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Environmental isotope systematics of the groundwater system of southern Kuwait

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Abstract The carbonate Dammam Formation of Eocene age and the unconformably overlying clastic Kuwait Group of rocks of Mio-Pliocene age are the two aquifers that provide useable groundwater (salinity 5000 mg/l or less) in Kuwait. These aquifers extend beyond the political limits of the country to Saudi Arabia and Iraq. A detailed environmental isotopic $(^{2/1}H, ^{18/16}O, ^{13/12}C, ^{3}H, ^{14}C)$ characterization of the groundwater system of southern Kuwait (a regional aquifer extending beyond the political limits of the country to Saudi Arabia and Iraq) has been carried out to understand its hydrodynamics so as to evolve a better conceptual flow model of the aquifer system. From the study, it was observed that the groundwater salinity of the Kuwait Group aquifer increases generally from south-west to north-east, although locally a few of them show low values. Groundwater samples from the Dammam Formation aquifer are characterized by a relatively low mineralization, compared with those of Kuwait Group aquifer. The water in the Kuwait Group aquifer in the south-western part of the country is Na–Cl type and in the Dammam Formation aquifer is Na–Cl to SO_4 –Na (Cl $> SO_4$) type. A wide range of d-excess of the groundwater samples was seen (Kuwait Group aquifer $+16.0$ to -20.6 ‰; Dammam Formation aquifer: $+22.8$ to -19.6 ‰), indicating that the groundwater system contains more than one type of water with different origin (recharge area) and history (time, evaporation, climate). In both the aquifers, the groundwater samples from south and central parts and along the coast showed negative *d*-excess values with heavier 18 O and 2 H,

indicating older recharge and greater degree of evaporation prior to recharge. The $\delta^{18}O$ and δ^2H of the initial recharge waters, respectively, are -8.8 and -40% for the Kuwait Group aquifer and -7.2 and -32% for the Dammam Formation aquifer. The corrected 14 C ages (Tamer's model) of groundwater samples of Kuwait Group aquifer ranged from \sim 5000 to 24,000 a, B.P, and that of Dammam Formation aquifer ranged from ~ 6000 to 20,000 a, B.P. The intermediate groundwater in the southwest and central parts of Kuwait Group aquifer is recharged during humid period (\sim 5000 to 10,000 a, B.P), whereas deeper groundwater in the south is recharged during arid period (\sim 9000–16,000 a, B.P). The recharge to the Dammam Formation aquifer mostly occurred during a cooler (humid) phase in the past. The Dammam Formation aquifer water is hydraulically well mixed below 350 m depth. Interconnection between the two aquifers established near the coast and south-west border of the country. The results of the study were used to refine the existing conceptual groundwater flow model for the aquifer system.

Keywords Kuwait Group aquifer - Dammam Formation aquifer - Hydrodynamics - Groundwater age - Palaeo-climate

Introduction

The carbonate Dammam Formation of Eocene age and the overlying clastic sediments of Kuwait Group of Mio-Pliocene age are the two main aquifers that yield useable water (salinity ≤ 5000 mg/l) in Kuwait. Except for the localized small accumulations of freshwater lenses in North Kuwait (Milewski et al. [2014\)](#page-18-0), most of the usable brackish water (salinity 2500–5000 mg/l) in these aquifers

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occurs in the southern and south-western parts of the country. In the water-starved arid climate of the country, useable (both fresh and brackish) reserves of groundwater constitute a strategic resource. Although desalination provides bulk of the freshwater consumed in the country, the brackish groundwater is heavily exploited for agriculture, animal husbandry, industrial activities, and mixing with desalinated water to make it potable.

Large-scale exploitation of the brackish groundwater resources in Kuwait started in the 1970s through the development of the well fields in these areas (Al-Awadi et al. [1998\)](#page-18-0). Prior to this date, the general hydraulic gradient in these aquifers was towards the north-east and east towards the discharge zone along the Arabian Gulf with an upward vertical component. The groundwater saturating these aquifers was in chemical equilibrium with the respective aquifer materials and had, therefore, some subtle difference in quality. With continued exploitation of these aquifers, the vertical component of the hydraulic gradient has changed its direction downward in the central and southern parts of the country. With the change in the flow direction, water from the Kuwait Group aquifer is flowing to the Dammam Formation aquifer in these areas, and as a result the hydrochemical equilibrium is expected to be disturbed. This could have some impacts on the quality of the water currently pumped from the aquifers. The drop in potentiometric heads of the aquifers due to continued production could also affect the cost of utilization of the aquifers.

The environmental isotopes, both stable and radioactive, of water and its dissolved constituents, to name a few $^{2/1}$ H, $^{18/16}$ O, $^{13/12}$ C, $^{15/14}$ N, $^{34/32}$ S, $^{11/10}$ B, $^{87/86}$ Sr, 14 C, 3 H amongst others, provide valuable information on the source, age, flow paths, geochemical evolution, vulnerability to contamination, and categorization of contaminant of groundwater. Today, the isotopic characterization of an aquifer system is considered a modern and powerful hydrological tool to understand the aquifer system, leading to an optimum development and exploitation pattern of groundwater resources in any given locality.

A detailed isotopic characterization $(2^{11}H, 18/16O, 13/12C,$ ${}^{3}H, {}^{14}C$) of the Kuwait Group and Dammam Formation aquifers of Kuwait was carried out to understand the hydrodynamics of groundwater system in terms of origin, age, and flow paths of water within the aquifers, in conjunction with in situ physicochemical and hydrochemical data, so as to evolve a better conceptual flow model of the aquifer system. A better conceptual flow model of the aquifer system could help in understanding the impacts of the production on the potentiometry and the associated hydrochemical equilibrium in the aquifers and on the produced water quality to ensure the continued sustainable management of the available brackish water resources of the country.

