

Hydrochemistry assessment of groundwater quality in Al-Ain city, UAE

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Abstract Groundwater is the main source for irrigation purposes in Al-Ain city. Urbanization and agricultural activities are considered potential sources of groundwater pollution in this area. Therefore, assessment of groundwater quality is very important to detect and prevent contamination for effective groundwater management. This paper focuses on the impact of urbanization on the groundwater resources of the gravel alluvial aquifer in the vicinity of Al-Ain city (northeast of Abu Dhabi Emirate). Groundwater samples were collected from 28 wells in Al-Ain city. The chemical monitoring revealed high spatial variability in chemical parameters as influenced by climate, matrix aquifer changes in geological formations, and water table depth. Results show that changes in groundwater chemistry in the aquifer are mainly controlled by evaporation, silicate mineral dissolution, evaporite dissolution, cation exchange, and mixing by upward leakage from Jabal Hafit limestone aquifer. The concentration increases were accounted for primarily by dissolved sodium, chloride, and sulfate. The high total dissolved solids (TDS) of shallow groundwater beneath the city of Al-Ain (up to 5640 mg/L) are mainly controlled by evaporation. Groundwater quality was better in the northeast and the east areas (near Oman Mountains) compared to the south area (northern edge of Jabal Hafit).

Keywords Arid zone · Shallow alluvial aquifer · Groundwater quality

Introduction

Groundwater usually constitutes the main source of water supply in arid regions. The wild growth of cities and dramatic increase of the urban populations put a huge stress on this natural resource, particularly in arid and semi-arid regions. In these areas, groundwater represents the only viable resource for years (Morris et al. 2003; Foster 2001). The effects of urban development on groundwater have been studied in several locations (Foster et al. 1998; Foppen 2002; Alderwish et al. 2004; Foster 2001; Arunprakash et al. 2014; Marghade et al. 2015; Yu et al. 2015). Foster et al. (1998), for example, have studied the effects of urbanization on the groundwater contamination of the cities of Hat Yai (Thailand) and Santa Cruz (Bolivia). Elevated concentrations of ammonium, chloride, and sulfate occur in the semi-confined aquifer beneath the city of Hat Yai centre as a result of the poor quality of canal seepage. In the city of Santa Cruz, groundwater in the deeper aquifer (below 100 m) is of excellent quality. However, the uppermost aquifer (above 40 m) shows substantial deterioration with elevated nitrate and chloride concentrations beneath the more densely populated districts. Foppen (2002) investigated the impact of wastewater infiltration on groundwater quality and drinking water supply in Sana'a, the capital of the Yemen Arab Republic. Results obtained show that all groundwater samples collected have high concentrations of almost all major ions and leached elements from wastewater. Cation exchange and acidification have taken place due to low flow and nitrification process. Alderwish et al. (2004) investigated

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the impacts of rapid urbanization on groundwater of arid zone alluvial environments in Cairo. Cairo is located in the alluvial valley of the Nile underlain by alluvial sediments consisting of sand and gravel with interbedded silt and clay. The main aquifer beneath Cairo area consists of sand and gravel of Late Pleistocene age. Results show that ammonium, nitrate, iron, and manganese concentrations at a number of sites exceed drinking water standards. Nitrate concentrations (up to 100 mg/L) are attributed to sewers leakage and industrial discharge in urban areas. Hydro-geochemical characteristics of the densely populated city of Chennai, India were assessed by Arunprakash et al. (2014) by understanding the reverse ion exchange process, seasonal variation of chemical parameters, rock–water interaction and suitability of groundwater for irrigation purposes. Groundwater contamination in a fast growing city of Nagpur, India was assessed by principal component analysis. This study suggests that variation in groundwater chemistry is mainly due to reverse ion exchange, silicate weathering and also mainly due to anthropogenic activities. Study on groundwater contamination with volatile organic carbon in metropolitan cities of Korea indicated that leakage from public garages at the sampling points was correlated with groundwater contamination while the detection of both toluene and chloroform in groundwater was correlated with sewage collection and disposal system due to urban and industrial activities (Yu et al. 2015). These studies indicated the variation in groundwater quality due to urbanization. Howard (2014) suggests that the key to manage groundwater quality problems in the world's rapidly growing cities is the full involvement of all stakeholders in the decision-making process. Urban contamination of groundwater is given most important in major cities of the world, whereas groundwater geochemistry is altered by many other natural and anthropogenic activities. Few studies which mainly affect the groundwater geochemistry may include seawater intrusion in fresh water aquifer system (Khairy and Janardhana 2013; Venkatraman et al. 2014), rock–water interaction (Gultekin et al. 2010; Thakur et al. 2015), surface and groundwater interaction (Parimalarenganayaki and Elango 2014), arsenic contamination (Pazand and Javanshir 2013), fluoride contamination (Brindha et al. 2011; Machender et al. 2014), mines water geochemistry (Murkute 2014; Adamu et al. 2014; Ma et al. 2015), geochemical changes due to agricultural activities (Mohamed et al. 2007; Taylor and Gazis 2014; Krishnakumar et al. 2014).

Groundwater resources in UAE can be divided into renewable (shallow aquifers) and non-renewable resources (deep aquifers) (Elmahdy and Mohamed 2012, 2013a, b). The renewable water resources occur mostly in shallow alluvial aquifers formed by percolating rainfall (Sherif et al. 2011a, b). On the other hand, the non-renewable deep

groundwater aquifers were formed during two ancient wet periods (6000–9000 and 25,000–30,000 years ago) (Wood and Imes 1995; Elmahdy and Mohamed 2015). The recharge of shallow aquifers depends mainly on rainfall events and surface runoff, and thus may vary considerably from year to year. Due to the high evaporation rate and surface water runoff in mountains areas, only 10 to 14 % of the total precipitation percolates to recharge the shallow groundwater aquifers in UAE (Elmahdy and Mohamed 2014a, b). Yet, many groundwater aquifers in GCC(Gulf Cooperation council) countries are being mined in an uncontrolled and unplanned manner (Mohamed et al. 2010a, b).

Management of groundwater potential is being very important in semi-arid and arid regions due to very less rainfall and high evaporation rate (Mohamed and Almualla 2010a, b). The most important water resource problems in the United Arab Emirates are the depletion of aquifers in several areas, such as at Al-Ain and Al Dhaid; saline water intrusion, and water quality degradation, such as that associated with the oil industry and agricultural activities (Rizk and Alsharhan 2003). Many studies have been already done on the groundwater quality in parts of the Abu Dhabi Emirate. Groundwater is mostly brackish and non-renewable (Al Katheeri 2008; Al Katheeri et al. 2009). Previous studies have been based on chemical and isotopic tools to provide general geological, hydrogeological, and water quality characterization of the aquifer. These studies have focused on the Jabal Hafit Limestones aquifer (Murad et al. 2012) where groundwater exhibits specific chemical composition with high SO_4^{2-} , and other elements concentrations (Cl^- , Na^+ , Ca^{2+} , Mg^{2+}) which could reflect the influence of carbonates and evaporite sediments, and the Al Jaww plain (Ahmad 2010). Howari (2004) studied the impact of urbanization on soil in the vicinity of Al-Ain landfill through sixty-four surface soil samples by analyzing heavy metals (cadmium, chromium, copper, nickel, lead and zinc). Results show that soils are contaminated by copper due to urbanization.

Hydrochemical assessment has been used to evaluate the groundwater quality in the shallow unconfined alluvial aquifer beneath the city of Al-Ain (north-eastern part of Abu Dhabi Emirate). The aims of this work are: (1) to understand the groundwater chemistry of the unconfined alluvial aquifer and (2) to evaluate the groundwater quality. The methodology exposed in this article is useful for differentiating between processes affecting groundwater. This is of high importance in aquifer conservation because conservation efforts are mainly addressed to the processes.

Study area

Al-Ain area is located in the east of the Emirate of Abu Dhabi, near the Oman border at approximately 24°03'N–

