Hydrochemistry of Umm Er Radhuma Groundwater

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Abstract

Umm Er Radhuma Aquifer (UER) is the most important groundwater aquifer in Saudi Arabia, extending over 1.6 M·km² in the eastern part of the Arabian Peninsula, forming the main aquifer throughout the Rub’ Al-Khali (RAK). Groundwater salinity increased from west to east, reaching more than 27,000 mg/L near the border with the United Arab Emirates, where a Na+-Ca2+-Cl−-SO42− water type dominated. Gibbs diagrams indicated that the dissolution/precipitation of carbonates and evaporation/precipitation of minerals, especially anhydrite, gypsum, and halite account for the solutes and salinity in groundwater. Most of the samples plot above the 1:1 line of (Ca2+ + Mg2+) against HCO3−, indicating other sources of Ca2+ and Mg2+ in the groundwater along with dolomite and calcium carbonate minerals. Phreeqc model indicated that the main clay minerals are kaolinite and gibbsite which had major effect on the cation exchange process as indicated by the Chloro-Alkaline index (CAI), where most of groundwater samples had values greater than zero which indicated the occurrence of reverse ion exchange between the groundwater and its host aquifer. The water type Na+-Ca2+-Cl−-SO42− dominated in the eastern part of the aquifer as the anaerobic conditions prevailed and the reduction of sulphate took place.

Keywords

Hydrochemistry, Umm Er Radhuma Aquifer, Groundwater, Water-Rock Interaction

1. Introduction

Groundwater chemistry is a function of many chemical and physical factors such as the mineral composition, lithology of the aquifer, oxidation reduction reac-
tions, natural or artificial recharge and discharge, weathering, exchange reactions (Elango & Kannan, 2007). Understanding the hydrochemistry of groundwater is of great importance, especially in such arid areas like Saudi Arabia where groundwater provides the major water supply.

The Kingdom of Saudi Arabia is commonly regarded as a dry country due to low precipitation and high evaporation rate. The mean annual rainfall across the Arabian Peninsula is less than 200 mm, and the temperature reaches more than 50°C in summers. Though no perennial surface water in the kingdom, groundwater is the most important natural water resource which provides the kingdom with water supply for domestic and agricultural purposes. Among the most important groundwater reservoirs in Saudi Arabia is Umm Er Radhuma aquifer (UER) as many of Arab Gulf states depend on it for different purposes. It is extending over 1.6 M·km² in the eastern part of the Arabian Peninsula, forming the main aquifer throughout the Rub’ al Khali (RAK) Desert where it is located in the southern areas of Saudi Arabia (Figure 1). RAK is considered the world’s largest continuous sand desert, covering an area of 522,340 km².

The Umm Er Radhuma (UER) aquifer has been investigated geologically, hydrogeologically since the early 1940s. Some of the previous research is summarized by Powers et al. (1966), Sogreah (1968), Watuki (1968, 1971), Italoconsult (1969), Dinçer et al. (1974), BRGM (1976, 1979), GDC (1979), Shampine et al. (1979), Al Bassam (1983, 1987), MOWE (2008). MEWA (2017) studied the general hydrochemistry of Umm Er Radhuma aquifer. However, further hydrochemistry investigations are required to identify in detail the origin and sources of salinity in the groundwater. This is what the current paper is trying to seek.