Hydrogeology of Kuwait

The State of Kuwait is situated at the north-eastern corner of the Arabian Peninsula. It comprises an area of approximately 17,600 km^2 extending between latitudes 28°30'N and $30^{\circ}05'$ N and between longitudes $46^{\circ}33'E$ and $48^{\circ}33'E$. In addition to the mainland, Kuwait also includes a few islands such as Bubiyan, Failaka, and Al-Qubbar. There is little difference in the country's altitude with the highest point in the country being 306 m above mean sea level.

The climatic conditions in the State of Kuwait are hot and arid with scanty rainfall. Based on the 1996 to 2007 records maintained by Kuwait Institute for Scientific Research (KISR), the mean total rainfall rate was 118 mm a year with rainfall mainly during November–April, and the average annual temperature was 26° C. The weather is warm to hot in October and mild to cold, with thunderstorms sometimes in November. The weather is coldest in January with temperature reaching about 12 °C (The recorded maximum and minimum temperature, respectively, was 50.8 °C in June 1954 and -4 g °C in 1964).

The main lithostratigraphy units forming the bedrock of Kuwait are unconsolidated to semi-consolidated clastic sediments of the Kuwait Group (post-Eocene Age), which unconformably overlies the dolomitic Dammam Formation of the Eocene Age. The generalized stratigraphy of the Tertiary sediments in Kuwait and surrounding areas is given in Fig. [1.](#page-2-0) The Dammam Formation and Kuwait Group of rocks age are the two aquifers that provide useable groundwater (salinity $\langle 5000 \text{ mg/l} \rangle$ in Kuwait. These aquifers extend beyond the political limits of the country to Saudi Arabia and Iraq (Al-Awadi et al. [1998](#page-18-0)). The aquifers in the Kuwait Group appear to be layered semi-confined system with a free water table in the uppermost horizon, and the Dammam Formation acts as a semi-confined to confined aquifer. In spite of the lithologic heterogeneity within the Kuwait Group aquifer and the variation in the degree of karstification within the Dammam Formation, the two aquifers are hydraulically connected. Under natural undisturbed conditions, there is an upward hydraulic gradient component from the Dammam Formation to the Kuwait Group aquifer. The generalized groundwater flow system in Kuwait is given in Fig. [2.](#page-3-0)

Sampling programme

From November 2012 to February 2013, 60 rainwater samples were collected from the installed rain gauges at ten locations spread across Kuwait for the environmental isotopic analyses $(^{2}H,~^{18}O,~^{3}H)$. The meteorological parameters at the rain gauge stations such as air temperature,

| GENERALIZED STRATIGRAPHY | HYDROGEOLOGICAL UNITS | | | | | |
|---|---|--|---|-----------------------|-----------------|--|
| Quarternary sediments $(< 30 \, \text{m})$ Unconformity | | Unconsolidated sands and gravels, gypsiferous and calcareous silts and clays | | Localized Aquifers | | |
| Kuwait Group | \cdot T \circ \overline{I} o \overline{I} | | | Dibdibba Aquifer | | |
| Mio-Pliocene sediments of Hadrukh, Dam and Hofuf Formations in | I _a r T I | Gravelly sand, sandy gravel, calcareous and gypsiferous sand, | | Upper Aquifer | | |
| Saudi Arabia; Ghar, Fars and Dibdibba Formations of Kuwait and southern Iraq | T | calcareous silty sandstone, sandy limestone, marl and shale; locally cherty | | Aquitard | | |
| $(200-300 \text{ m})$ | r r | | | Lower Aquifer | | |
| Unconformity | $I_{\bar{I}}$. | Localized shale, clay and calcareous silty sandstone | | Aquitard | | |
| | $\begin{array}{c c}\n\hline\n\text{A} \\ \hline\n\end{array}$ | Cherty limestone | | | | |
| | | | | | Upper | |
| Dammam Formation $(60-200 \text{ m})$ | | Chalky, marly, dolomitic and calcarenitic limestone | | Aquifer | Middle Lower | |
| | فہ 70 | Nummulitic limestone with lignites and shales | Aquitard; locally aquiclude where Rus Formation is predominantly anhydritic | | | |
| Rus Formation $(20-200 \text{ m})$ | | Anhydrite and limestone | | | | |
| Umm Er Radhuma (UER) Formation (300-600 m) | | Limestone and dolomite (calcarenitic in the middle) with localized anhydrite layers | | Aquifer | | |
| | | | | | | |
| Disconformity | | Shales and marls | Aquitard | | | |
| Aruma Group $(400 - 600$ m) | | Limestone and shaly limestone | | Aquifer | | |

Fig. 1 Generalized stratigraphy of the tertiary sediments in Kuwait and surrounding areas (Source: Mukhopadhyay et al. [1996\)](#page-18-0)

humidity, pressure, wind direction, and speed were also measured continuously during the study.