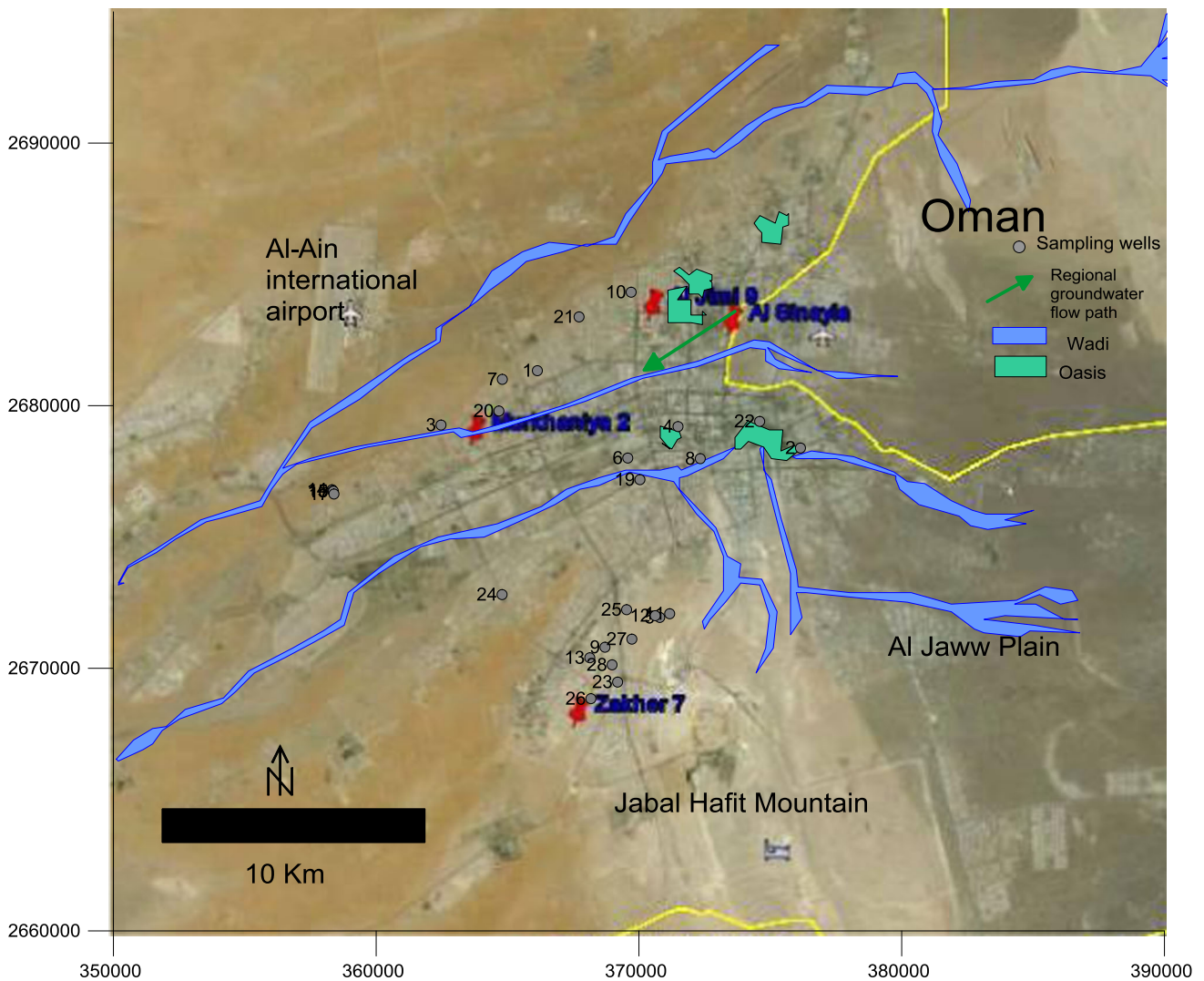
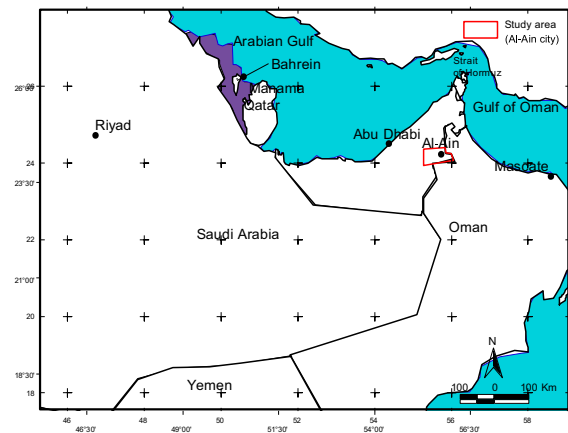


Fig. 1 The study area with groundwater sample locations

24°22'N and 55° 28'E (Fig. 1). The study area is characterized by an arid climate with an average annual temperature of 27 °C, a potential evaporation of 3975 mm/year, and an annual rainfall of 132 mm (1971–1997). The

city is one of the largest oases of the Arabian Peninsula (El-Ghawaby and El-Sayed 1997). There are no perennial surface water resources within the Emirate of Abu Dhabi, apart from the spring at Ayn Al Fayda. In the study area the

surface drainage has an intermittent flow regime because of prolonged droughts periods. Two main wadis including wadi Tuwayya to the north and wadi Al-Ain to the south are shown in Fig. 1.

Al-Ain basin is surrounded by three main geomorphological provinces: (a) Al Jaww plain and the Omani Mountains to the east, (b) the hilly area where bedrocks crop out to the south-east, and (c) the dune covered scarps to the north and south (El-Ghawaby and El-Sayed 1997). The topographic surface contour map of Al-Ain area depicts a generally low relief surface containing a westerly directed trough axis (El-Ghawaby and El-Sayed 1997). The geological formations of Quaternary-Holocene deposits detected in the inter-dune trough zone for a thickness of 10–30 m in Al-Ain area consist of near-surface and surficial sediments of alluvial, aeolian and local sabkha origin (Sabkah is a flat area between a desert and an ocean, characterized by a crusty surface consisting of evaporite deposits (including salt, gypsum, and calcium carbonate), windblown sediments, and tidal deposits) (El-Ghawaby and El-Sayed 1997). The Quaternary–Holocene alluvial deposits overlie the Tertiary section in Al-Ain depression composed of alluvial gravel deposits indicating old courses of buried paleo channels. These alluvial deposits range, size-wise, from cobbles, boulders and pebbles at the eastern part, where valleys debouch from Al Jaww plain, to pebbles and coarse sand where the main valleys become masked by the sand dunes to the west of Al-Ain town. The bulk of the alluvium has been deposited after transport within the wadi network draining westward and northward from the ophiolitic and carbonate source rocks of the Oman Mountains and Jabal Hafit, respectively.

The most important geological characteristics of the Al-Ain include the Jabal Hafit Mountain composed of limestone (Murad et al. 2012; Rizk and Alsharhan 2003). The Jabal Hafit rocks are well-bedded massive limestone which has been locally dolomitized (Zaineldeen 2011). It is composed of a 1500 m thick sequence of interbedded limestone and marl with gypsum and dolomite (Zaineldeen 2011), and evaporite formations of Lower Eocene to Miocene age. The temperature and conductivity logs indicate the possibility of a confined-flow carbonate system. High temperatures (between 36.5 and 51.4 °C) occur in this aquifer at the depths ranging between 93 and 102 m (Khalifa 1997). Groundwater in Jabal Hafit region is slightly alkaline, sodium chloride rich, high total dissolved solids (TDS) content between 3900 and 6900 mg/L (Khalifa 1997), thermal and brackish, hence it is not suitable for human consumption. The environmental isotopes (^{18}O , ^2H , and ^3H) in Jabal Hafit thermal water and its surrounding region indicate that recent recharge (about past 1950) occurs at high elevation (Khalifa 1997; Murad and Krishnamurthy 2004).

Two aquifers can be distinguished in this study region. These are the eastern gravel aquifer and the western gravel aquifer. Al-Ain is located on the western gravel aquifer. The eastern gravel aquifer is composed of a series of alluvial formations between promontories of rock spurs extending into the Gulf of Oman. Quaternary alluvium of the western gravel aquifer is composed of an approximately 60 m sequence of sand and gravel with thin interbeds of silt and clay. The regional groundwater flow of gravel aquifer in the Al-Ain area comes from rain, which falls on the western flank of the Northern Oman Mountains and runs through wadis where it infiltrates and recharges the aquifer (Murad and Krishnamurthy 2004; Imes et al. 1993, Bright et al. 1996). Groundwater movement is generally from east to west in the study region. The hydraulic head map for the sand and gravel aquifers shows that the eastern mountains are the main recharge areas for groundwater in the United Arab Emirates, whereas the Arabian Gulf and the Gulf of Oman are the main discharge areas (Woodward and Menges 1991; Al Sharhan 2003). Groundwater samples of western gravel aquifer generally indicate enrichment during infiltration due to the residence of water in surface depressions of clay leading to high evaporation of water before recharge (Murad et al. 2012; Mustafa et al. 2015). The aquifer contains fresh groundwater that drains from the wadi towards the sea. The low chloride concentrations suggest younger water. A detailed geologic and hydrologic map of this study region is represented by various researchers (Tang et al. 2001; Al Sharhan 2003; Murad and Krishnamurthy 2004; Murad et al. 2012).

Water table depth

The water table depth ranges from 3 m (Well number 27, Shiab Al Ashkar, near the northern edge of Jabal Hafit) to 15.25 m below ground surface (Well number 2, Al Niyyadat, central city, near Al-Ain oasis east of the study area and the border of Oman near Al Jaww plain). The water table depth displayed a spatial variability at the study site. The water table depth decreases from the NE (near Oman border and Oman Mountains) to the SW, similar to the general direction of the groundwater flow (east to west), and to the south (northern edge of Jabal Hafit Mountain) (Fig. 2a). It increases to the west (west of the city of Al-Ain) towards the sand dunes.

Sampling and analysis

Understanding the groundwater chemistry is based on sampling and analysis of water from 28 wells localized in the shallow unconfined aquifer. The locations of the sampled wells are shown in Fig. 1. The analytical work of this

