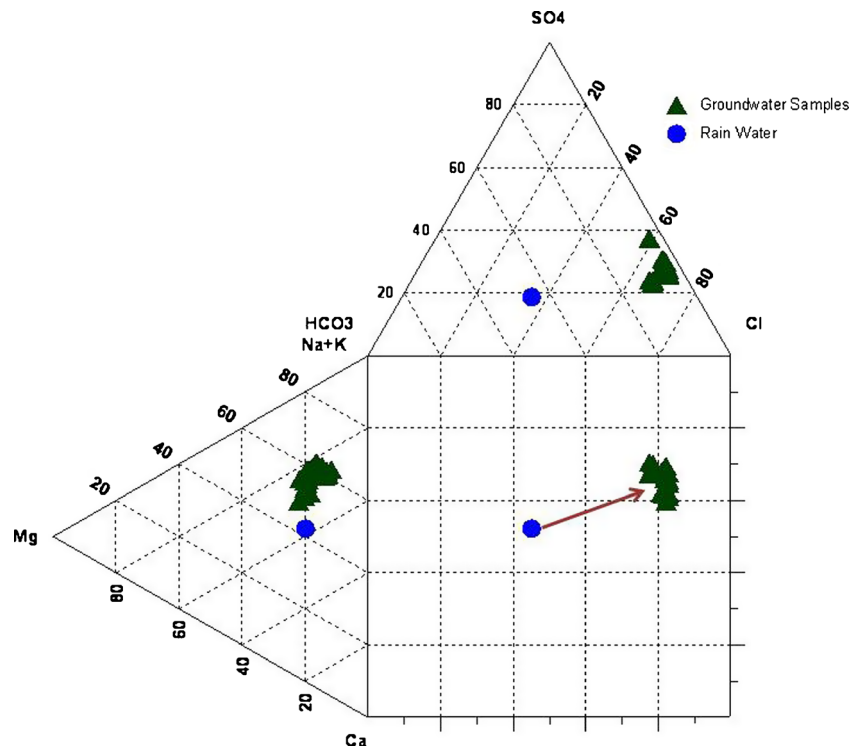
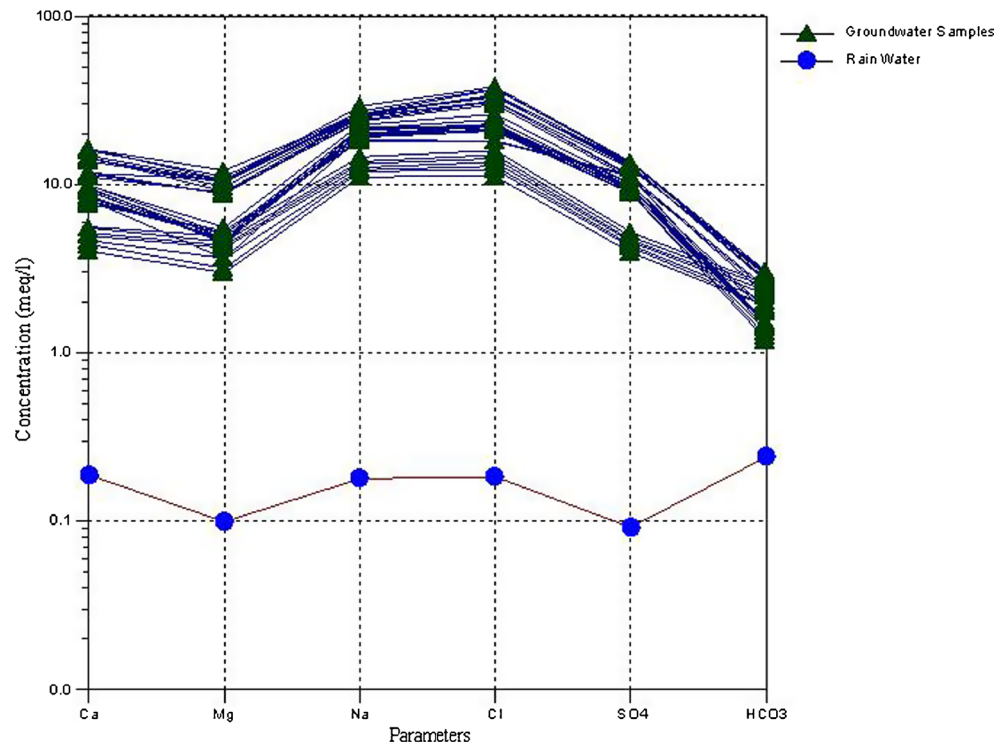


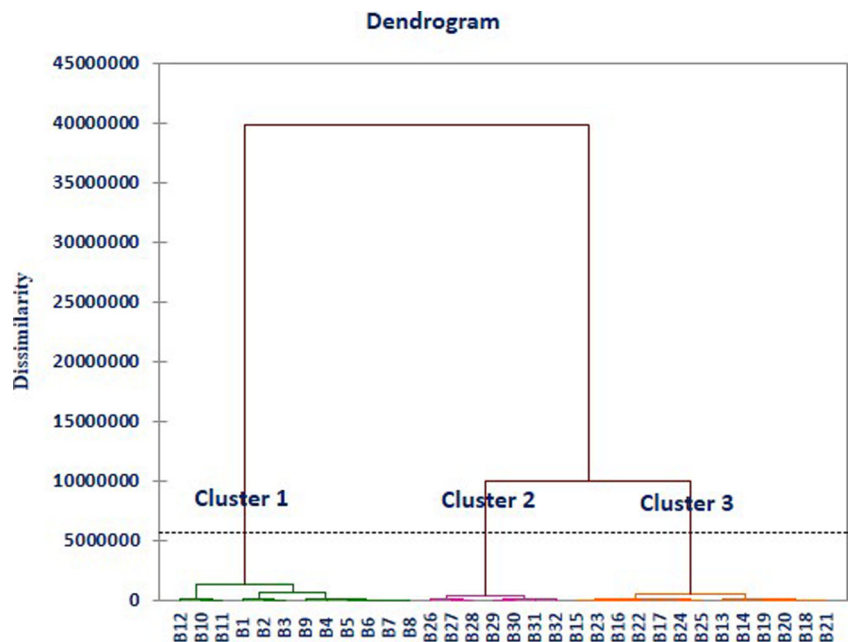
Fig. 7 Plot of Schoeller's for the samples of groundwater of the Madinah area



PCA is applied on the normalized data set (23 parameters) to recognize the major variables affecting the quality of groundwater of the Madinah area. Factors with eigenvalue ≥ 1.0 are considered significant (Kim and Mueller 1987) and are retained in order to understand the data structure (Jackson 1991), which has expressed that the selected PCs are able to carry more information than single original variables. Four major PCs were extracted, which accounted 86.05 % variance of the original data structure. The results of the PCs are given in Table 3.