Thirty groundwater samples were collected from the Kuwait Group and Dammam Formation aquifers for the in situ physicochemical parameters [temperature (T), electrical conductivity (EC), pH, dissolved oxygen (DO)], hydrochemistry (major cations and anions), and isotopic analyses $(^{2/1}H, ^{18/16}O, ^{13/12}C, ^{3}H, ^{14}C)$. The sampling locations are shown in Fig. [3.](#page-4-0) Prior to the selection of sampling locations, a thorough study on the available well

Fig. 2 Generalized groundwater flow system in Kuwait (Source: Senay et al. [1987](#page-19-0))

lithologs was made, to ensure that groundwater samples cover all the zones of the Kuwait Group and Dammam Formation aquifers.

The samples were analysed for environmentally stable 18 O and 2 H isotopes using liquid water isotope analyser (LGR Make) at the Water Research Center (WRC) of Kuwait Institute for Scientific Research (KISR). The ²H and 18 O results are expressed in the standard δ -notation with respect to Vienna Standard Mean Ocean Water (V-SMOW) (precision ± 0.5 and ± 0.1 ‰, respectively). The environmentally stable ${}^{13}C$ and radioactive ${}^{3}H$ and ${}^{14}C$ isotopes analyses were carried out at the Laboratory of Radio Analysis and Environment, National School of Engineers of SFAX, Tunis, Tunisia, through International Atomic Energy Agency (IAEA), Vienna, Austria. δ^{13} C was measured using isotope ratio mass spectrometer in the form of carbon dioxide gas (standard: Pee Dee Belemnite; precision ± 0.5 ‰). Environmental ³H content of water samples was analysed using liquid scintillation counter after electrolytic enrichment and expressed in tritium units (TU) (precision ± 0.5 TU). Environmental ¹⁴C analyses were carried out using accelerated mass spectrometry, and the results are expressed in percentage modern carbon (pMC) (precision ± 0.5 pMC). The samples were analysed for major cations and anions using ion chromatograph (DIONEX) at WRC,

KISR. The major ions are reported in mg/l units (charge balance error ± 5 %). The in situ physicochemical parameters were measured in the field. The results of analyses are given in Tables [1](#page-5-0), [2](#page-7-0) and [3](#page-8-0).

Results

Potentiometric head

In keeping with the regional flow pattern, all the aquifers had initial hydraulic gradients towards north and east. As Kuwait is situated in discharge zone, the vertical gradient has been upwards (i.e. from the Dammam Formation aquifer to the Kuwait Group aquifer) before the regular high volume production of these aquifers that started in the 1960s. With the large-scale exploitation of the aquifers (mainly the Dammam Formation aquifer) starting in the 1960s, the vertical hydraulic gradient had reversed downward in the central part of the Kuwait by mid-1980s, as indicated by the monitoring of the potentiometric heads in these two aquifers. The potentiometric head map prepared on the basis of the water level data for the entire country is presented in Fig. [4](#page-9-0). The maps indicate that the general groundwater flow direction is towards the discharge zones Fig. 3 Sampling locations of rainwater (*) and groundwater (•)

near the Arabian Gulf where the water becomes almost stagnant or of very slow movement.

Hydrochemistry

Most groundwater samples collected are characterized by high total mineralization. The groundwater salinity of the Kuwait Group aquifer increases generally from south-west (from about 3500 mg/l, brackish water) to north-east (reaching to more than 64,500 mg/l, salty and brine water, although locally a few of them showed low values. Groundwater samples from the Dammam Formation aquifer are characterized by a relatively low mineralization, compared with those of Kuwait Group aquifer, with total dissolved solids (TDS) ranging from 2500 mg/l in the south-west to 6900 mg/l in the north-east and the central part of the country.

Based on the relative abundance of different anions in the water, the water in the Kuwait Group aquifer in the south-western part of the country is Na–Cl type (Fig. [5\)](#page-10-0) and in the Dammam Formation aquifer is Na–Cl to SO_4 – Na $(Cl > SO₄)$ type. The brackish water in the Dammam Formation aquifer in the southern, south-western, and central parts of Kuwait ranges in salinity between 2500 and 6900 mg/l with salinity increasing towards east and northeast. The water type changes from sulphate–chloride to chloride–sulphate in the same direction. The water becomes saline to brine $(>10,000 \text{ mg/l}$ and more) further to the east, north-east, and north-west with chloride predominating over sulphate (chloride–sulphate type). This change in water type can be related to the movement of the groundwater from its recharge zone in Saudi Arabia to its zone of discharge near the Arabian Gulf where water becomes almost stagnant or of very slow movement (Mukhopadhyay et al. [1996](#page-18-0)).

δ^2 H- δ^{18} O relationships in rainwater

The δ^2 H– δ^{18} O of the rainwater samples show a large variation (δ^2 H -4 to +1 ‰ and δ^{18} O -4 to +1 ‰), with enriched values during February–May and depleted values in November and December (Table [2](#page-7-0); Fig. [6\)](#page-10-0). The regression line for the rainwater samples of Kuwait (i.e. Kuwait Meteoric Water Line, KWML) is:

$$
\delta^{2}H(\mathcal{C}_{oo}) = 6.1(\pm 0.3) * \delta^{18}O + 11.1(\pm 0.4)[n = 35, R^{2} = 0.96]
$$
 (1)

The KMWL falls above the global meteoric water line (GMWL) [GMWL defines the relationship between ²H and 18 O in precipitation on a global scale and has the relation: $\delta^2 H = 8 * \delta^{18} O + 10$ (Craig [1961](#page-18-0))].