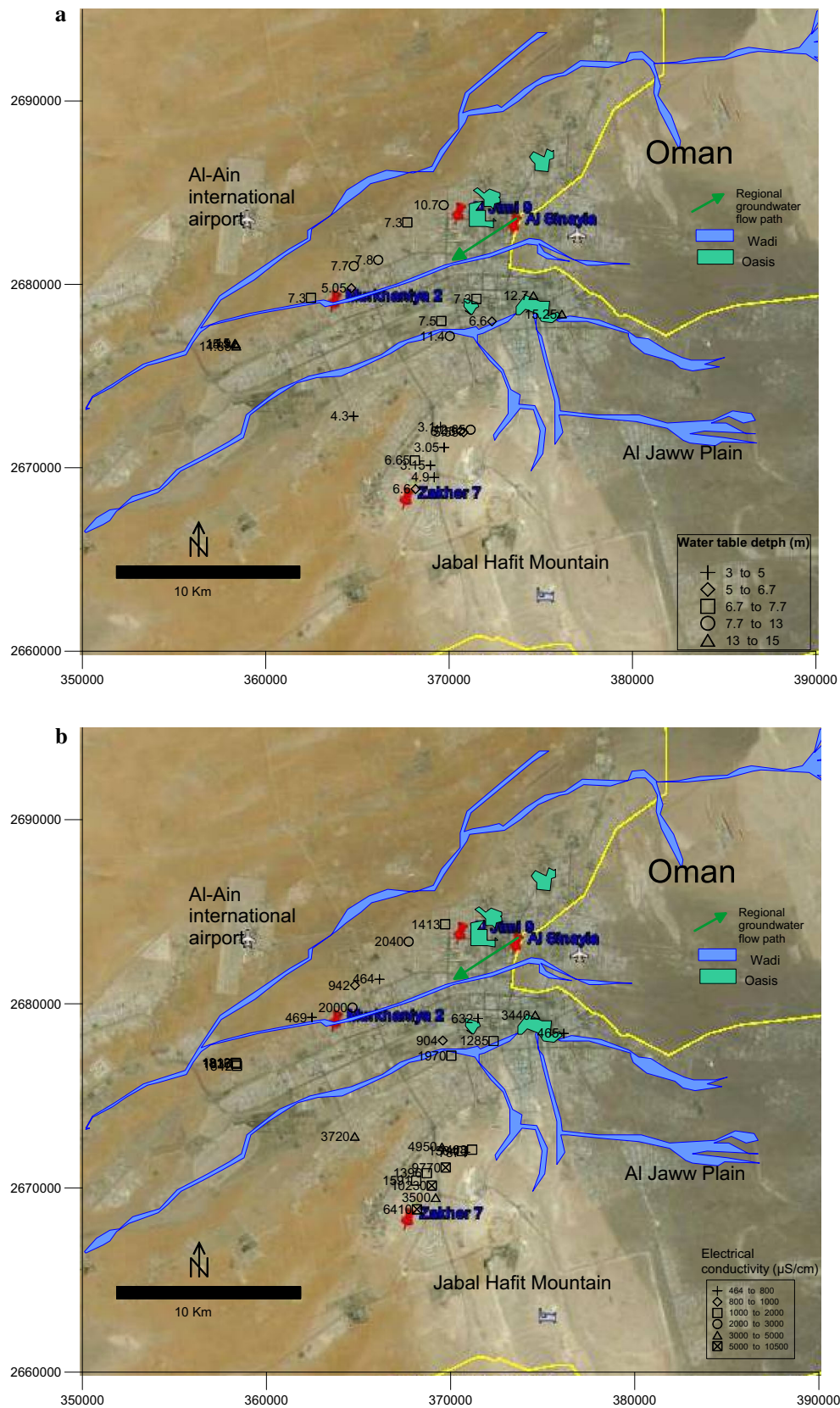


Fig. 2 Spatial variation of **a** water table depth (m), **b** electrical conductivity (µS/cm), **c** total dissolved solids (mg/L)

Fig. 2 continued

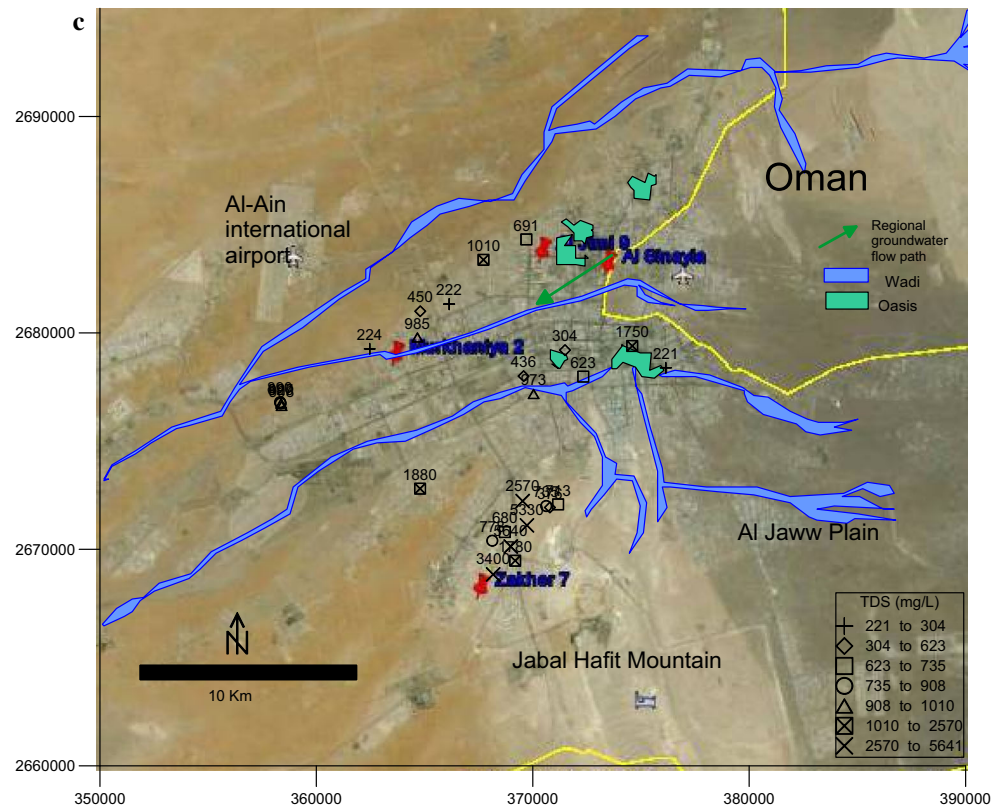


Table 1 Statistics of hydro-chemical analysis of all samples (EC in $\mu\text{S}/\text{cm}$, TDS in mg/L , pH in pH unit, and all others in meq/L)

	Min	Max	Median	Mean	Standard deviation
EC	464.00	10230.00	1701.50	2492.82	2525.70
TDS	221.00	5640.00	834.00	1283.57	1391.58
pH	7.4	8.4	7.8	7.8	0.3
Ca^{2+}	0.90	20.71	2.69	4.18	4.69
Mg^{2+}	0.54	25.54	2.33	5.03	6.02
Na^+	0.40	86.40	10.02	16.90	20.70
K^+	0.001	1.271	0.299	0.406	0.344
HCO_3^-	0.54	2.43	1.28	1.27	0.41
Cl^-	0.17	65.08	9.28	13.82	15.37
SO_4^{2-}	1.02	71.14	5.37	11.08	15.15
NO_3^-	0.000	0.177	0.081	0.090	0.044

study was performed at the United Arab Emirates University in Al-Ain. Immediately after the groundwater sampling, the pH was measured using Orion 420 field. The electrical conductivity (EC) was measured with a conductivity meter Orion 150 in the laboratory. Cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) analyses were performed using a flame photometer 416. Samples were analyzed with ICS-200 Dionex ion chromatography and spectrophotometer Cary 50 UV visible Varian for anions (Cl^- , NO_3^- , F^-). The measurement of bicarbonate was done by titration at the laboratory. Charge balance errors for the groundwater

range from -9 to 6 % (standard deviation = 3). Only three samples have errors more than ± 5 %.

Results and discussion: sources of mineralization and geochemical processes

For a proper management of the groundwater quality, it is important to know the geochemical processes controlling the natural mineralization, and those which contribute to the degradation of the chemical quality. Water-rock interaction (mineral dissolution, cation exchange) and

atmospheric inputs (rain and dust) are natural sources of groundwater mineralization. The baseline quality may be modified by mixing the groundwater from different origins, by evaporation process which concentrated the components, by the microorganisms that consume some elements. Contents of elements give information on the residence time and thus the paths and the speeds of movement within the aquifers, and the climatic conditions which favor their concentrations by evaporation. The main chemical processes that control the groundwater mineralization are ion exchange reactions, dissolution of minerals, concentration by evaporation and leaching of ions from pollutants. The alluvium from this shallow aquifer is mainly formed from the Ophiolite (ultramafic rocks) of the Oman Mountains and is underlain by the Jabal Hafit limestone aquifer. The cementation of these gravels is mainly by calcium carbonate, calcium magnesium carbonate or gypsum. Sabkha deposits are also noticed in the area. Jabal Hafit is located south of Al-Ain and composed by interbedded limestone (CaCO_3 , with MgCO_3) and marl (CaCO_3 with clays) with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). These geological formations can influence the groundwater geochemistry. The geology of Jabal Hafit has significant impact on the hydrogeology of the area. The water bearing formations of the study area are mainly composed of alluvial deposits underlain by clay, gypsum, limestone and marl lithofacies (Murad et al. 2012). The shallow unconfined aquifer has a low flow due to the presence of silts and clays. This characteristic allows all chemical reactions to have necessary time to take place and contribute to increase the groundwater salinity in addition to the impacts of urbanization, upward leakage from Jabal Hafit limestone aquifer, and evaporation process.

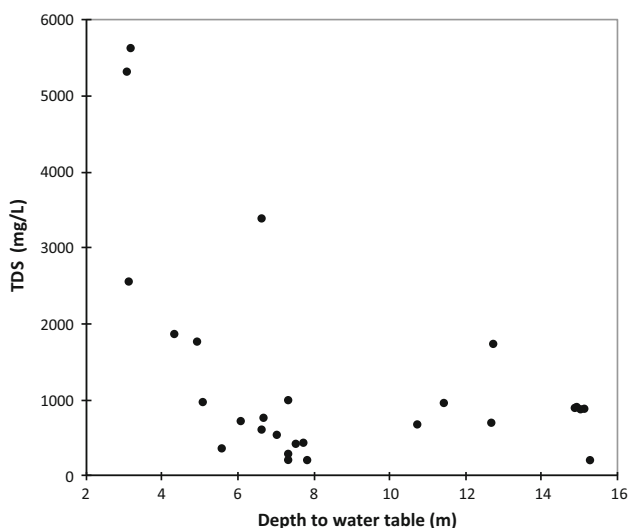


Fig. 3 Relationship between total dissolved solids (TDS) and depth to the water table