The PC1 accounts for 40.986 % of the total variance, displaying strong positive loading on Na, K, Cl, and Al, while it displays a moderate positive loading on EC, TDS, Ca, Mg, SO₄, Mn, Pb, Cu, Cd, Cr, Ni, Zn, and As. PC1 shows a weak positive loading on Fe, Se, and V. The major variables constituting PC1 are related to the hydrochemical variables originating from mineralization of groundwater and Na-rich silicates. The Cl mainly originated from cyclic salting in agricultural areas and from sewage and fertilizers.

Fig. 8 A dendrogram showing the three clusters of groundwater samples in the Madinah area



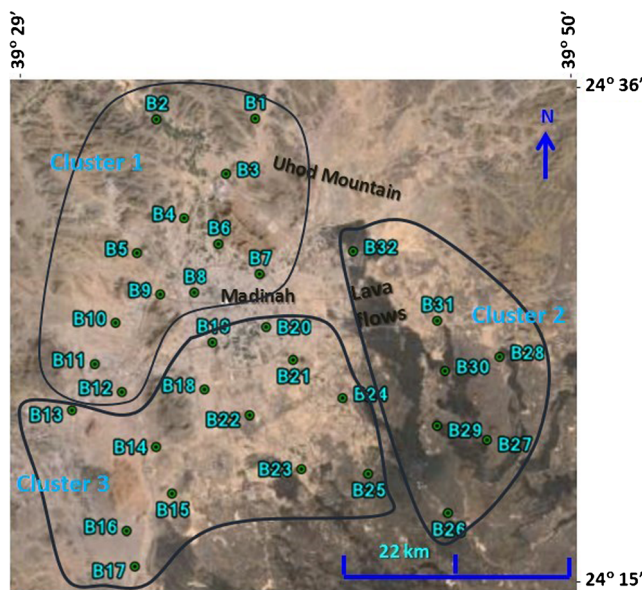


Fig. 9 Map showing the three clusters of groundwater samples in the Madinah area

The PC2 accounted 31.648 % of the total variance, showing strong positive loading on Fe, while it displays a moderate positive loading on Mn, Cu, Cd, Ni, Zn, and As. PC1 shows a weak positive loading on Pb and Cr. The major variables constituting PC2 are related to the leaching and dissolution processes and from intensive fertilizers use for agricultural purposes. Out of the total variance, 7.400 % is explained by PC3 and is mainly carried by Se, V, and Co. Moreover, 6.011 % of the total variance of water quality is displayed by Hg with a strong positive loading under PC4. PC4 shows a weak positive loading on Se.

Ionic ratios

In order to understand and illustrate the hydrogeochemical processes, concentrations of different major elements and their interrelationship were studied. If the groundwater facies formed in different conditions, the ratios of certain ions may have obvious differences, which can infer the evolution of different groundwater facies (Reddy and Kumar 2010).

Particular ratios calculated to conclude the probable source of the groundwater and to disclose the probable processes that prevailed in the study area (Hounslow 1995). The influence of weathering of silicate mineral on the groundwater composition is supported upon further examination of the aqueous geochemistry. Values of $Cl^-/\text{sum anions}$ 0.59–0.70 (<0.8) are indicative of rock weathering.

The $Mg/(Ca + Mg)$ values of the groundwater vary from 0.31 to 0.48 (<0.5), which indicate the weathering of limestone–dolomite (Hounslow 1995).

The $Ca/(Ca + SO_4)$ values of the groundwater samples vary from 0.40 to 0.55 (≈ 0.5), which indicate the dissolution of

Table 3 Factor loading and eigenvalues of principal components

Variables	PC1	PC2	PC3	PC4
EC ($\mu\text{S}/\text{cm}$)	0.741	-0.668	-0.015	-0.026
TDS (mg/l)	0.741	-0.668	-0.015	-0.026
Ca (mg/l)	0.706	-0.688	-0.024	-0.026
Mg (mg/l)	0.624	-0.704	-0.249	-0.036
Na (mg/l)	0.762	-0.610	0.120	-0.036
K (mg/l)	0.882	-0.425	0.048	-0.001
HCO_3 (mg/l)	0.288	-0.564	-0.593	-0.150
SO_4 (mg/l)	0.694	-0.637	0.141	0.036
Cl (mg/l)	0.758	-0.642	-0.045	-0.034
Fe (mg/l)	0.421	0.860	0.060	-0.022
Mn (mg/l)	0.740	0.532	-0.114	0.179
Pb (mg/l)	0.652	0.341	-0.100	-0.218
Cu (mg/l)	0.735	0.640	-0.116	-0.026
Cd (mg/l)	0.692	0.573	-0.132	0.050
Cr (mg/l)	0.725	0.397	0.298	0.018
Ni (mg/l)	0.720	0.654	-0.086	-0.001
Zn (mg/l)	0.716	0.624	-0.076	0.086
As (mg/l)	0.518	0.672	-0.191	-0.098
Se (mg/l)	0.464	-0.096	0.563	0.401
Hg (mg/l)	0.131	-0.146	0.167	0.868
V (mg/l)	0.357	0.114	0.556	-0.403
Co (mg/l)	0.127	0.008	0.618	-0.418
Al (mg/l)	0.757	0.620	-0.121	0.037
Eigenvalue	9.427	7.279	1.702	1.383
Variability (%)	40.986	31.648	7.400	6.011
Cumulative %	40.986	72.634	80.033	86.045

Italicized values are coefficients that have correlation greater than 0.75 and are considered as strong and indicate high proportion of its variance explained by the factor; between 0.50 and 0.75 are considered as moderate loading, while coefficients having 0.30–0.50 correlation are considered as weak significant factor loading, indicating that much of that attribute's variance remains unexplained and it is less important (Reghunath et al. 2002)

gypsum (Hounslow 1995). The SI for gypsum vary from -0.62 to -1.44.