Table 1 Results of chemical analysis of groundwater samples

Table 1 continued

Not many studies have been reported on the isotopic composition of rainwaters in this region. Michelsen et al. [\(2015](#page-18-0)) carried out an isotopic study on 28 rain events that occurred in Riyadh between 2009 and 2013 and found that the rain samples showed $\delta^{18}O$ and δ^2H values scattering between -6.5 and $+9.5$ % and between -30 and $+50$ % V-SMOW, respectively. The isotopic variations observed in the rainwater samples at Riyadh are comparatively larger than seen at Kuwait. For comparison purpose, the North Oman Meteoric Water Line (NOMWL) $(\delta^2 H = 8 \delta^{18} O + 16$; Gat and Carmi [1970\)](#page-18-0) is also shown in the figure.

Relation between the isotopic composition of rainwater and climatic factors

The Middle East region is under the influence of three types of moisture influx, namely the Mediterranean and Atlantic Ocean (winter season—from December to February) and the monsoon front (autumn season— September to November). Generally, isotopic composition of rainwater samples depends on the origin of moisture source (inland, sea), geographical (latitude, longitude, altitude), rainfall characteristics (amount, intensity) and climatic and meteorological conditions (temperature, relative humidity, atmospheric pressure, wind direction, and speed).

To understand the effect of various climatic factors on the isotopic composition of rainwater, a continuous measurement of atmospheric temperature $({}^{\circ}C)$, relative humidity (%), rainfall (mm), barometric pressure (mbar), wind direction (degree), wind speed at 1, 4, 6, 8 10 m height (m/s), solar radiation (W/m²), etc. were continuously measured at all rainwater sampling locations using standard methods.

From the daily averages of the measured climatic and meteorological parameters figure, it was observed that in late November and December, at rainwater sampling locations away from the coast such as Um Omara and Al-Wafra the rainy days are associated with high-speed winds, whereas at locations close to coast (KISR, Al-Mutla, Ras Al-Subiyah, etc.) that is not the case. This indicates that high-speed winds are responsible for bringing the moisture from a distance source (Mediterranean Sea/Atlantic Ocean) for condensation (rain-out process). Also, it was observed that rainfall is proportional to relative humidity and wind speed. In February, the relative humidity and amount of rainfall are less and wind speed is much higher compared to late November and December. This probably indicates monsoonal winds.

| Location | Months | $\delta^{18}O$ (%o) | $\delta^2 H$ (%) | d -Excess $(\%_0)$ | Location | Months | $\delta^{18}O$ (%o) | δ^2 H (‰) | d -Excess $(\%_0)$ |
|--------------------|--------------|---------------------------------|--------------------------|--------------------------|---------------------------|----------|--------------------------|--------------------------|--------------------------|
| Al-Taweel | Nov 2012 | -1.0 | $+3.8$ | $+11.8$ | KOC North Kuwait Nov 2012 | | -3.3 | -6.7 | $+19.7$ |
| | Dec 2012 | -1.9 | -1.6 | $+13.6$ | | Dec 2012 | -3.3 | -6.8 | $+19.6$ |
| | May 2013 | $\overline{}$ | $\overline{}$ | $\overline{}$ | | May 2013 | -3.8 | -18.1 | $+12.3$ |
| Um Al-Haiman | Nov 2012 | -1.4 | $+1.2$ | $+12.4$ | Um Omara | Nov 2012 | -2.9 | -6.0 | $+17.2$ |
| | Dec 2012 | -1.2 | $+2.3$ | $+11.9$ | | Dec 2012 | -2.7 | -5.2 | $+16.4$ |
| | Feb 2013 | $\qquad \qquad -$ | $\overline{}$ | $\overline{}$ | | Feb 2013 | -0.8 | $+5.4$ | $+11.8$ |
| | Mar 2013 | -0.8 | $+9.9$ | $+16.3$ | | Mar 2013 | -0.8 | $+6.0$ | $+12.4$ |
| | Apr 2013 | $\overline{}$ | $\overline{}$ | - | | Apr 2013 | $\overline{}$ | $\overline{}$ | $\overline{}$ |
| | May $2013 -$ | | - | - | | May 2013 | -2.7 | -8.0 | $+13.6$ |
| Al- Huwaimliyah | Nov 2012 | $\hspace{0.1mm}-\hspace{0.1mm}$ | - | $\overline{}$ | Ras Al-Subiyah | Nov 2012 | -0.7 | $+4.3$ | $+9.9$ |
| | Dec 2012 | -0.9 | $+2.1$ | $+9.3$ | | Dec 2012 | -4.0 | -12.6 | $+19.4$ |
| | Feb 2013 | -0.5 | $+8.4$ | $+12.4$ | | Feb 2013 | $+0.5$ | $+13.2$ | $+9.2$ |
| | Mar 2013 | -0.5 | $+3.9$ | $+7.9$ | | Mar 2013 | $\overline{}$ | | $\overline{}$ |
| | Apr 2013 | $\overline{}$ | $\overline{}$ | $\overline{}$ | | Apr 2013 | $\overline{}$ | | $\overline{}$ |
| | May 2013 | $\overline{}$ | $\overline{}$ | $\overline{}$ | | May 2013 | -3.8 | -18.1 | $+12.3$ |
| KISR | Nov 2012 | -1.7 | $+1.3$ | $+14.9$ | Al-Wafra | Nov 2012 | $\overline{}$ | | $\overline{}$ |
| | Dec 2012 | -1.6 | -0.3 | $+12.5$ | | Dec 2012 | -2.7 | -5.7 | $+15.9$ |
| | Feb 2013 | -0.1 | $+9.2$ | $+10.0$ | | Feb 2013 | $+0.9$ | $+16.9$ | $+9.7$ |
| | Mar 2013 | $+0.9$ | $+16.5$ | $+9.3$ | | Mar 2013 | $+0.8$ | $+17.9$ | $+11.5$ |
| | Apr 2013 | | $\overline{}$ | - | | Apr 2013 | $+1.0$ | $+18.1$ | $+10.1$ |
| | May 2013 | $\overline{}$ | $\overline{}$ | $\overline{}$ | | May 2013 | $\overline{}$ | - | - |
| Al-Mutla | Nov 2012 | -3.1 | -6.1 | $+18.7$ | Ras Az-Zoor | Nov 2012 | $\overline{}$ | $\overline{}$ | $\overline{}$ |
| | Dec 2012 | -3.2 | -7.2 | $+18.4$ | | Dec 2012 | -2.6 | -6.1 | $+14.7$ |
| | Feb 2013 | -0 | $+12.6$ | $+12.6$ | | Feb 2013 | $+0.4$ | $+12.9$ | $+9.7$ |
| | Mar 2013 | $+0.3$ | $+12.4$ | $+10.0$ | | Mar 2013 | $+0.2$ | $+12.3$ | $+10.7$ |
| | Apr 2013 | | | - | | Apr 2013 | $\qquad \qquad -$ | - | $\overline{}$ |