Physicochemical parameters

Statistical data for the groundwater samples are presented in Table 1. The groundwater is slightly basic ($7.4 < \text{pH} < 8.4$) with a composition dominated by Na^+ , Cl^- , and SO_4^{2-} . The concentration of solutes is very variable (electrical conductivity 444–10230 $\mu\text{S}/\text{cm}$, median of 1701.0 $\mu\text{S}/\text{cm}$) (Fig. 2b). The total dissolved solids (TDS) values follow a similar trend to electrical conductivity (221–5640 mg/L, median of 834 mg/L) (Fig. 2c), indicating that the groundwater quality varied greatly from fresh to saline. This large variation in salinity in space may reveal some of the processes affecting the groundwater. The groundwater shows no patterns in changing TDS concentrations along groundwater flow paths (NE–SW) at the smaller scale of the study area (Al-Ain depression) as a

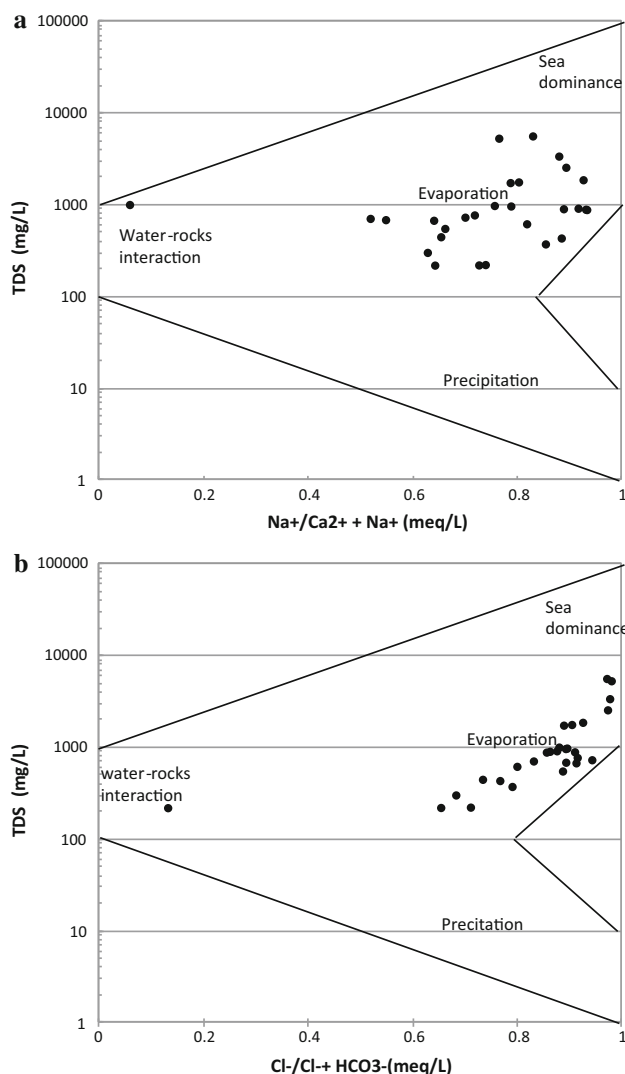


Fig. 4 Gibbs diagram of the groundwater samples collected from the study area **a** $\text{Na}^+/\text{Ca}^{2+} + \text{Na}^+$ (meq/L) **b** $\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-$ (meq/L)

result of geological and environmental changes. Therefore, aquifer mineral dissolution reactions with the aquifer substrate are not a dominant process controlling increases in groundwater salinity. The highest TDS and EC values were obtained at the northern edge of Jabal Hafit mountain, indicating the influence of the Jabal Hafit limestone aquifer below (Murad et al. 2012). The TDS show a high positive correlation with ionic mass ($R^2 = 0.98$). The TDS contents of the groundwater are predominantly Na and Cl. In these shallower wells (−15.25 to −3 m), high and variable electrical conductivity and TDS are recorded (Fig. 3). Therefore, groundwater TDS values may reflect shallow zone processes such as evaporation, vertical mixing and evaporite (gypsum) dissolution near the water table during the recharge process. This high TDS in this shallow unconfined aquifer can be explained by high evaporation (arid zone) and controlled also by recharge processes (infiltrating diffuse rainfall is evaporated and heavy rainfall events transport saline pore water contained in the

unsaturated zone). This high TDS can also be the result of upward leakage from the Jabal Hafit limestone aquifer, leaching from sabkha deposits and gypsum veinlets. The correlations between the concentration of each major element and TDS are used to highlight the different mechanisms that contribute to the salinization of groundwater. In general, the concentrations of Na, Ca, Mg, K, Cl and SO_4 are well correlated to the TDS. The coefficients of determination of these correlations (R^2) are 0.95, 0.84, 0.81, 0.80, 0.98, and 0.90, respectively. This reflects the participation of these ions to the acquisition of the groundwater mineralization. However, the concentrations of HCO_3 did not show a clear correlation with TDS, indicating low participation of these ions to the groundwater mineralization. The participation of SO_4 , Ca, and Mg to the groundwater mineralization can be the result of the dissolution of sulfate (CaSO_4 anhydrite, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)), carbonate (dolomite $\text{CaMg}(\text{CO}_3)_2$, calcite, aragonite, limestone CaCO_3) contained in the aquifer matrix and the

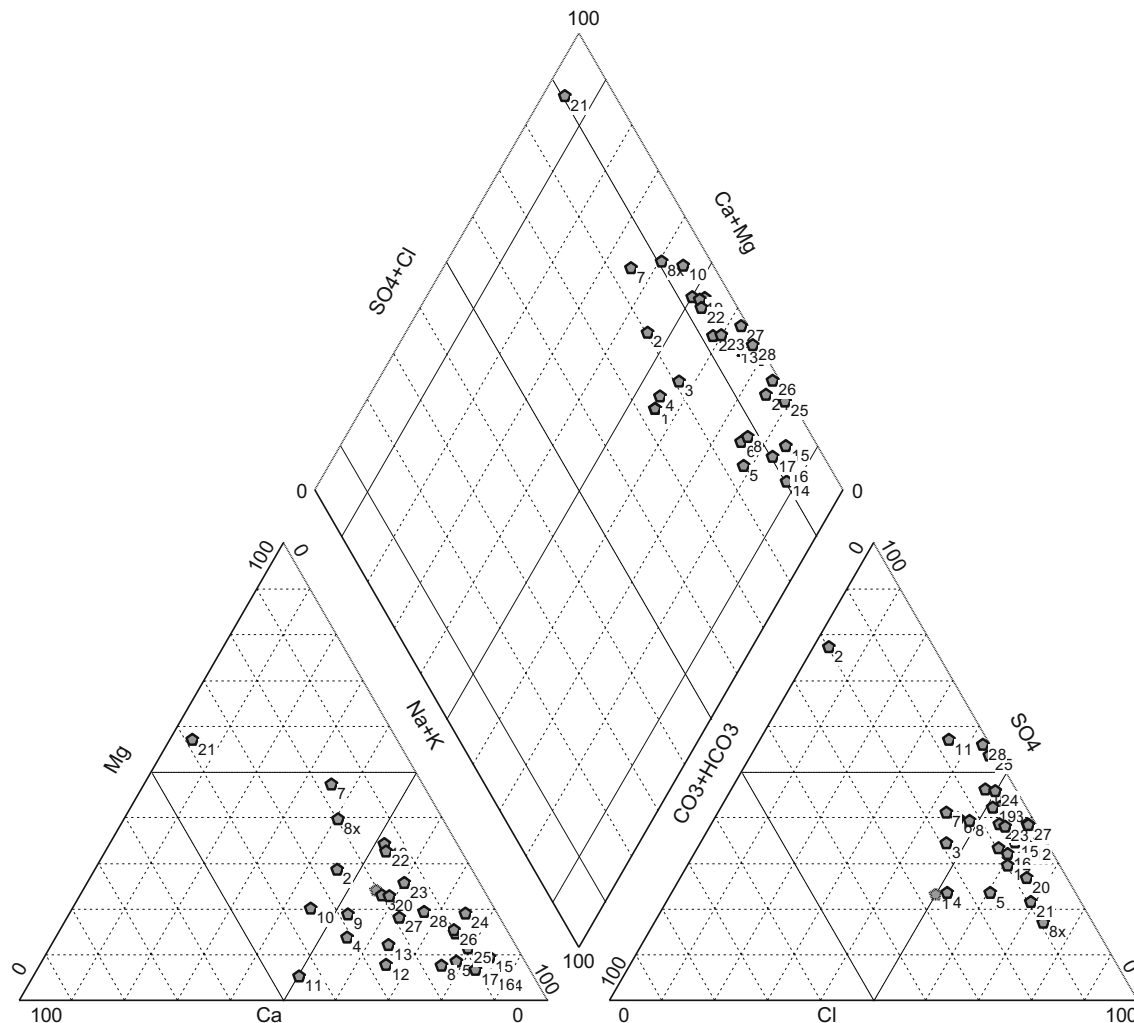


Fig. 5 Piper diagram of the groundwater samples collected from the study area

Jabal Hafit limestone aquifer which could mixed with the shallow gravel aquifer by upward leakage. Similarly, the participation of Ca and SO₄ in salinity indicates a strong dissolution of gypsum, which is confirmed by the strong correlation between these two ions ($R^2 = 0.73$). The mechanism controlling water chemistry and the functional sources of dissolved ions can be assessed by plotting the ratios of Na⁺ to (Na⁺ + Ca²⁺) and Cl⁻ to (Cl⁻ + HCO₃⁻) as function of TDS (Gibbs 1970). Gibbs diagrams of the water samples (Fig. 4) clearly show that samples have become saline by evaporative enrichment. Only two samples with TDS less than 1000 mg/L show that the mineralization is controlled by water–rocks interaction. Many researchers (Tweed et al. 2012; Scanlon et al. 2003, 2007) show that evaporation process in (semi)-arid zone greatly increases the concentration of ions leaching to higher salinity. It is also known that thick unsaturated zones in (semi)-arid regions contain a reservoir of salts that accumulated over thousands of years (Allison et al. 1990; Philipps 1994; Walvoord et al. 2004) and can be flushed into underlying aquifers.