Silicate weathering

Weathering of silicate is considered as an important source for elevated concentrations of sodium besides calcium in groundwater. However, halite is present in the alluvium of Madinah, therefore, if the dissolution of halite is controlling the presence of Na, then the ratio of Na/Cl would be roughly equivalent to 1 (Table 4), but if the Na/Cl ratio is more than 1, it is usually interpreted as sodium liberated from the weathering of silicate (Meybeck 1987). The values of Na/Cl ratio are nearby or above 1.00 (0.71–1.02, median = 0.92), indicating to some extent that weathering of silicate and the dissolution of halite are the main reactions causing the release of Na into groundwater. The silicates of the Madinah area are mostly consisted

Table 4 Chemical analysis results of nutrients, irrigation water parameters and hydrochemical coefficients in the area of study (conc. in mg/l)

Well no.	NO ₃	NO ₂	NH ₄	PO ₄	F	B	SAR	RSC	MH	Mg/ (Ca + Mg)	Ca/ (Ca + SO ₄)	Cl/sum anions	Na/Cl
B1	45.05	0.010	BDL ^d	0.29	0.00081	0.26	7.94	-23.99	39.27	0.39	0.55	0.70	0.77
B2	116.71	0.010	BDL	0.21	0.00145	0.25	7.40	-24.17	41.02	0.41	0.54	0.70	0.73
B3	91.52	0.020	BDL	0.09	0.00124	0.23	6.94	-25.25	42.83	0.43	0.54	0.69	0.71
B4	47.08	0.010	BDL	0.41	0.00072	0.29	7.27	-22.36	41.64	0.42	0.52	0.68	0.76
B5	61.44	0.041	0.01	0.45	0.00123	0.24	7.92	-19.60	47.90	0.48	0.48	0.68	0.79
B6	34.71	0.053	0.01	0.09	0.00110	0.29	7.33	-21.67	42.12	0.42	0.53	0.69	0.76
B7	48.11	0.011	BDL	0.29	0.00052	0.19	7.41	-21.31	40.32	0.40	0.53	0.68	0.76
B8	42.57	0.012	0.01	0.35	0.00054	0.29	7.60	-21.32	42.63	0.43	0.51	0.68	0.80
B9	42.67	0.011	0.04	0.14	0.00054	0.24	7.41	-20.55	38.26	0.38	0.54	0.67	0.81
B10	37.81	0.004	0.04	0.34	0.00185	0.28	7.85	-17.86	43.30	0.43	0.51	0.70	0.80
B11	41.34	0.013	0.03	0.28	0.00052	0.22	7.54	-18.32	42.69	0.43	0.51	0.70	0.77
B12	67.12	0.022	0.03	0.31	0.00077	0.29	7.50	-17.62	44.65	0.45	0.51	0.69	0.79
B13	41.66	0.044	0.04	0.42	0.00073	0.26	8.14	-13.59	36.11	0.36	0.50	0.69	0.86
B14	55.38	0.022	0.04	0.32	0.00114	0.23	7.86	-13.19	33.72	0.34	0.51	0.68	0.89
B15	75.41	0.014	BDL	0.35	0.00148	0.18	7.72	-12.21	32.72	0.33	0.50	0.67	0.92
B16	105.34	0.012	0.01	0.31	0.00057	0.27	7.47	-11.90	35.65	0.36	0.48	0.67	0.90
B17	134.22	0.021	0.01	0.41	0.00052	0.26	7.89	-10.52	31.00	0.31	0.48	0.67	0.92
B18	47.36	0.012	0.01	0.42	0.00065	0.26	8.09	-12.26	33.67	0.34	0.49	0.68	0.93
B19	168.43	0.021	BDL	0.39	0.00159	0.24	8.02	-12.61	32.23	0.32	0.50	0.67	0.94
B20	110.28	0.011	0.01	0.05	0.00126	0.31	8.15	-12.70	33.77	0.34	0.48	0.66	0.98
B21	49.25	0.012	BDL	0.27	0.00083	0.26	8.07	-12.22	33.39	0.33	0.48	0.66	0.96
B22	65.48	0.042	BDL	0.19	0.00139	0.20	7.75	-11.63	36.05	0.36	0.47	0.66	0.94
B23	69.57	0.024	BDL	0.15	0.00095	0.25	8.00	-11.52	37.80	0.38	0.47	0.67	0.96
B24	109.54	0.016	BDL	0.24	0.00068	0.34	7.10	-11.50	40.75	0.41	0.40	0.59	0.99
B25	58.67	0.012	BDL	0.25	0.00056	0.33	7.22	-11.60	38.82	0.39	0.42	0.59	1.02
B26	22.36	0.011	BDL	BDL	0.00064	0.21	5.92	-5.12	42.74	0.43	0.50	0.66	1.00
B27	27.46	0.022	BDL	BDL	0.00202	0.25	6.12	-5.69	42.00	0.42	0.51	0.67	0.97
B28	19.57	0.037	BDL	BDL	0.00122	0.19	5.98	-6.27	43.93	0.44	0.52	0.67	0.95
B29	18.32	0.014	BDL	BDL	0.00088	0.18	5.89	-6.96	45.89	0.46	0.52	0.67	0.93
B30	18.74	0.014	BDL	BDL	0.00075	0.15	6.09	-7.16	45.68	0.46	0.52	0.67	0.93
B31	18.64	0.017	BDL	BDL	0.00087	0.17	6.10	-7.60	45.33	0.45	0.53	0.67	0.92
B32	18.22	0.048	BDL	BDL	0.00091	0.16	6.35	-7.97	46.88	0.47	0.52	0.67	0.91
WHO ^a	50	3	0.5	0.4-0.5 ^b	1.5	2.4							