Table 2 Isotopic results of rainwater samples

As mentioned earlier, the rainwater samples collected in November and December are depleted in δ^2 H compared to February samples. However, the climatic and meteorological parameters fairly remained the same during those months. Hence, the observed difference in isotopic composition of rainwater collected in November/December and February is attributed to origin of moisture source. The moisture source from the Mediterranean Sea/Atlantic Ocean will be depleted owing to far-off distance of the source from Kuwait (continental effect).

δ^2 H- δ^{18} O relationships in groundwater samples

The δ^2 H and δ^{18} O of most of the groundwater samples of both the Kuwait Group aquifer and Dammam Formation aquifer (Fig. [7](#page-11-0)) showed that they fall below the KMWL with their regression equation (called as regression line or evaporation line), respectively, being:

$$
\delta^2 H = 1.6 * \delta^{18} O - 20.3 [n = 14, R^2 = 0.59]
$$
 (2)

$$
\delta^2 H = 3.5 * \delta^{18} O - 11.7 [n = 16, R^2 = 0.60]
$$
 (3)

Also, it is seen from the figure that the groundwater samples showed large variations in their isotopic composition.

δ^{13} C, ¹⁴C, and ³H content of groundwater samples

Groundwater samples measured very low environmental ³H values (Kuwait Group aquifer 0.16 to 1.01 TU; Dam-mam Formation aquifer 0 to 0.73 TU (Table [3\)](#page-8-0). Since most of the groundwater samples measured very low tritium values (close to the analytical error; ± 0.5 TU), they are mostly old groundwaters and not modern groundwaters. Hence, 14 C content of the dissolved inorganic carbon (DIC) of the groundwater samples was analysed and found to range from 4.6 to 38.3 pMC in the Kuwait Group aquifer and from 6 to 17.5 pMC in the Dammam Formation aquifer. The δ^{13} C values range from -8.1 to -13.6 ‰ for the groundwaters of Kuwait Group aquifer and from -7.3 to -12.3% for the groundwaters of the Dammam Formation aquifer.

Corrections to apparent 14 C ages are normally done based on either mass balance of 13 C or major chemical

a Kuwait Group and

b Dammam Formation aquifers

constituents. Several mass balance correction models have been proposed in the literature. The most popular correction models are the 13 C-based Pearson's model (Pearson [1992\)](#page-19-0), the chemistry-based Tamer's model (Tamer [1967](#page-19-0)), and the Fontes and Garnier model (Fontes [1992\)](#page-18-0), a combination of chemistry and 13 C.

Kuwait Group and Dammam Formation aquifers showed decrease in ¹⁴C values with enrichment in $\delta^{13}C$ along the flow path (Fig. [8](#page-11-0)). Dissolution of carbonatebearing minerals (calcite, aragonite, dolomite, etc.) and oxidation of organic matter through bacterial reduction are the two dominant processes that govern the ${}^{13}C_{\text{DIC}}$ systematics of a sedimentary aquifer system. While the first process enriches $\delta^{13}C_{\text{DIC}}$, the second depletes it by producing $HCO₃$ (depleted in ¹³C) from the oxidation of organic matter along the flow paths. Pearson's model and Tamers' model take into account carbonate dissolution and soil gas $CO₂$ dissolution.

Hence in the present study, Pearson's model and Tamers' model were used to obtain the ^{14}C ages of the groundwater samples, along with other models (Vogel's model and statistical model) (Table [4\)](#page-12-0). As shown in the table, the Pearson's model ages are relatively higher compared to the other models except for two sampling sites. Tamer's model ages for Kuwait Group aquifer range from 5069 to 23,976 a, B.P, and that for the Dammam

Fig. 5 Piper diagram of groundwater samples

Fig. 7 δ^{18} O versus δ^2 H of groundwater samples

Formation aquifer range from 5874 to 20,074 a, B.P 1^{14} C radioactivity at time t, $A_t = A_0 e^{-\lambda t}$, where ' λ ' is its radioactive decay constant $(=1.2097 \times 10^{-4} \text{ a}^{-1})$].