Hydrochemical facies

The groundwater samples are characterized by major ions patterns Na⁺ >> Ca²⁺ > Mg²⁺ > K⁺ for cations and Cl⁻ > SO₄²⁻ >> HCO₃⁻ for anions. Major dissolved ion

contents are plotted on a Piper diagram (Fig. 5) showing that the chemical composition of the groundwater is predominantly Na-Cl-SO₄ type (82 % of the samples). Two other hydrochemical facies appeared in the Piper plot: Ca-Mg-Cl-SO₄ type (14 % of the samples), and Mg-Cl type (only one sample). The trilinear diagram of cations shows that in 82 % of the samples Na²⁺ is the dominant cation and Cl⁻ is the dominant anion in 93 % of the samples.

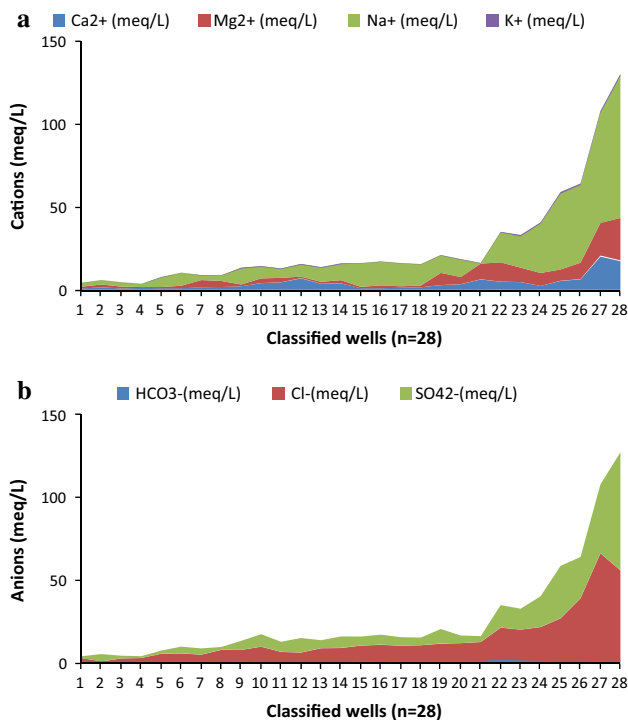


Fig. 6 Distribution of **a** cations and **b** anions with increasing salinity (electrical conductivity); each indentation on the x-axis corresponds to an analysis of major ions

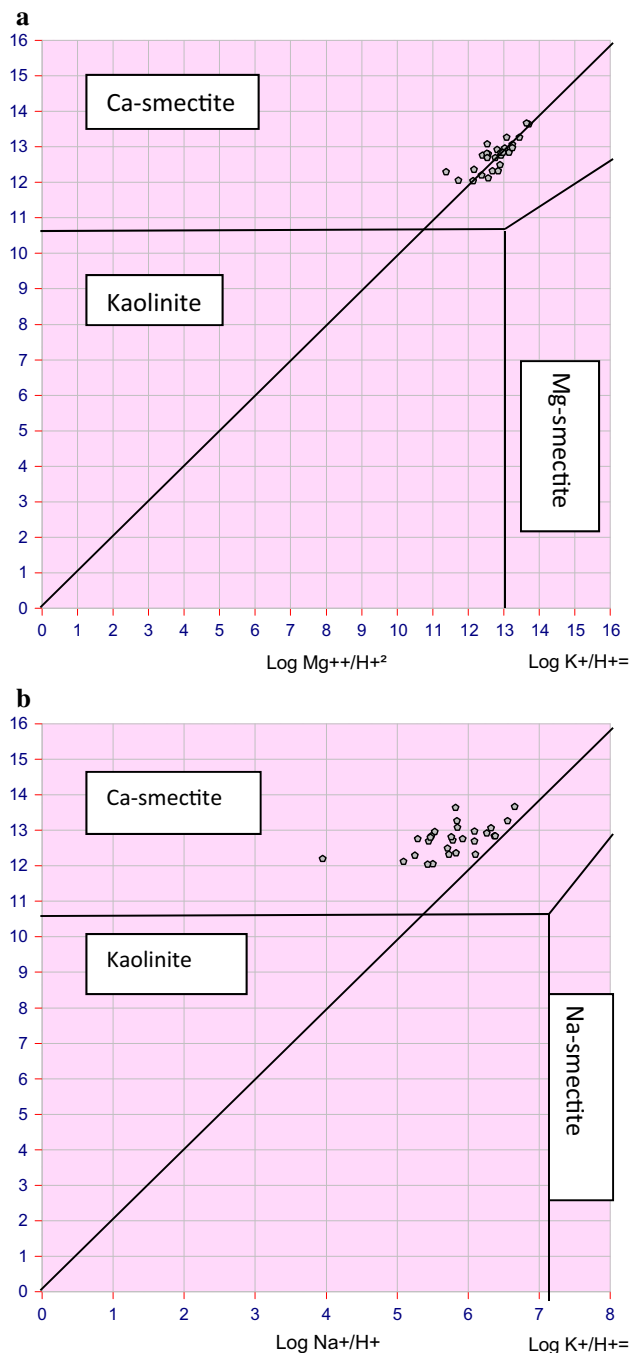


Fig. 7 Stability diagram of mineral phases in the system: **a** CaO-Na₂O-Si₂O-Al₂O₃-H₂O: Ca²⁺-Mg²⁺, **b** CaO-Na₂O-Si₂O-Al₂O₃-H₂O: Ca²⁺-Na⁺ phases relative to groundwater samples

Ca^{2+} , Mg^{2+} and HCO_3^- are never predominant. Only one sample shows Mg^{2+} as a dominant cation (well number 21 at Eidan Al Ridda, Al Towwaya). The presence of weathered dolomite in Jabal Hafit could be the main reason for elevated magnesium in groundwater at this location. SO_4^{2-} is predominant in only four samples. The chemical facies Na-Cl reflects a low flow in the aquifer. This allows the predominance of Na (ion exchange processes) against Ca. The high concentrations of chloride in all samples can be linked to evaporation (arid zone) in the shallow aquifer (depths of water table range from 3 to 15.25 m). A more quantitative approach of the hydro-chemical variations is obtained by plotting the ionic concentrations in the way of increasing mineralization (Fig. 6a, b). The highest mineralization is linked to an increase of the Na^+ , Cl^- and SO_4^{2-} . The increase of Ca^{2+} and Mg^{2+} is not significant except in few samples. This is corroborated by the high

standard deviations obtained for Na^+ (20.7), Cl^- (15.4), and SO_4^{2-} (15.1) and low standard deviations for Mg^{2+} (6.0), Ca^{2+} (4.7), and HCO_3^- (0.4). This observation is in agreement with the natural origin of the hydro-chemical sides Na-Cl- SO_4 .

Stability fields and saturation indices

To test the groundwater equilibrium with the silicate mineral phases, chemical analyses have been reported in the stability diagrams of the systems Na_2O - MgO - Al_2O_3 - SiO_2 - H_2O . Groundwater samples lie in the domain of stability of montmorillonite (Ca-smectite) (Fig. 7). All the samples are located over the smectite saturation line, so smectite is expected to form better than kaolinite because of the arid climate condition. This is in agreement with the clay phase present in the aquifer, and climatic conditions (arid, low

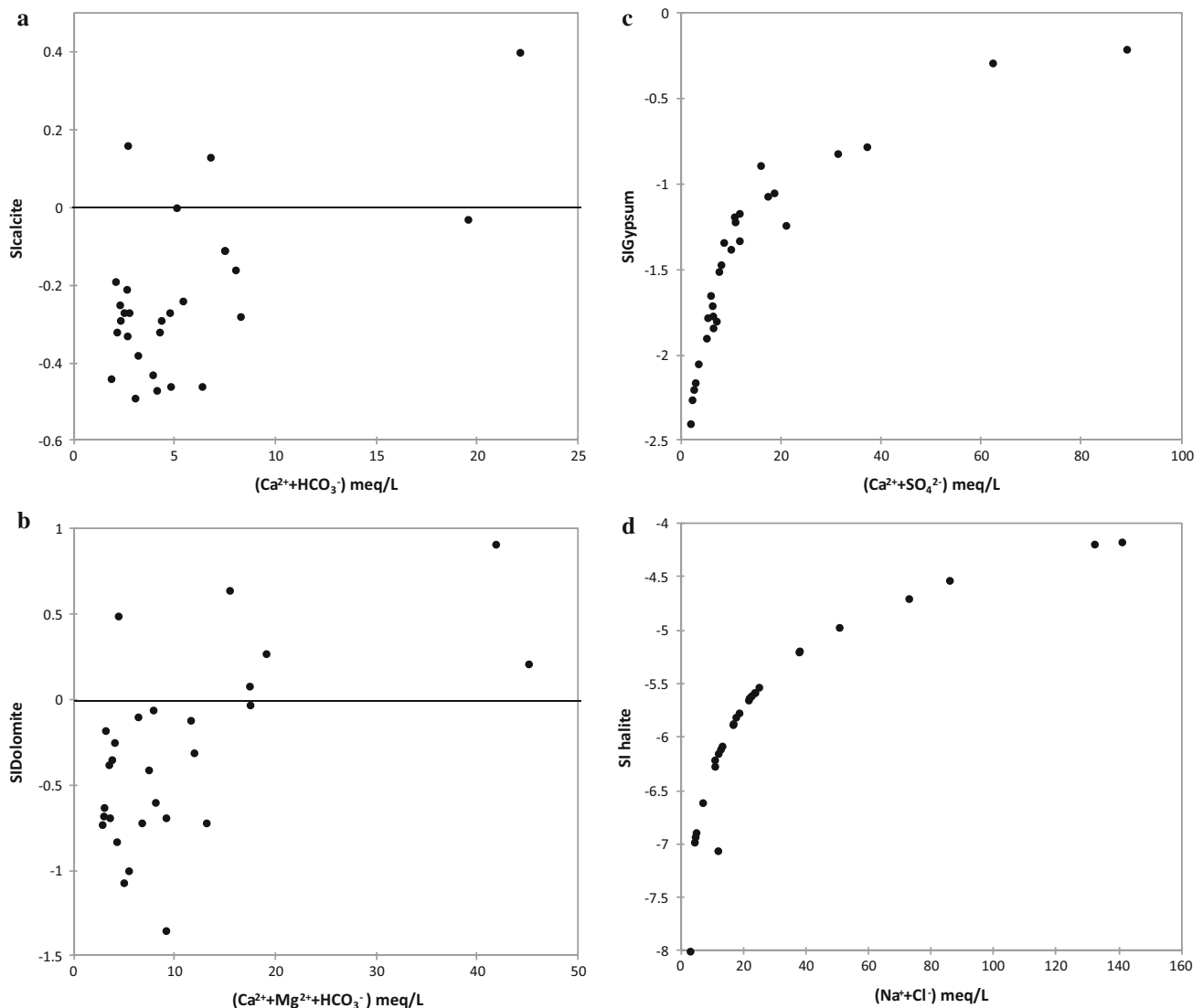


Fig. 8 Plot of the PHREEQC calculated saturation indices (SI) for **a** calcite, **b** dolomite, **c** gypsum, and **d** halite