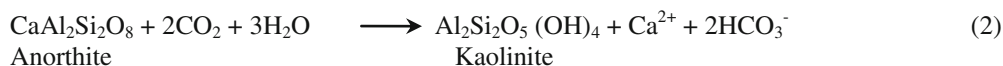
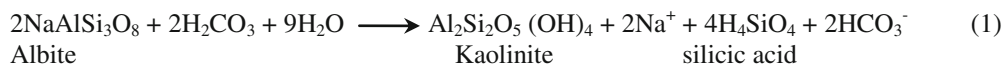
SAR sodium adsorption ratio, RSC residual sodium carbonate, MH magnesium hazard, BDL below detection limit

^a WHO (2011); maximum limit for drinking

^b Carney (1991)

of basalt, andesite, gabbro, diorite, and few rocks of granitic nature. Thus, Na and Ca are predictable to be freed during

weathering processes of these rocks according to the following reactions:



In calcite case, the equilibrium of water–mineral is controlled by the following reaction:



Moreover, the dissolution of silicates and carbonates releases HCO_3^- into the groundwater system of the area of study, where high concentrations of HCO_3^- were found to range between 72.66 and 186.41 mg/l. Thus, the reaction between groundwater and weathered rocks is main practice in Madinah.

Minerals equilibrium

Using the approach of saturation indices, it is probable to expect the reactive mineralogy of the subsurface from groundwater results without assembling the specimens of the solid part and examining the mineralogy (Deutsch 1997). In the current work, to define the chemical balance between minerals and water, SI of certain minerals were estimated. If the groundwater is saturated ($\text{SI} > 0$) with respect to a mineral, it is susceptible to deposit (precipitation) some of the solute load. Also, if it is undersaturated ($\text{SI} < 0$), it will yield more mineral into the solution (dissolution). The groundwater becomes in equilibrium with a specific mineral, wherein the case of the calculated SI of a specific mineral is zero. The SI of a mineral is calculated based on the following equation (Lloyd and Heathcote 1985):

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

where IAP is the ion activity product, and K_{sp} is the solubility product of the mineral.

The SI values of carbonate and sulfate minerals of groundwater of the Madinah area (Table 5) revealed that the groundwater situation is in slightly to moderately undersaturation condition with respect to these minerals ($\text{SI}_{\text{aragonite}} -0.22:-0.84$, $\text{SI}_{\text{calcite}} -0.07:-0.70$, $\text{SI}_{\text{dolomite}} -0.20:-1.66$, $\text{SI}_{\text{gypsum}} -0.62:-1.44$, $\text{SI}_{\text{anhydrite}} -0.88:-1.67$). The groundwater of the Madinah area is strongly undersaturated with halite ($\text{SI}_{\text{halite}} -4.72:-5.60$). The SI of different minerals are illustrated in Fig. 10.

The studied minerals are intense in the soil zone, since high evaporation degrees cause their deposition. Rainfall or irrigation water dissolves these minerals from the soil zone then flushes into the groundwater system. This causes an increase of the saturation indices of minerals in the system of groundwater.

Nutrients

Nutrients, which include nitrate, nitrite, ammonia, phosphate, fluoride, and boron in groundwater, were analyzed to investigate the anthropogenic effects and the pollution extent in the study area (Table 4). Groundwater pollution with nitrate (NO_3) is familiar in several parts of the world. The USEPA

has agreed with 10 mg N/l as the maximum contaminant level (MCL) for NO_3 in water used for drinking (Federal Register 2002), as drinking of water with elevated nitrate is a reason of methemoglobinemia, which is a possibly serious disorder in children (Exner et al. 2010).

Nitrate originates from many sources such as agricultural activities especially fertilizers, animal wastes, plant remains, industrial, and sewage disposal. The World Health Organization's guiding limit for nitrate in drinking water is 50 mg/l (SASO 1984; WHO 2011). The concentrations of nitrate range between 18.22 mg/l at well B32, which is located at the eastern part (Aqool) area, and 168.43 mg/l at well B19, which is located in the center of the city (Table 4). Forty-four percent of the groundwater samples have NO_3 concentration more than 50 mg/l, which suggest the influence of agricultural activities and sewage disposal. The distribution of nitrate in the Madinah groundwater is presented in Fig. 11. This figure shows that the nitrate has different trends of increase. It is noticed that there are two zones having the highest value of nitrate, wherein they are located in the center of the city, where it is densely populated area, and in the northern part near Uhud Mountain, where it is densely cultivated area.

Table 4 shows that the concentration of nitrite in groundwater samples of the area of study is lower than guideline value (3 mg/l) for drinking purposes (WHO 2011). The decreased concentrations of ammonia may be owing to adsorption of clay particles and to the action of bacteria on oxidizing ammonia to nitrate and nitrite (APHA 1988). Ammonia in drinking water is not of immediate health relevance. The values of ammonia in the Madinah groundwater samples indicate very low concentrations reach 0.04 mg/l, or they were below detection limit (Table 4).

The main phosphate source in water might be from the contamination produced from fertilizer use and anthropogenic practices or from the minerals in parent rock (Zanini et al. 1998; Krapac et al. 2002; Daesslé et al. 2006). The maximum limit allowed for phosphate in drinking water varies from 0.4 to 0.5 mg/l (Carney 1991). The concentration of phosphate in the Madinah groundwater (Table 4) is under the maximum limit allowed for drinking.

The breakdown of the fluorine-rich minerals is a possible source of fluoride. As well, it may have originated due to runoff, infiltration of fertilizers, industrial wastes, and manure treatment system (Smedley et al. 2002; Edmunds and Smedley 2013). The concentration of fluoride is lower than 1.5 mg/l in the groundwater samples of the area of study (WHO 2011; Table 4).