Discussion

Origin of cloud mass

The large variation seen in the δ^2 H and δ^{18} O of rain-water of Kuwait (Fig. [6](#page-10-0)) is a typical characteristic seen in arid and semi-arid regions. Comparatively, a higher intercept of KMWL (~ 11.1) than GMWL indicates the difference in climatic conditions (relative humidity and temperature) under which the cloud is formed at its source. A lesser slope of the KMWL (\sim 6.1) in Eq. [\(1](#page-4-0)), compared to the Global Meteoric water Line (GMWL), along with positive δ -values of the rainwater samples, indicates evaporation of falling raindrops (i.e. secondary evaporation) of the less intense rains occurring under dry atmospheric conditions. Owing to the fact that Kuwait receives scanty rain (118 mm annual) with very low intensity, a clear amount effect in the isotopic composition of the precipitation was not observed. Thus, the observed large variation in the isotope composition of precipitation is attributed to the varying moisture sources and thus the associated continental effect not due to amount effect.

Dansgaard [\(1964](#page-18-0)) defined the d-excess as d-excess = δ^2 H–8 * δ^{18} O. The *d*-excess is a useful tracer of vapour source and has been related to meteorological conditions at vapour source regions and to vapour recycling over the continents. The d-excess indicates the effect

Fig. 8 δ^{18} O versus *d*-excess of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

of secondary evaporation. The global mean value of dexcess is approximately $+10$ ‰. Different studies have used the d-excess parameter to investigate the sources of water vapour over the Middle East region (Celle-Jeanton et al. [2001\)](#page-18-0).

As mentioned before, the Middle East region is under the influence of three types of moisture influx, namely the Mediterranean, Atlantic Ocean, and the monsoon front. The d-excess value of the rainwater samples was computed (Table [2](#page-7-0)) and found to range between $+19.7$ % (November–December) and $+7.9$ ‰ (February–May). The low values of d-excess during February–May probably indicate that the source of moisture could be the nearby Arabian Gulf with a component of recycled water through secondary evaporation during condensation under dry atmospheric conditions. A high *d*-excess value $(+19.7 \text{ %})$ with depleted isotopic values in December rainwater samples at Kuwait Oil Company (KOC)—North Kuwait $(\delta^{18}O = -3.3\%$ and $\delta^2 H = -6.8 \%$ = -9.9 % = μ Mediterranean rains, as the air mass originating from the Mediterranean Sea is generally characterized by relatively large d-excess $(d = +22 \text{ %})$ (Gat and Carmi [1970\)](#page-18-0).

As the cloud mass moves from a source area towards the continent, depletion in the isotopic composition of rainwater occurs (continental effect). Also, the rainwater samples collected during November–December showed a decreasing trend in their d-excess values from north to south, possibly reflecting the direction of the Mediterranean moisture-bearing winds in those months or indicating the multiple sources of the atmospheric moisture or both. During February–May, d-excess of the rainwater samples does not change significantly across the country and the source of moisture could be nearby Arabian Gulf with a component of recycled water through secondary evaporation during condensation under dry atmospheric conditions. The higher d-excess in case of NOMWL is attributed to the Mediterranean source.

δ^2 H and δ^{18} O composition of the initial recharge waters

Figure [7](#page-11-0) shows that the regression (evaporation) lines of Kuwait Group and Dammam Formation aquifer,

Screen Depth (m)

Screen Depth (m

Screen Depth (m)

Depth

 \mathbf{E}

creen

respectively, intersect the δ^{18} O and δ^2 H axis (shown as vertical arrows with KG and DM) at $\delta^{18}O = -8.8 \%$ and $\delta^2 H = -40\%$ and $\delta^{18}O = -7.2\%$ and $\delta^2 H = -32\%$. The intersected values represent the isotopic composition of initial waters at the recharge area, and hence, the same can be used to confirm the location of the recharge areas in the highlands of Saudi Arabia and to estimate volumetric mixing between the two aquifers.

It is interesting to note in the figure that the initial recharge waters of the underlying Dammam Formation aquifer are relatively less depleted than that of the overlying Kuwait Group aquifer. This suggests that the Kuwait Group aquifer was recharged relatively during more humid period than the Dammam Formation aquifer. Also, the regression lines for the Kuwait Group and Dammam Formation aquifers intersect each other on the GMWL.

Interrelationship between the aquifers

The knowledge of possible interconnection between different aquifers in a multi-aquifer system is very essential for groundwater resource evaluation as well as for forecasting water-quality issues (increase or decrease) by leakage from above or below, particularly in case of carbonate aquifers, as the interconnection may be difficult to establish by piezometric studies alone owing to highly heterogeneous and non-isotropic nature of the geology. Stable isotopes such as ${}^{2}H$ and ${}^{18}O$ along with radioactive 3 H and 14 C can be used to establish interconnection between the various aquifers.

Fig. 9 δ^{13} C versus ¹⁴C plot of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

Fig. 10 d-Excess versus screen depth of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

The Kuwait Group groundwaters near the coast (HS-116, WT03), at the central parts (SU-85A), and near the south-west border (UG 62) fall on regression line for the Dammam Formation aquifer (Fig. [7](#page-11-0)), indicating that possibly the two aquifers are interconnected at those places. Similarly, the groundwaters of the Dammam Formation at the south (near Al-Wafra) fall on the regression line for the Kuwait Group aquifer, indicating the interconnection between the two aquifers. The piezometric study of the two aquifers also corroborates the same.