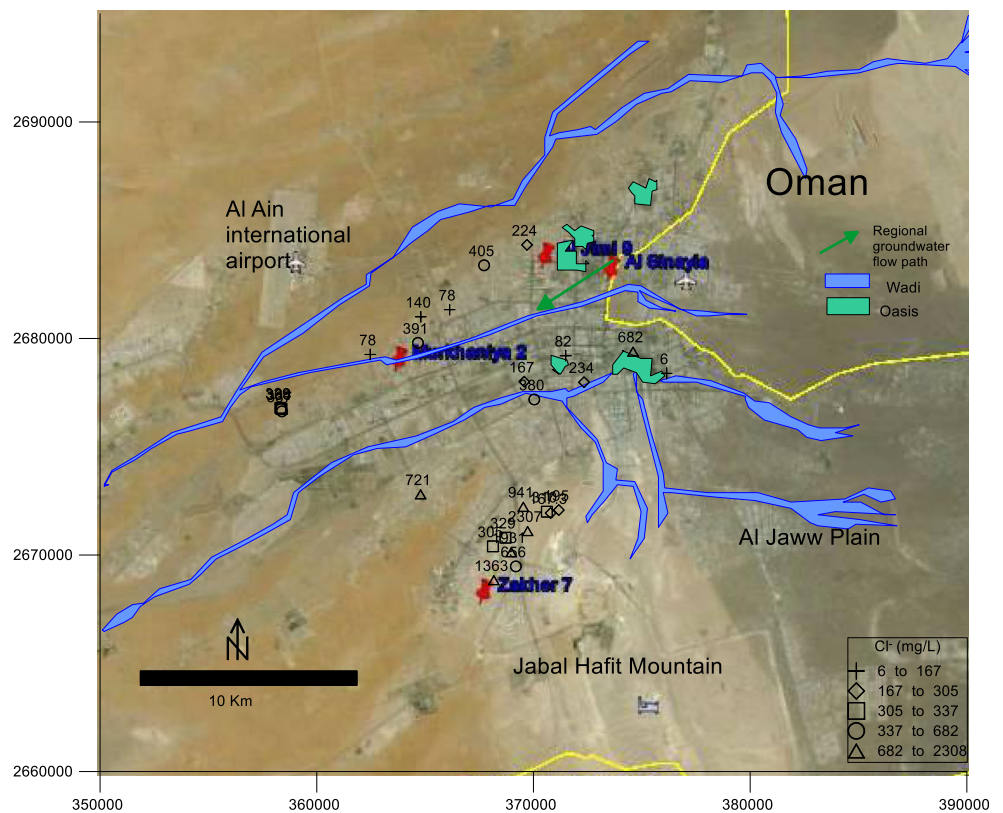
rainfall and low soil moisture), thereby promoting the formation of montmorillonite (Appelo and Postma 1999). For example, Montmorillonite has a strong cation exchange capacity (CEC) compared to kaolinite. Freeze and Cherry (1979) suggest that when the dominant clay resulting from the silicate weathering is montmorillonite, groundwater flow is restricted and is associated with a low flow in the aquifer. This implies a longer residence time of groundwater in the aquifer, and allows the water–rock interactions in the aquifer to have necessary time to take place. The stability diagrams indicate that silicate weathering is one of the main sources of groundwater mineralization.

To assess dissolution–precipitation processes, saturation indices (SI) of some mineral phases were calculated with PHREEQC v2.16 (Parkhurst and Appelo 1999). The saturation indices indicate that the groundwater in the study area is under saturated with respect to calcite (SI = -0.5 - 0.4, median -0.3), dolomite (SI = -1.4 - 0.9, median -0.4), gypsum (SI = -2.4 - -0.2, median -1.4) and halite (SI = -8.0 - -4.2, median -5.8) (Fig. 8). Thus, the changes in groundwater composition are consistent with dissolution of carbonates (calcite, dolomite), sulfates (gypsum) and halite. Carbonates (calcite and dolomite) show a slight oversaturation for few samples indicating that those minerals precipitated in the aquifer.

Major ions

The chloride contents range from 0.2 to 65.1 meq/L (median of 9.3 meq/L). Figure 9 shows the spatial variations of Cl contents. The highest concentrations were recorded to the south (northern edge of Jabal Hafit Mountain) and the lowest at the northeast (near the recharge zone), same as the spatial variation of sulfate concentrations. This spatial variation is positively correlated to the spatial variations of the electrical conductivity. Chloride is usually used as a tracer of water movement because of its conservative characteristic (non volatile, not taken up by plants, rarely found in the solid phase, and extremely soluble). Chloride moves conservatively in water through the hydrologic cycle. The chloride concentrations are plotted against all elements. The data defined notable correlation with Na ($R^2 = 0.90$), Ca ($R^2 = 0.81$), Mg ($R^2 = 0.81$), and SO_4 ($R^2 = 0.82$) (Fig. 10) showing that those ions are from the same sources as Cl. The ratios of Na/Cl (median 1.2), Ca/Cl (median 0.3), and Mg/Cl (median 0.3) in the samples are in the same range of the ratios in the rain water of the region (median of 1.15, 0.3, and 0.3, respectively), but the ratio of SO_4/Cl is lower in the groundwater (median of 0.7) than in the rain water (median 5.0). Groundwater is compared with the rainwater as the ^{36}Cl data from groundwater

Fig. 9 Spatial variation of Cl^- (mg/L)



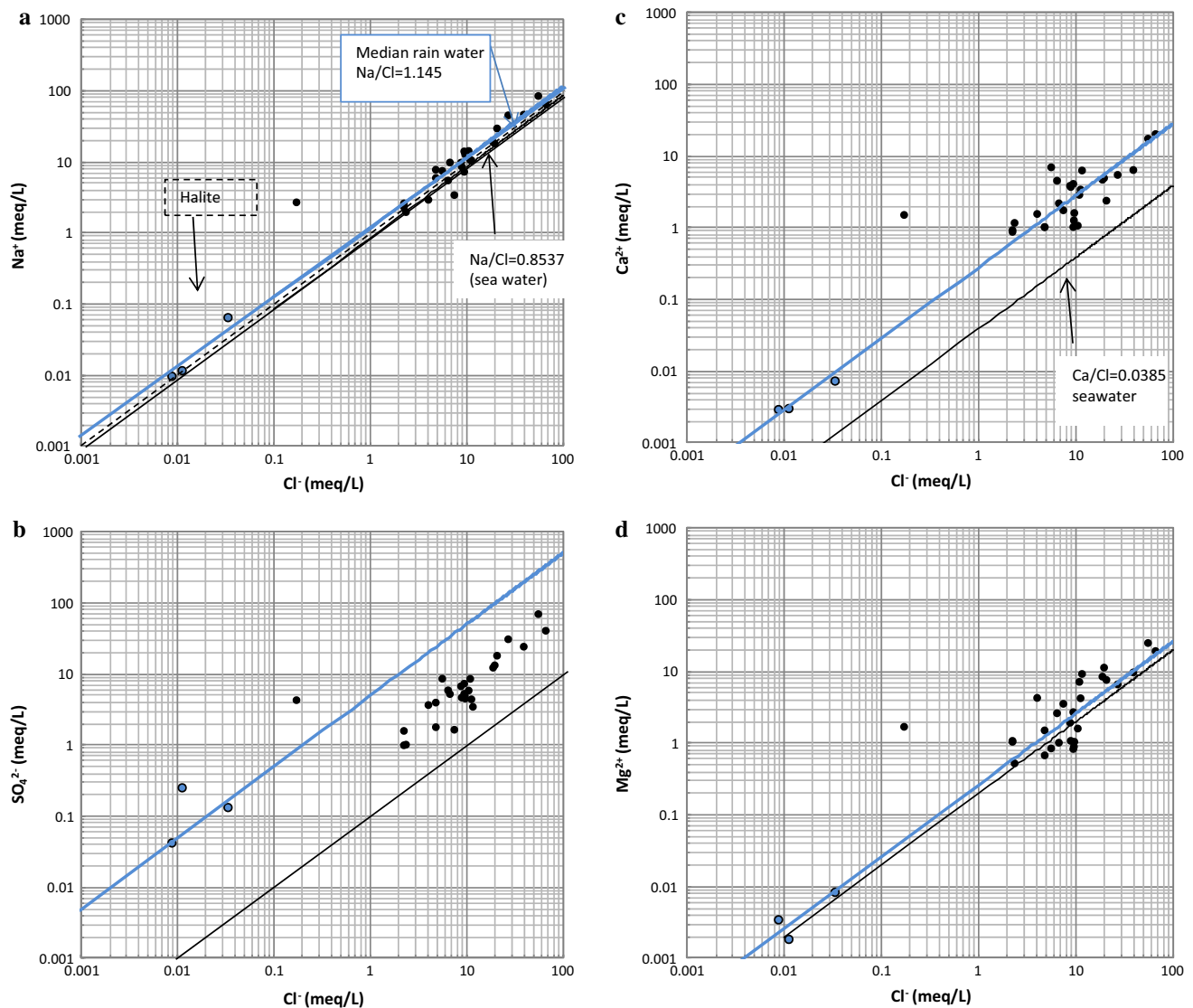


Fig. 10 Bivariate plots of **a** Na^+ , **b** SO_4^{2-} , **c** Ca^{2+} , and **d** Mg^{2+} versus Cl^- concentration in the groundwater samples

of the United Arab Emirates indicate that the recharge to the aquifers is modern (Murad and Krishnamurthy 2004).