Boron concentrations vary widely and depend on the surrounding geology and wastewater discharges (WHO 2011). The pollution of groundwater with boron is also from dissolution processes of the sediments, under reducing conditions or from agricultural activities (e.g., fertilizers, pesticides). The guideline value of boron is 2.4 mg/l (WHO 2011). The boron

Table 5 The saturation indices of specific minerals in Madinah groundwater

Well location	Aragonite	Calcite	Dolomite	Gypsum	Anhydrite	Halite
B1	-0.24	-0.09	-0.30	-0.64	-0.88	-4.72
B2	-0.25	-0.11	-0.30	-0.65	-0.89	-4.76
B3	-0.22	-0.07	-0.20	-0.65	-0.88	-4.78
B4	-0.26	-0.12	-0.31	-0.67	-0.91	-4.81
B5	-0.39	-0.25	-0.46	-0.77	-1.01	-4.81
B6	-0.29	-0.14	-0.35	-0.70	-0.94	-4.82
B7	-0.31	-0.17	-0.43	-0.69	-0.92	-4.82
B8	-0.34	-0.19	-0.44	-0.70	-0.94	-4.82
B9	-0.25	-0.10	-0.35	-0.69	-0.93	-4.85
B10	-0.43	-0.29	-0.62	-0.62	-1.04	-4.86
B11	-0.47	-0.32	-0.69	-0.79	-1.03	-4.87
B12	-0.46	-0.31	-0.64	-0.83	-1.06	-4.90
B13	-0.60	-0.45	-1.08	-0.86	-1.10	-4.97
B14	-0.61	-0.46	-1.14	-0.86	-1.10	-5.02
B15	-0.71	-0.56	-1.36	-0.89	-1.13	-5.09
B16	-0.77	-0.63	-1.44	-0.91	-1.15	-5.12
B17	-0.84	-0.69	-1.66	-0.94	-1.17	-5.13
B18	-0.71	-0.56	-1.35	-0.89	-1.13	-5.05
B19	-0.68	-0.53	-1.32	-0.86	-1.10	-5.05
B20	-0.68	-0.54	-1.30	-0.86	-1.09	-5.05
B21	-0.71	-0.57	-1.36	-0.88	-1.11	-5.07
B22	-0.76	-0.61	-1.40	-0.91	-1.15	-5.11
B23	-0.83	-0.68	-1.51	-0.96	-1.19	-5.10
B24	-0.80	-0.65	-1.39	-0.88	-1.11	-5.21
B25	-0.76	-0.61	-1.36	-0.87	-1.10	-5.21
B26	-0.84	-0.70	-1.45	-1.44	-1.67	-5.60
B27	-0.81	-0.66	-1.40	-1.38	-1.62	-5.54
B28	-0.77	-0.62	-1.27	-1.36	-1.60	-5.51
B29	-0.71	-0.56	-1.13	-1.33	-1.57	-5.47
B30	-0.67	-0.53	-1.06	-1.32	-1.55	-5.43
B31	-0.63	-0.48	-0.97	-1.28	-1.52	-5.40
B32	-0.61	-0.47	-0.92	-1.26	-1.50	-5.35

concentration in the Madinah groundwater (Table 4) is under the guideline value for drinking purpose.

Trace constituents

The various trace component sources in the groundwater of Madinah might have originated from leaching and dissolution processes and from intensive fertilizer use for agricultural purposes.

The analyses of Fe, Mn, Pb, Ni, Zn, Cu, Cd, Cr, As, Se, Hg, V, Co, and Al constituents of Madinah groundwater are shown in Table 6. According to the standards of WHO (2011) for drinking uses, the concentrations of the analyzed trace components of Madinah groundwater show normal contents for Fe, Mn, Cu, Zn, Se, Hg, V, and Co, whereas the concentrations of Pb, Cd, Cr, Ni, As, and Al show high content in some

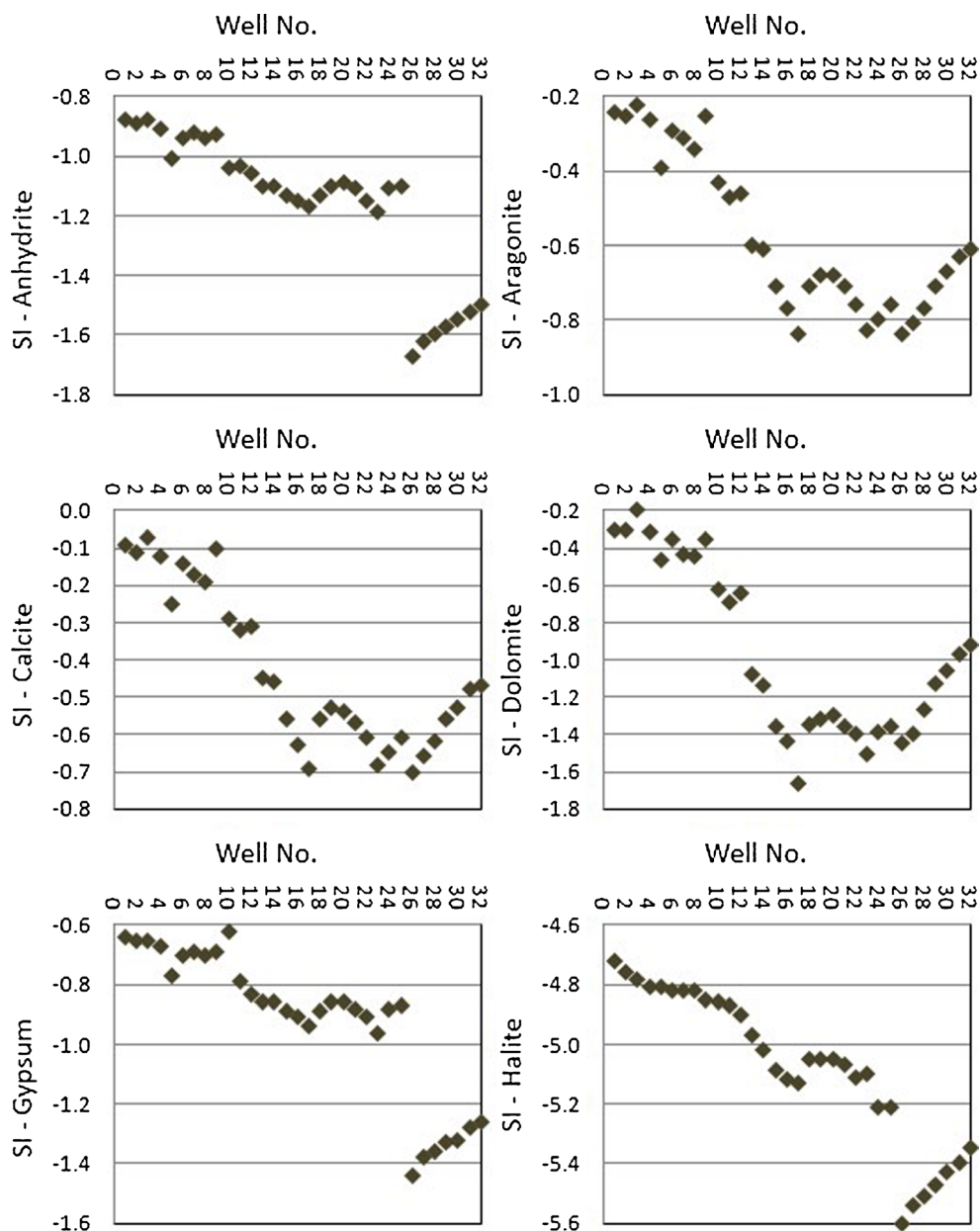
samples (B11, B12, B13, B14), which are located in the southwestern part of the study area. This may be due to the human activities in the industrial area found in the southwestern parts of Madinah. Close to the Madinah area, the wastewater of several manufactures (e.g., paints, dyes, tannery) and car workshops are disposed in badly designed landfills. The wastewater is overloaded with elevated concentrations of trace components, which are the principal sources of pollution of groundwater.