2. Geology and Hydrogeology

The Late Paleocene to Early Eocene sediments of Umm Er Radhuma formation
had deposited during major transgression where marine conditions prevailed on the Arabian Peninsula as far as Jordan, Iraq, Oman and Yemen (Ziegler, 2001). Calcareous shales deposited at the base of the formation followed by thick succession of carbonate rocks. The sedimentation took place on a wide carbonate shelf, which was distorted partly by tectonic movements during the movement of the Arabian plate into a series of deeps and shallows (Figure 2). A compressional force during the movement led the hypersaline groundwater from the Wasia-Biyadh aquifer to be injected through the deep faults into the overlying beds. This process might interpret the dolomitization of Umm Er Radhuma limestone, in which the dolomite replaced calcite and aragonite in association with the precipitation of secondary anhydrite. On the other hand, the dolomitization in the southern portion might be attributed to the leakage from the overlying anhydrite and evaporates bed (Rus formation). Thick calcarenite beds and reef type carbonates are contained in the central and southern part of the formation which were deposited around paleo-highs. Marls and shales occur between the carbonate units of the upper part of the formation, while cherts occur sporadically throughout the central and southern part. The formation crops out along the northwest-southeast trending belt from Rafha in the north to east of Al Kharj with a mean thickness of about 350 m, and it gets thicker in the central part of the Rub’ Al Khali Basin, reaching more than 600 m (MEWA, 2017). The transmissivity ranges between $7.2 \times 10^{-5}$ m$^2$/s from $5.2 \times 10^{-1}$ m$^2$/s, and the conductivity varies between $2.9 \times 10^{-7}$ m/s and $8.8 \times 10^{-3}$ m/s, with an average of $1.6 \times 10^{-5}$ m/s. The wide range of the values is caused by the varying degree of karstification. The storage coefficient varies between $3 \times 10^{-4}$ and $3 \times 10^{-3}$ while the specific yield ranges from Sy = 1% to 7% (MEWA, 2017).

**Figure 2.** Schematic diagram illustrating the dolomitization of the limestone through interaction with high saline groundwater from the underlying aquifers.
3. Materials and Methods

Groundwater Sampling and Laboratory Analyses

The data in this paper was carried out by the Ministry of Environment Water and Agriculture in association with the Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) as an internal report project, titled “Detailed Groundwater Resources Studies in The Rub’ Al Khali Desert”, in addition to a historic data compiled from BRGM (1976). 44 groundwater samples have been collected by the GIZ during field trips from November 2010 to December 2011. Three samples were taken at each well for TDS, major cations, and major anions. Forty four Groundwater samples have been collected in 100 ml polyethylene screw-cap bottles which were rinsed three times with the water to be sampled. All samples were filtered using 0.45 μm filter and preserved by cooling. Additionally, nitric acid (HNO3 70%) has been added to samples dedicated for cation analysis for further preservation. Field measurements included pH, EC, T, dissolved oxygen, bicarbonate and hydrogen sulfide using a flow-through-cell and multi-parameter pocket meters (Multi 340i, WTW, Germany). Moreover, groundwater samples were collected for trace elements in 250 ml polyethylene bottles. Samples were then shipped in cooling boxes to the hydrochemical laboratory in Darmstadt Technical University, Germany. The following standard analytical techniques were applied to investigate the hydrochemical composition of groundwater samples:

- Ion chromatography (IC; major ions);
- Atomic Adsorption Spectrometry (AAS; Fe2+);
- Photometric tests (B, SiO2);
- Gravimetry (TDS);
- Atomic Adsorption Spectrometry, ICP/MS, and ICP-OES (trace elements).

Phreeqc is a computer program written in the C programming language which has been designed to conduct a broad variety of aqueous geochemical calculations. Phreeqc has capabilities for 1) calculation of speciation and saturation-index, 2) reaction-path and advective-transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface-complexation reactions, and ion-exchange reactions, and 3) inverse modeling, which identifies the mole transfers that account for composition changes between waters a long flow path (Parkhurst, 1995).

4. Results and Discussion

According to the statistical summary of the hydrochemical data of the groundwater samples of Umm Er Radhuma aquifer (Table 1 & Figure 3), most of the samples are fresh (<1000 mg/l) to slightly saline near the outcrops (Figure 3), where it is characterized by a Ca$^{2+}$-SO$_4^{2-}$ water type. Low salinity is also observed in the Dhofar Mountains (Oman) due to freshwater recharge that may be responsible for the lower saline groundwater tongue extending from the Dhofar Mountains to the north. However, salinity increases from west to east, where the
Figure 3. TDS distribution of the groundwater samples for Umm Er Radhuma aquifer.