Na^+ concentrations range from 0.4 to 86.4 meq/L (median of 10.02 meq/L), with an average concentration of 16.9 meq/L and a standard deviation of 20.7. The K^+ contents range from 0.001 to 1.27 meq/L (median of 0.3 meq/L), with an average concentration of 0.4 meq/L and a standard deviation of 0.3. A plot of ($\text{Na} + \text{K}$) versus total cations shows that the ratio of $\text{Na} + \text{K}$ versus total cations (median ratio of 0.6) tends to be higher than the ratio of ($\text{Ca} + \text{Mg}$) versus total cations (median of 0.38) showing that alkalis are dominant cations. Na increase with Cl and Na/Cl ratios ranges from 0.04 to 1.74. Only one sample (well number 2, Al Niyadat, Central District) shows a high Na/Cl ratio (16.35) with low Cl content. In an $\text{Na} + \text{K}$ versus Cl diagram (Fig. 11), most samples plot

near the equiline (halite dissolution line). This suggests that halite dissolution occurs in the aquifer and is associated with the presence of local sabkha sediments in the Quaternary-Holocene deposits. In addition, the rain evaporates before reaching the aquifer and may produce an evaporated salt deposit which can dissolve and may influence the groundwater chemistry.

SO_4^{2-} concentrations range from 1.02 to 71.14 meq/L (median of 5.37 meq/L). The highest concentrations (more than 1000 mg/L; 20.82 meq/L) were found in the south (northern edge of Jabal Hafit Mountain) and the lowest concentrations (<500 mg/L; 10.41 meq/L) in the north (near Oman border, and at the east of the city of Al-Ain) (Fig. 12). The SO_4^{2-} concentrations show a notable correlation with ($\text{Ca} + \text{Mg}$) ($R^2 = 0.82$), and with each of alkali earths ($R^2 = 0.73$ and 0.8 for Ca and Mg , respectively).

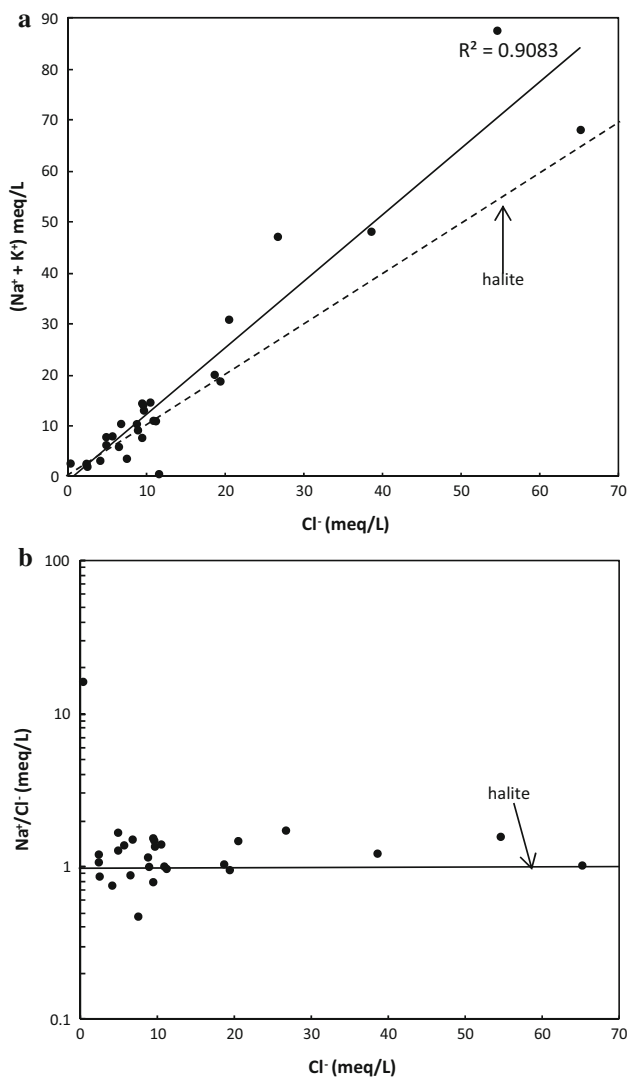
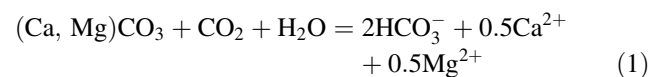


Fig. 11 Plots of **a** $\text{Na}^+ + \text{K}^+$ versus Cl^- and **b** $\text{Na}^+ / \text{Cl}^-$ versus Cl^- in groundwaters

This suggests that the chemistry of the groundwater is likely controlled by dissolution of sulfate minerals (gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Where confined by silts and clays, dissolution of sulfate minerals and halite is the dominant process which controlled the major ion chemistry by contributing calcium and sulfate, and allowing Ca/Na and Ca/Mg exchange with the solid phases in the aquifer. The clay minerals are formed due to the weathering and they are responsible for the changes in the chemistry of groundwater due to ion exchange. Also a high correlation appears between the concentrations of SO_4 and Na. Assuming that gypsum is the source of SO_4 , the correlation between Na and SO_4 ($R^2 = 0.94$) indicates that Ca tends to be exchanged with Na in the aquifer matrix.

The concentration of Ca^{2+} varied between 0.9 and 20.7 meq/L (median of 2.7 meq/L and average of 4.1 meq/L)

with the standard deviation of 4.7, whereas the concentration of Mg^{2+} varied between 0.5 and 25.5 meq/L (median of 2.3 meq/L and average of 5.0 meq/L) with the standard deviation of 6.0. Ca^{2+} and Mg^{2+} are well correlated ($R^2 = 0.76$), and show a strong correlation to SO_4^{2-} as shown before. This suggests that Ca^{2+} and Mg^{2+} can have other sources such as limestone and dolomite other than sulfate. The molar Ca/Mg ratios of these samples range from 0.3 to 8.2 with a median and an average of 0.8 and 1.4, respectively, and a standard deviation of 1.5. The average value indicates that dolomite contributes solutes to the groundwater (Eq. 1). Waters in contact with limestone typically have Ca/Mg ratios of approximately 2.0:1 to 1.5:1 (Mandel and Shifan 1981).

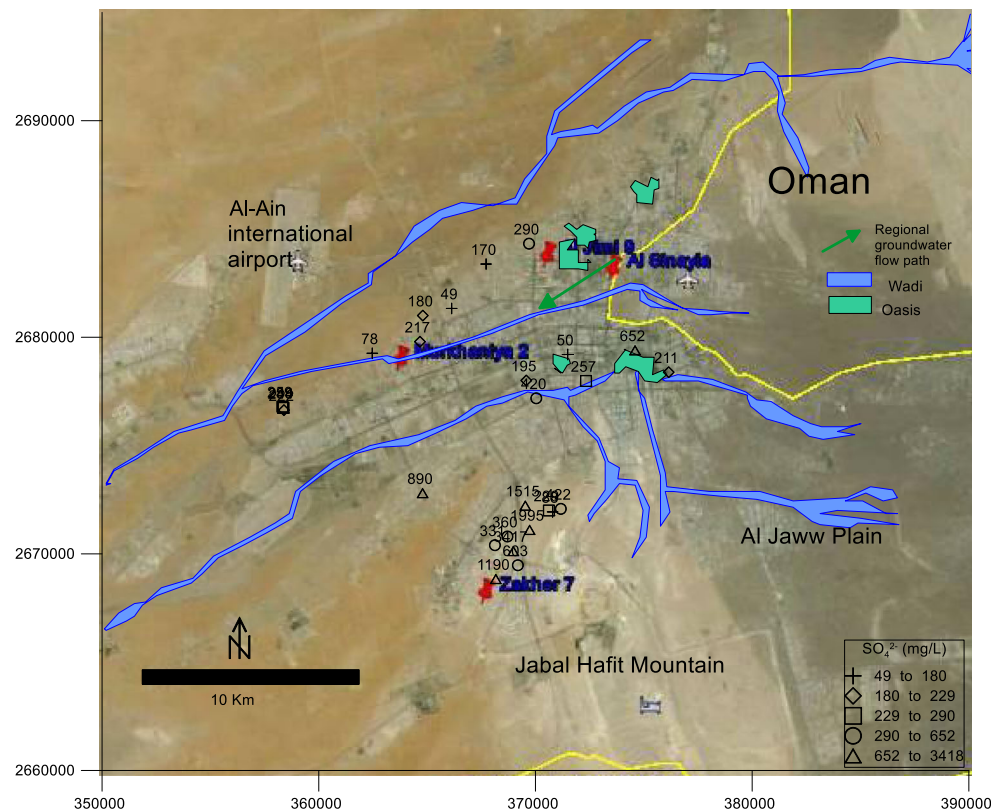


HCO_3^- concentrations are low, ranged between 0.5 and 2.4 meq/L (median of 1.3 meq/L) and display any correlation with the other chemical components. The relative good correlations observed between elemental ratios are between Ca/Na vs Mg/Na ($R^2 = 0.99$) and Ca/Na vs HCO_3^-/Na ($R^2 = 0.97$). An Na-normalized Ca versus Na-normalized Mg and Na-normalized HCO_3^- plot (Fig. 13; after Gaillardet et al. 1999) shows that the groundwater samples are influenced by evaporite dissolution and silicate weathering.