Groundwater quality assessment

Drinking purposes

WHO (2011) sets no standard limits for TDS, sodium, chloride, bicarbonate, sulfate, potassium, calcium, and magnesium

Fig. 10 Diagrams of SI of the minerals anhydrite, aragonite, calcite, dolomite, gypsum, and halite



and their health effects. The taste is the only established. However, the standards of nitrate and nitrite were based on health concerns. The normal concentrations of trace components existent in drinkable groundwater have no impact on human health.

Tastiness of water with a lower TDS values (<600 mg/l) is usually good. Levels higher than about 1000 mg/l for TDS (WHO 2011) make the water unpalatable. The existence of high TDS levels might also be unpleasant to users due to extreme scaling in heaters, water pipes, household appliances, and boilers.

Nevertheless, the groundwater of the area of study has high TDS concentrations exceeding 1000 mg/l. Forty-four percent

of the groundwater samples have NO_3 values more than 50 mg/l, and Pb, Cd, Cr, Ni, As, and Al show high content in some samples, which are considered unsafe for drinking purposes. Consequently, Madinah groundwater is unsafe for purpose of drinking.

Irrigation purposes

The evaluation of groundwater for agricultural purposes is governed by irrigation parameters, e.g., TDS, magnesium hazard (MH), sodium adsorption ratio (SAR), and residual sodium carbonate (RSC).

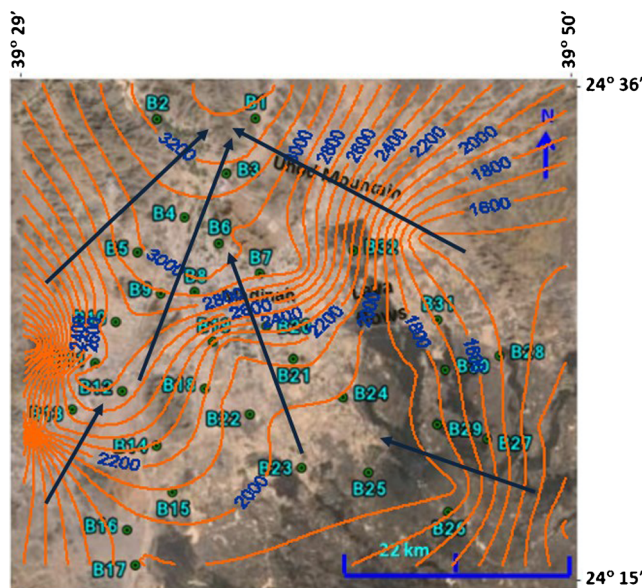


Fig. 11 Distribution of NO₃ in the Madinah area

SAR is a useful tool to measure the danger of sodium on agriculture (Fetter 1994). SAR is calculated using the following equation:

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

where the used ions are in milliequivalent per liter.

The parameter SAR is of great importance due to the elevated content of Na in agricultural water may elevate the hardness of soil hardness and may decrease the permeability of the soil. The values of SAR (Table 4) in the Madinah groundwater varied from 5.89 to 8.15 (i.e., <10), which indicate that the water is excellent for agricultural activities (USSL 1954).

To evaluate the groundwater suitability for the irrigation, Wilcox diagram (1955) was used (Fig. 12) for the groundwater of the area of study.

The usage of salty waters in pervious rocks may raise the groundwater salinity. Figure 12 shows the groundwater points of Madinah on the diagram of Wilcox. It is clear that the samples of groundwater are assembled in three areas, namely C3S2, C4S2, and C4S3 that show medium to high sodium and high to very high salinity.

In the area of study, the groundwater could be safely used for irrigation purposes on practically all types of soils; nevertheless, it might be sensible to retain control on the salinity by appropriate managing and via choosing plants that possess good tolerance for the salts.

The suitability of groundwater for irrigation purposes is affected by higher concentrations of carbonate, bicarbonate, calcium, and magnesium in groundwater. Hence, RSC is

generally used to specify the groundwater suitability for irrigation, and it is estimated by using the following equation (Eaton 1950; McLean et al. 2000):

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

in which, all ions are in milliequivalent per liter. The estimated values of RSC (Table 4) for Madinah groundwater samples vary between -5.12 and -25.25. The results of RSC show that all the groundwater samples are below 1.25, so it is of a good category for irrigation (USSL 1954).

The values of MH for irrigation water are obtained using an equation proposed by Szabolcs and Darab (1964), and it is as follows:

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

in which, all ions are in milliequivalent per liter.

If the values of MH >50, then the water is unsafe for irrigation purpose. The estimated MH values (Table 4) for water samples from the Aqool area vary from 31.00 to 47.90, which indicate that they are suitable for irrigation activities.

Referring to the calculations of TDS (Table 2), SAR, RSC, and MH (Table 4) for the samples of Madinah groundwater, it is realized that they are moderately appropriate for activities of irrigation work.

Conclusions

Expanding urbanization and intensified land use for agriculture and industrial activities threatened the limited water resources of Saudi Arabia. Besides rare precipitation and over-exploitation of groundwater, the level of groundwater was declined, and groundwater was deteriorated. Thus, the quality and quantity of groundwater are of ultimate importance.