Table 1. Chemical analyses data for the groundwater of Umm Er Radhuma aquifer (in ppm).

| Well     | LAT      | LONG     | pH  | EC µS/cm | TDS  | Ca²⁺  | Mg²⁺  | Na⁺  | K⁺  | Cl⁻  | HCO⁻₃ | SO₄²⁻ |
|----------|----------|----------|-----|----------|------|-------|-------|------|-----|------|-------|-------|
| GHFH-801 | 21.02850 | 55.16011 | 7.19| 15,910   | 10,900| 477.0 | 271.0 | 2570 | 76.1| 5180 | 216.6 | 972.0 |
| OLTD40   | 22.39989 | 53.96625 | 7.90| 16,500   | 10,800| 501.0 | 186.0 | 2920 | 93.9| 5300 | 308.1 | 697.0 |
| S-397    | 23.44653 | 50.89114 | 7.38| 591.0    | 4810  | 591.0 | 250.0 | 998.0| 53.9| 734.0 | 115.9 | 2330 |
| OLTD13   | 23.86678 | 51.30725 | 8.79| 9670    | 6870  | 485.0 | 199.0 | 1340 | 72.6| 2360 | 137.3 | 1830 |
| OLTD52   | 22.19956 | 55.50636 | 7.00| 33,800   | 4100  | 1050  | 395.0 | 5130 | 113.0| 8150 | 176.1 | 2210 |
| OLTD39   | 22.46494 | 53.98664 | 6.80| 17,720   | 10,700| 569.0 | 193.0 | 3060 | 98.2| 5690 | 332.5 | 651.0 |
| JZTD2    | 18.76103 | 49.44333 | 7.34| 12,320   | 7285  | 630.0 | 362.0 | 1660 | 95.1| 3270 | 48.8  | 1940 |
| MKSR-801 | 21.26433 | 49.54578 | 6.72| 2610    | 2309  | 254.0 | 99.5  | 213.0| 34.5| 142.0 | 277.6 | 1160 |
| 7-S-11   | 20.53239 | 47.59878 | 6.79| 2740    | 1744  | 210.7 | 78.6  | 224.3| 10.0| 594.8 | 173.9 | 395.3 |
| Location          | Latitude | Longitude | Depth (ft) | Temperature (°F) | Pressure (psi) | Flow Rate (gpm) | Efficiency (%) |
|-------------------|----------|-----------|------------|------------------|---------------|----------------|----------------|
| 7-S-25            | 22.71242 | 53.28344  | 7.75       | 66,000           | 49,500        | 2520           | 896.0          |
| SUHL-801          | 21.59570 | 53.18430  | 7.15       | 5390             | 3739          | 201.1          | 102.5          |
| KharkherNewWell   | 18.90000 | 51.18339  | 7.68       | 2270             | 1932          | 194.0          | 105.0          |
| JZTD1             | 18.08494 | 47.96872  | 7.09       | 2730             | 1770          | 101.0          | 52.2           |
| KIDNSRAK-804      | 21.71410 | 53.34540  | 7.47       | 7530             | 5782          | 453.0          | 176.0          |
| RAK-05O           | 19.25069 | 49.84586  | 6.96       | 2480             | 1887          | 242.3          | 98.1           |
| PYDH-LKSR-801     | 22.14967 | 48.23289  | 6.90       | 1650             | 1044          | 118.9          | 47.1           |
| RAK-08O           | 20.83889 | 49.79500  | 6.97       | 2660             | 1885          | 303.4          | 106.9          |
| RAK-08O           | 20.83889 | 49.79500  | 6.97       | 2660             | 1885          | 303.4          | 106.9          |
| RAK-06            | 20.39725 | 50.96567  | 7.05       | 2730             | 2010          | 236.2          | 111.2          |
| PAYD-801          | 22.04542 | 48.19744  | 7.40       | 572              | 44.3          | 190.6          | 28.9           |
| TKMN-803          | 22.20667 | 49.65689  | 7.45       | 2590             | 194.7         | 237.9          | 119.4          |
| RAK-EX-04         | 21.26444 | 49.54583  | 6.77       | 2680             | 1948          | 294.4          | 113.2          |
| RAK-EX-07         | 22.07611 | 49.66111  | 7.40       | 2860             | 2524          | 271.5          | 120.6          |
| RAK-EX-05A        | 21.16306 | 49.54611  | 7.10       | 3200             | 3546          | 505.0          | 192.2          |
| HFER-RBKL-801     | 23.09711 | 48.98550  | 6.87       | 1749             | 1140          | 50.5           | 84.1           |
| Well Al Bragh     | 21.79833 | 49.05378  | 7.27       | 1399             | 1000          | 104.0          | 55.9           |
| HDDH-801          | 21.79567 | 50.24681  | 7.05       | 2760             | 2320          | 257.0          | 107.0          |
| S-610             | 23.28025 | 51.09647  | 7.28       | 4960             | 3690          | 332.0          | 162.0          |
| S-646             | 23.31478 | 51.00728  | 7.26       | 5310             | 3780          | 286.0          | 151.0          |
| S-612             | 23.02275 | 51.10889  | 7.30       | 5220             | 3650          | 268.0          | 148.0          |
| Grada-01          | 22.27097 | 51.15928  | 7.34       | 8500             | 5200          | 257.0          | 140.0          |
| Grada-WW1         | 22.28719 | 51.14258  | 7.36       | 7970             | 4990          | 284.0          | 154.0          |
| 7-S-64            | 18.57017 | 48.78839  | 7.07       | 1777             | 1220          | 124.0          | 48.2           |
| Sul_12            | 20.07320 | 54.99260  | 7.01       | 8880             | 5358          | 386.0          | 110.0          |
| 7-S-29            | 19.71080 | 53.96380  | 7.34       | 3520             | 2575          | 183.0          | 122.0          |
| W7-S-84           | 19.91240 | 54.04070  | 7.27       | 3730             | 2573          | 142.9          | 106.3          |
| RAK-05E           | 19.25117 | 49.84561  | 6.95       | 2430             | 2145          | 300.8          | 106.8          |
| FRIS-801          | 20.40790 | 50.94010  | 7.00       | 2930             | 2260          | 189.2          | 88.8           |
| 7-S-XX            | 18.85581 | 51.12736  | 7.03       | 2200             | 1730          | 206.0          | 110.0          |
| KharkherBGCenter  | 18.89780 | 51.10250  | 6.99       | 2300             | 1905          | 215.4          | 116.0          |
| Kharkher_Desal    | 18.85967 | 51.13067  | 6.97       | 2230             | 1821          | 231.0          | 120.0          |
| 7-S-28            | 20.13660 | 54.93510  | 8.21       | 5550             | 3710          | 121.3          | 110.7          |
| ST16              | 19.34767 | 51.71422  | 6.90       | 2460             | 1530          | 143.0          | 72.4           |
| UumAlMulahWell    | 18.80419 | 50.02075  | 6.92       | 2810             | 2399          | 302.5          | 123.9          |
| 7-S-53            | 19.21733 | 51.25808  | 7.00       | 2200             | 1749          | 175.0          | 92.2           |
| S-699A            | 20.56910 | 53.09450  | 7.07       | 4010             | 2825          | 233.0          | 97.7           |
| S-688A            | 20.60100 | 52.72340  | 7.17       | 3260             | 2717          | 717            | 757.0          |
total dissolved solids (TDS) value reached more than 27,000 mg/L near the border with the United Arab Emirates, where a Na⁺-Ca²⁺-Cl⁻-SO₄²⁻ water type dominates (Figure 4).