Groundwater ages and recharge processes

Highly lesser slopes of the δ^2 H $-\delta^{18}$ O regression lines of the groundwater samples of both Kuwait Group and Dammam Formation aquifers (Eqs. [2](#page-7-0), [3\)](#page-7-0), in comparison with that of the KMWL, indicate an evaporation effect in their stable isotopic composition. The evaporation effect could be due to either near-surface evaporation in the unsaturated zone during recharge or a secondary evaporation of falling raindrops or both.

Although most of the groundwater samples from both the aquifers indicate evaporation effect (Fig. [7](#page-11-0)), the samples from the Kuwait Group aquifer at sites SU-85A (in the central part) and UG-65 (near the Saudi Arabia border in the south-west) fall on the KMWL with depleted isotopic values. This indicates that these groundwaters are nonevaporated precipitational recharge. Similarly, some of the groundwater samples of the Dammam Formation aquifer located in the south-west border (SH-C-32, SH-D-6, SH-E-25, SW-4) fall close to the KMWL with depleted values, which again possibly indicates that they are non-evaporated precipitational recharge.

The conversion of stable isotopes to d -excess is also being exploited as a complementary tool to understand the

groundwater samples

processes of recharge (Abass et al. [2010](#page-18-0)). The calculated dexcess values of the groundwater samples are given in Table [3](#page-8-0) and Fig. [9.](#page-13-0) A wide range of d-excess of the groundwater samples is seen (Kuwait Group aquifer: $+16.0$ to -20.6 %; Dammam Formation aquifer: $+22.8$ to -19.6%). Most of the groundwater samples from the Kuwait Group aquifer (Fig. [9a](#page-13-0)) have d-excess value less than the global mean value (\sim +10 ‰). This indicates the evaporation of recharging rainwaters prior to infiltration. However, since the KMWL (Fig. [6](#page-10-0)) shows a lesser slope (6.1) than that of the GMWL (\sim 8), the raindrops undergoing evaporation during their fall could also be another contributing factor to the lesser d-excess of groundwater.

In the Dammam Formation aquifer, some of the groundwater samples have d-excess value close to a value of 20 (Fig. [9](#page-13-0)b), which is a typical value for moisture sources from Mediterranean Sea. There is no correlation between d-excess and the screen depth of the wells (Fig. [10\)](#page-13-0). It is also interesting to note that the samples from central, south, and along the coast (i.e. away from the recharge area located at Saudi Arabia) of both the aquifers showed negative d-excess values with heavier 18 O and 2 H (shown in eclipse in the figure) indicating greater degree of evaporation prior to recharge. Thus, the d-excess of the groundwater samples indicates that the groundwater system is a mixture of so many types of water with different origin (recharge source) and history (time, evaporation, climate).

The corrected 14 C ages showed large variation for both the Kuwait Group and Dammam Formation aquifers (Fig. 11). The ^{14}C age of a groundwater system is governed by its flow paths through the geological formation and the distance from the recharge area. From the ¹⁴C versus $\delta^{18}O$ plot, it can be seen that in the case of Kuwait Group aquifer, three different groups of groundwater are discerned: Group 1 (samples at intermediate depths in the south-west and central parts)—low ¹⁴C ages (\sim 5000 B.P)

Fig. 12 δ^{18} O versus δ^{13} C of groundwater samples

Fig. 13¹⁸O versus screen depth of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

and depleted δ^{18} O isotopic values (-4.5 to -5.7 ‰); Group 2 (samples at deeper depths in the south-western part and at shallow depths along the coast)—intermediate 14 C ages

Fig. 14 δ^{13} C versus screen depth of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

(\sim 8000–10,000 B.P) and intermediate δ^{18} O isotopic values $(-2.5 \text{ to } -3.5 \text{ %})$; and Group 3 (deeper ($> 300 \text{ m}$) samples from the south—higher ¹⁴C ages (\sim 9000–16,000 B.P) and enriched δ^{18} O isotopic values (\sim 0–1 ‰). This suggests that the deeper groundwater in the south is recharged during arid phase, whereas the intermediate groundwater in the southwest and central parts is recharged during the humid phase. The deeper groundwater in the south-western part and the shallow groundwater along the coast are of mixed water of several origins.

The samples from the Kuwait Group aquifer at sites SU-85A (in the central part) and UG-65 (near the Saudi Arabia border in the south-west) (ref. Figure [3](#page-4-0)), falling on the KMWL with depleted isotopic values and having low 14 C values (38.3 and 29.2 pMC, respectively) and measurable tritium content (0.51 and 0.75 TU, respectively) (ref. Table [3](#page-8-0)), possibly indicate a mixing between (young) recent non-evaporated precipitational recharge and old waters in the aquifer system.

Fig. 15¹⁴C versus screen depth of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

In the Dammam Formation aquifer, there are two groups of groundwater, namely Group 1 (wells in the central part and with depth less than 350 m)—enriched δ^{18} O isotopic values (0 to -2%)—and Group 2 (wells in the south-western part and with depth more than 350 m)—depleted δ^{18} O isotopic values (-5 to -7 ‰), although the range of 14 C ages of both the groups are the same. Out of the two groups, Group 2 samples do not show evaporation effect, as they fall on the KMWL (Fig. [7](#page-11-0)) and they are very old waters $(>8000 \text{ a}, B.P)$. Highly depleted δ^{18} O values and higher 14 C model ages of the deeper groundwater in the south-western part suggest that they were recharged in the past at cooler climatic conditions (humid phase). Since the Group 2 samples fall close to the intercept between the KMWL and the regression line for the Dammam Formation, it appears that the recharge to the Dammam Formation significantly occurred during over 8000 a, B.P.