Therefore, a hydrogeochemical investigation was conducted to identify the pollution sources at the groundwater system of Madinah. The present work also includes groundwater characteristics and a groundwater quality assessment. This groundwater quality assessment will serve as an important part in optimizing the available water resources and sustaining a desired water quality to satisfy the competing needs of socioeconomic development and maintaining healthy ecosystems. In order to investigate the pollution sources of Madinah, groundwater samples have been collected from 32 locations and were analyzed for major, minor, and nutrient constituents.

Elevated values of salinity were detected in northern part of Madinah. The high values of salinity are found in highly agricultural and residential areas. The varied concentration

Table 6 The chemical analysis concentrations (mg/l) of minor constituents in the area of study

Well no.	Fe	Mn	Pb	Ni	Zn	Cu	Cd	Cr	As	Se	Hg	V	Co	Al
B1	0.05050	0.01540	0.01710	0.0010	0.02720	0.00610	0.00152	0.02870	0.00308	0.00239	0.00034	0.00464	0.00071	0.00750
B2	0.05010	0.01340	0.01580	0.0010	0.01740	0.00850	0.00430	0.05820	0.01196	0.00592	0.00026	0.01698	0.00053	0.00849
B3	0.05540	0.11240	0.00220	0.0120	0.01570	0.00430	0.00540	0.05400	0.00041	0.00983	0.00071	0.01184	0.00044	0.00083
B4	0.04670	0.01140	0.00910	0.0010	0.02640	0.00580	0.00910	0.03010	0.00343	0.01271	0.00052	0.00863	0.00004	0.00076
B5	0.04870	0.01640	0.00380	0.0010	0.03440	0.00520	0.00860	0.01690	0.00122	0.00792	0.00037	0.01406	0.00008	0.00685
B6	0.07540	0.01740	0.00330	0.0010	0.02840	0.00470	0.00160	0.01760	0.00070	0.00545	0.00032	0.00817	0.00007	0.00447
B7	0.06440	0.01340	0.00460	0.0010	0.02870	0.00360	0.00201	0.04510	0.00167	0.00790	0.00028	0.01410	0.00046	0.00416
B8	0.07640	0.03540	0.00320	0.0010	0.02820	0.00750	0.00245	0.03440	0.00026	0.01466	0.00027	0.03168	0.00139	0.00057
B9	0.06600	0.01651	0.00850	0.0010	0.02140	0.00220	0.00320	0.01184	0.00177	0.01179	0.00021	0.02066	0.00047	0.00036
B10	0.08430	0.03000	0.00550	0.0010	0.01170	0.00670	0.00430	0.03830	0.00158	0.00810	0.00017	0.04412	0.00041	0.00022
B11	0.61200	0.14120	0.02700	0.1400	0.29800	0.04600	0.06900	0.09640	0.01609	0.00900	0.00017	0.03239	0.00048	0.10400
B12	0.45400	0.22400	0.01260	0.1000	0.29200	0.05200	0.07600	0.07560	0.01807	0.01366	0.00071	0.01286	0.00053	0.10320
B13	0.67200	0.21720	0.01500	0.1800	0.29300	0.06800	0.02170	0.08110	0.03587	0.01190	0.00022	0.01286	0.00061	0.10900
B14	0.66700	0.17600	0.03700	0.1500	0.22900	0.07600	0.08300	0.11400	0.04512	0.00749	0.00026	0.04244	0.00046	0.10380
B15	0.18410	0.01540	0.02700	0.0180	0.09420	0.00420	0.00773	0.03110	0.00040	0.00976	0.00034	0.01835	0.00061	0.00021
B16	0.26670	0.01534	0.00351	0.0010	0.03470	0.00230	0.00368	0.07390	0.00287	0.00719	0.00053	0.03251	0.00032	0.00020
B17	0.12672	0.01367	0.00260	0.0170	0.08240	0.00240	0.00870	0.03530	0.00265	0.01091	0.00049	0.01441	0.00041	0.00064
B18	0.15410	0.01240	0.00550	0.0010	0.02280	0.00270	0.00245	0.08600	0.00049	0.01704	0.00057	0.02701	0.00064	0.00741
B19	0.25100	0.01340	0.01640	0.0010	0.06190	0.00280	0.00240	0.02930	0.00115	0.00881	0.00015	0.00200	0.00048	0.00817
B20	0.25450	0.01450	0.00220	0.0010	0.02230	0.00230	0.00300	0.01480	0.00021	0.01166	0.00071	0.01700	0.00062	0.00083
B21	0.27280	0.02670	0.00154	0.0010	0.02270	0.00650	0.00140	0.04410	0.00043	0.00790	0.00022	0.03309	0.00063	0.00074
B22	0.26720	0.01244	0.00147	0.0160	0.03140	0.00380	0.00500	0.05410	0.02000	0.00831	0.00019	0.01441	0.00068	0.00647
B23	0.26520	0.01512	0.00400	0.0010	0.02210	0.00690	0.00124	0.03430	0.00080	0.01066	0.00015	0.02701	0.00069	0.00487
B24	0.25630	0.01330	0.00300	0.0010	0.02280	0.00310	0.00300	0.04450	0.00013	0.00405	0.00012	0.00200	0.00051	0.00414
B25	0.22672	0.01942	0.00195	0.0150	0.03160	0.00870	0.00154	0.02640	0.00119	0.00239	0.00067	0.01700	0.00049	0.00057
B26	0.12662	0.01671	0.00270	0.0010	0.02230	0.00590	0.00213	0.01184	0.01500	0.00592	0.00024	0.00200	0.00021	0.00051
B27	0.29030	0.04840	0.00210	0.0010	0.02270	0.00460	0.00400	0.01940	0.00300	0.00595	0.00058	0.00200	0.00032	0.00871
B28	0.20470	0.01270	0.00800	0.0010	0.02260	0.00550	0.00930	0.01760	0.01300	0.00591	0.00028	0.00200	0.00012	0.00061
B29	0.20267	0.01954	0.00158	0.0100	0.03410	0.00420	0.00285	0.01372	0.00043	0.00594	0.00026	0.01441	0.00046	0.00068
B30	0.20266	0.01754	0.00164	0.0010	0.02870	0.00450	0.00620	0.01408	0.01220	0.00085	0.00017	0.01835	0.00063	0.00061
B31	0.20266	0.01364	0.00260	0.0010	0.02600	0.00470	0.00300	0.01592	0.00080	0.00081	0.00012	0.01441	0.00064	0.00014
B32	0.20289	0.01140	0.00163	0.0010	0.01170	0.00460	0.00600	0.01408	0.00013	0.00012	0.00011	0.01835	0.00042	0.00037
WHO ^a	NGL	NGL	0.01	0.07	NGL	2	0.003	0.05	0.01	0.7	0.006	NGL	0.11 ^b	0.1