Nitrate is an inorganic ion produced during various stages of the nitrogen cycle. In most oxygenated water, nitrate is the predominant ion because of rapid oxidation of nitrite (Reid and Wood 1976). Nitrate usually occurs in relatively small concentrations in uncontaminated water, and concentrations in the range of several milligrams per liter indicate contamination from human activities. NO_3^- is present in low concentration in all wells. Groundwater NO_3^- concentrations range from 0.00 to 11 mg/L.

Ion exchange

The extent of cation exchange processes in groundwater chemistry can be investigated by the relationship between the concentration of $(\text{Na}^+ - \text{Cl}^-)$ against $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$. The product of $(\text{Na}^+ - \text{Cl}^-)$ represents excess sodium, that is, sodium coming from the sources other than halite dissolution, assuming that Na^+ contributions of meteoric origin would be balanced by equivalent concentrations of Cl^- (Jankowski et al. 1998; McLean and Jankowski 2000). Also, the product of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ represents the calcium and/or magnesium that would be derived from processes other than silicate weathering, gypsum and carbonate dissolution. Figure 14 shows that the samples

Fig. 12 Spatial variation of SO_4^{2-} (mg/L)

have a slope of ~ -0.9 , close to the $y = -x$ line, suggesting that cation exchange probably has a strong influence on the groundwater chemistry related to the low flow and extended residence time in the groundwater aquifer.

Groundwater quality assessment

Most of the groundwater samples are within the limits for drinking water for major constituents according to international standards (WHO 2011). The TDS exceed the drinking water guideline value (<1000 mg/L) in eight samples located near Jabal Hafit. Sulfate exceeds the guideline value (<500 mg/L) in seven samples and nitrate concentrations are very low (<11 mg/L; guideline value = 50 mg/L).

Salinity and sodium adsorption ratio (SAR) are the two main criteria to evaluate irrigation water. Salinity hazard, measured by electrical conductivity, and sodium hazard (SAR), measured as the proportion of sodium to calcium and magnesium in a sample are the axes of a Wilcox plot; a diagram used to classify irrigation waters. Based on this classification (Fig. 15), groundwater of the unconfined alluvial aquifer of Al-Ain depression has high Sodium Adsorption Ratios values south (near Jabal Hafit Mountain) and west of the study area (Al Bateen and Al Shuaibah) and it is not suitable for irrigation. At the east of the study area,

groundwater has low and middle SAR, and can be used for irrigation.

Summary and conclusions

A hydrochemical study was conducted on the shallow unconfined alluvial aquifer of the city of Al-Ain (north-eastern of Abu Dhabi Emirate). The aquifer is less permeable with a high variability in lithology. As expected, the chemical monitoring revealed high spatial variability in chemical parameters. Groundwater is generally, with some variations, Na-Cl-SO₄ type. Major solutes in groundwater appear to be derived primarily from silicate weathering and evaporite dissolution. In addition, cation exchange has provided some of the solutes in the groundwater. Evaporation-driven salinization of shallow groundwater in arid zone results in relatively high groundwater salinity values. Major ion concentrations exhibited increases in depth and space because of evaporation process, water-rock interactions (e.g., mineral dissolution, ion exchange reactions), leaching of ions by upward and downward leakage from, respectively, Jabal Hafit limestone aquifer and sabka deposits, and leaching of ions from potential pollutant sources. The concentration increases were accounted for primarily by dissolved sodium, chloride, and sulfate. In

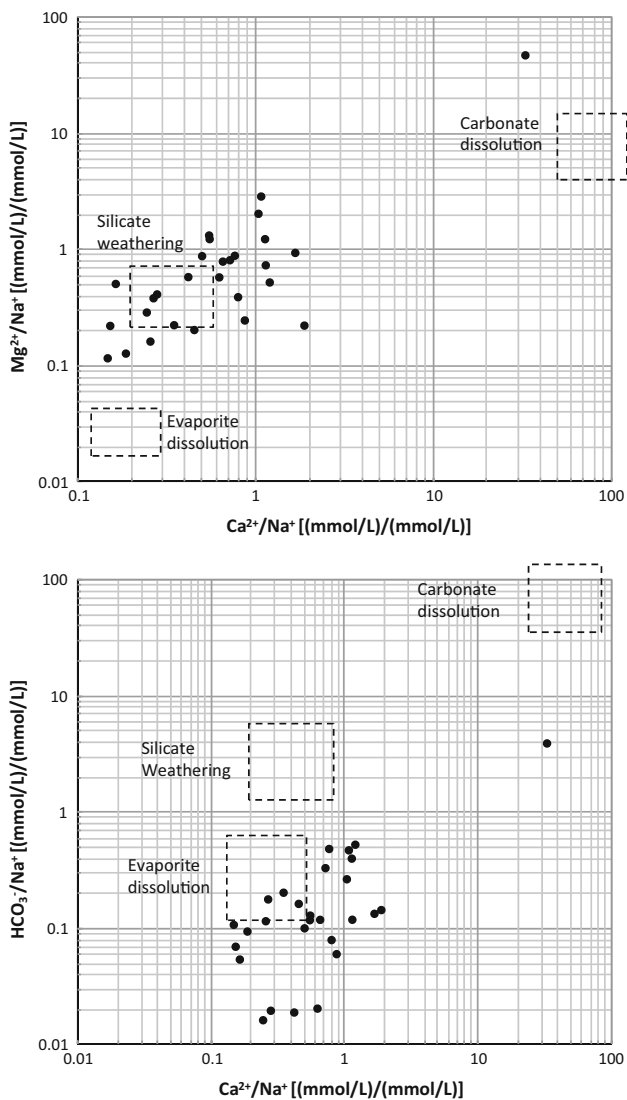


Fig. 13 Bivariate plots of Na^+ -normalized ($\mu\text{M}/\mu\text{M}$) Mg^{2+} versus Ca^{2+} and HCO_3^- versus Ca^{2+} to show trends of weathering. The dashed rectangular areas demonstrate global average compositions of groundwater with respect to evaporite dissolution, silicate weathering, and carbonate dissolution without mixing (following Gaillardet et al. 1999)

general, the chemistry of groundwater throughout the aquifer was a good quality. Many of the chemical constituents analyzed in each sample are less than the primary drinking water standards. To assess the mechanisms controlling groundwater chemistry in the Al-Ain depression, further study of sediment–water interactions is needed. To assess the sensitivity of the aquifer to the effects of land use changes (urbanization, agricultural practices), an integrated approach of hydrodynamics, hydro-geochemical, and

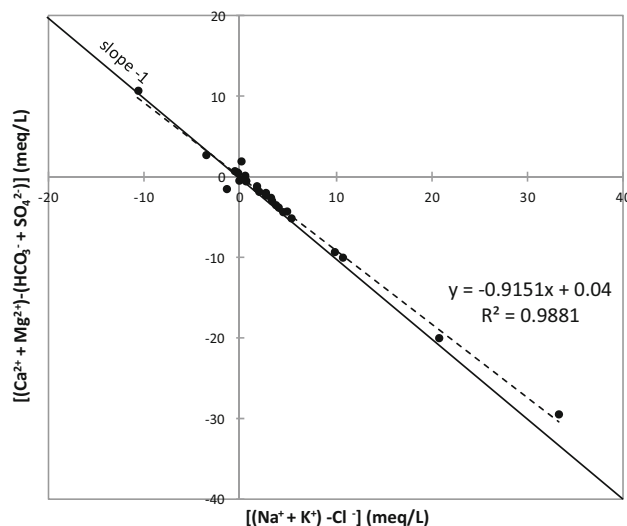


Fig. 14 Bivariate plot of $(\text{Ca}^{2+}$ and $\text{Mg}^{2+})$ less $(\text{HCO}_3^-$ and $\text{SO}_4^{2-})$ against $(\text{Na}^+$ and $\text{K}^+)$ less Cl^- to indicate the cation exchange reactions

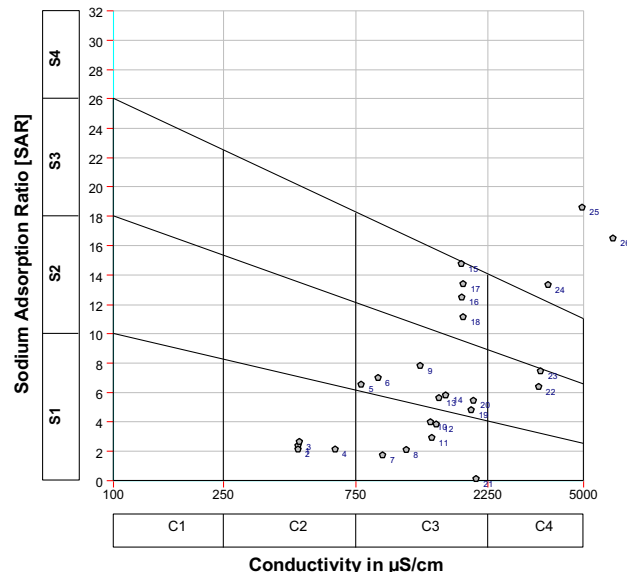


Fig. 15 Wilcox diagram of salinity and sodium adsorption ratio (SAR) hazards for all samples

hydro-biological studies must include all the compartments (groundwater, soils, waste disposals in landfill, and springs).

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