Fig. 16¹⁴C versus EC of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

The δ^{18} O versus δ^{13} C (Fig. [12](#page-15-0)) showed that both isotopically (δ^2 H and δ^{18} O) enriched and depleted groundwater contained similar range of enriched δ^{13} C values (-6) to -12%), which is indicative of samples away from the recharge areas.

The plot of well depth (screen depth) versus $\delta^{18}O$ and δ^2 H of the groundwater samples of Kuwait Group aquifer (Fig. [13a](#page-15-0)) revealed no good correlation in the shallow depths $(0-50 \text{ m})$, but at deeper depths $(>50 \text{ m})$ a fairly good correlation is observed. This suggests that the groundwater of Kuwait Group aquifer at shallow depths is fairly well mixed (no stratification), whereas at deeper depths they are probably stratified. At deeper depths, the groundwaters are isotopically depleted compared to the shallower depths. The variations in $\delta^{18}O$ and δ^2H isotopic values at shallow and deeper zones reflect the recharge histories and the associated isotopic content of the initial recharging rainwaters at the recharge area.

In the Dammam Formation aquifer, there are two groups of groundwater seen (Fig. [13b](#page-15-0)): Group 1—located at a depth less than 350 m and with enriched δ^{18} O and δ^{2} H isotopic values (0 to -2%) and Group 2—located at a

Fig. 17 EC versus screen depth of groundwater samples of a Kuwait Group and b Dammam Formation aquifers

depth more than 350 m and with depleted δ^{18} O and δ^{2} H isotopic values $(-5 \text{ to } -7 \text{ %})$, corroborating the findings from ¹⁴C versus δ^{18} O (Fig. [11](#page-14-0)).

A plot of δ^{13} C versus screen depth (Fig. [14\)](#page-15-0) and ¹⁴C versus screen depth (Fig. [15](#page-16-0)) also corroborates the aforementioned discussions on, stratification, or otherwise of the aquifers, recharge during older periods and climatic conditions, different flow paths, etc. Also, as seen from ^{14}C versus screen depth (Fig. [15a](#page-16-0)) in the Kuwait Group aquifer, samples located along the coast at shallow depths $(<57 \text{ m})$ are very old $(^{14}C \le 20$ pMC), compared to some of the deeper groundwater. These groundwater contains much higher EC $(41,600-77,730 \mu S/cm)$, compared to other Kuwait Group aquifer samples $(4550-8730 \text{ }\mu\text{S/cm};$ Fig. [16](#page-16-0)a) and the underlying Dammam Formation aquifer samples (3200–8730 μ S/cm; Fig. [16b](#page-16-0)). As substantiated by δ^{18} O (Fig. [11;](#page-14-0) Group 2), this indicates possibly mixed nature of groundwater with several origins along the coast.

The Dammam Formation aquifer samples contain low 14° C values: 6–28 pMC (Fig. [15b](#page-16-0)). The 14° C versus EC for both the Kuwait Group (Fig. [16](#page-16-0)a) and Dammam Formation (Fig. [16b](#page-16-0)) aquifers does not indicate any correlation, which is possibly due to various intermixing processes occurring between various formations along the flow.

A plot of EC versus depth of sample of the Kuwait Group aquifer (Fig. 17a) indicates that, except for the shallow groundwater along the coast (Group 2; Fig. [11](#page-14-0)) which shows large variation in EC $(18,330-77,730 \text{ }\mu\text{S/cm})$, the others show relatively lesser EC (50–8780 μ S/cm). In case of the underlying Dammam Formation aquifer (Fig. 17b), the groundwater samples below 350 m show similar EC (4530–3710), indicating probably the well-mixed condition.

Based on the above results and discussion, a refined conceptual flow model of the groundwater system is given in Fig. [18](#page-18-0).

Conclusions

A detailed environmental isotopic characterization of the one of the important shared aquifer systems in the region has been carried out for the first time. The aquifer system mostly contains palaeo-groundwaters, i.e. not part of the actively recharged systems, and hence, the resources may be finite and their exploitation is mining.

The aquifer system is quite complex, containing several types of water having different origin (recharge area) and history (time, evaporation, climate). The groundwater flow direction is rather quite complex and not distinct, although the general direction is from south-west to north-east towards the discharge zones near the Arabian Gulf where the water becomes almost stagnant or of very slow movement. Interconnection between the two main aquifers (Kuwait Group and Dammam Formation) established near the coast and south-west border of the country. The isotopic signatures of the initial recharge waters of the groundwater aquifer system deciphered which can be used for the confirmation of the location of recharge area which lies in the Saudi Arabia. Palaeo-climatic excursions between arid $({\sim}9000-16,000$ a, B.P) and humid phases $({\sim}5000-10,000$ a, B.P) during the Holocene and Late Pleistocene in this Gulf region has been obtained based on isotopic composition of deeper groundwaters (Tertiary sediments) as proxies from the present investigation and reported for the first time.

From the present study, the existing conceptual groundwater flow model for the aquifer system has been refined. The updated conceptual model will lead to a more precise numerical model that will help in devising plans to ensure the sustainable exploitation of the two aquifers without jeopardizing the quality and/or the volume of the

Fig. 18 Refined conceptual groundwater flow model of the aquifer system (modified after Senay et al. [1987](#page-19-0))

water produced. Also, as not abundant information on the isotopic characteristics of one of the shared aquifer systems in the region is available, the data generated from the present study will benefit water researchers and managers in the region.

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