NGL no guideline (not of health concern at levels found in drinking water)

^aWHO (2011); maximum limit for drinking

^bNagpal (2004)

ranges show the participation of numerous hydrochemical reactions inducing the chemistry of water.

Hydrochemical Piper, Durov, and Schoeller diagrams are constructed to show the relative concentrations of the major ions, which can summarize the main contrasts in hydrochemical composition among different water sources. In the present study, the groundwater is affected by evaporation, ion exchange, anthropogenic pollution, and water–rock interaction. The groundwater samples of the area of study show prevalence of Na, Ca, Cl, and SO₄ over Mg, K, and HCO₃.

CA and PCA were applied on the results of chemical analysis of groundwater samples to evaluate the spatial variability among the studied wells and to obtain relationship between parameters and sampling site in order to identify the factors and sources influencing groundwater quality. The CA allowed the formation of three clusters between the sampling wells reflecting differences on water quality at different locations. Four major PCs were extracted, which accounted 86.05 % variance of the original data structure.

The geochemical evolution of Madinah is from the composition of rainwater (Ca–HCO₃) to the composition of the

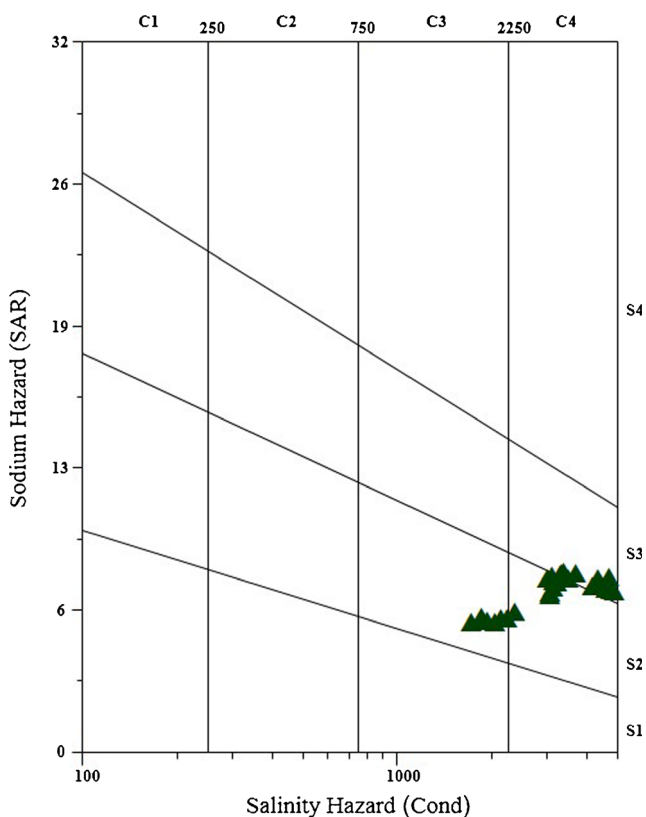


Fig. 12 Wilcox plot of TDS and SAR for groundwater samples in the area of study

groundwater (Na–Cl). The geochemical composition of the Madinah groundwater of the area of study is affected by the silicate mineral dissolutions and their reaction with the groundwater, which tend to change the quality of groundwater.

Chloride ion is the prevailing anion in the Madinah groundwater samples. The groundwater samples are characterized by Na–Cl facies, which point to final phase of the groundwater evolution.

Evidently, the groundwater is affected by evaporation, ion exchange, anthropogenic pollution, and interaction of water–rock. The groundwater samples of the area of study show prevalence of Na, Ca, Cl, and SO_4 over Mg, K, and HCO_3 . Ionic ratio of $\text{Cl}^-/\text{sum anions}$ indicates rock weathering of $\text{Mg}/(\text{Ca} + \text{Mg})$ indicates limestone–dolomite weathering, and $\text{Ca}/(\text{Ca} + \text{SO}_4)$ indicates gypsum dissolution. The calculated SI for minerals carbonate, sulfate, and halite in the Madinah groundwater show undersaturation phase.

Forty-four percent of the groundwater samples has NO_3 concentration more than 50 mg/l, which suggests the influence of agricultural activities and sewage disposal. The highest value of nitrate is located in the center of the city, where it is densely populated area and in the northern part near Uhud Mountain, where it is densely cultivated area. The concentration of nitrite, ammonia, phosphate, fluoride, and boron are below the guideline value for drinking purposes.

The concentrations of Pb, Cd, Cr, Ni, As, and Al show high content in some samples (B11, B12, B13, B14), which are located in the southwestern part of the study area. This may be due to the human activities in the industrial area found in the southwestern parts of Madinah. Close to this area, wastewater from several industries and car workshops is disposed in badly designed landfills. The wastewater is overloaded with elevated concentrations of trace components, which is the principal source of pollution of groundwater.

The groundwater of the area of study has high TDS concentrations exceeding 1000 mg/l; 44 % of the groundwater samples have NO_3 values more than 50 mg/l; and Pb, Cd, Cr, Ni, As, and Al show high content in some samples, which are considered unsafe for drinking purposes. Consequently, groundwater of the study area is not safe for drinking purposes. Referring to the results of TDS, SAR, RSC, and MH for the samples of Madinah groundwater, it is realized that they are moderately appropriate for activities of irrigation.

Managing of water resources needs to be urgently implemented to avoid public health impacts. Disposal of industrial wastewater in such insecure landfill must be prohibited to avoid further groundwater contamination.

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