Water-Rock Interaction and Sources of Solutes

Gibbs diagrams are considered an effective tool to identify the main geochemical processes which control the hydrogeochemical characteristics of groundwater in aquifers such as atmospheric precipitation, rock weathering, evaporation, and minerals precipitation. The diagrams describe the weight ratios of Na⁺/(Na⁺ + Ca²⁺) and Cl⁻/(Cl⁻ + HCO₃⁻) against TDS as shown in Figure 5, where most of the samples plot between the rock weathering and the evaporation zones. Therefore, the dissolution/precipitation of carbonates and evaporation/precipitation of minerals, especially anhydrite, gypsum, and halite are the major geochemical reactions which account for the solutes in groundwater.

The dissolution of carbonate minerals takes place when carbon dioxide infiltrates along with rainfall and surface water into the aquifer near the outcrops, leading to the formation of carbonic acid which dissociates carbonate minerals in the investigated aquifer according to the following equations:

\[
\begin{align*}
H_2O + CO_2 &= H_2CO_3 = H^+ + HCO_3^- \\
CaCO_3 + H^+ &\rightarrow Ca^{2+} + HCO_3^- \\
CaMg(CO_3)_2 + 2H_2O + 2CO_2 &\rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \\
CaSO_4 &\rightarrow Ca^{2+} + SO_4^{2-}
\end{align*}
\]

The dissolution of dolomite is well illustrated in Figure 6, where most of the cores of the dolomite rhombs undergo dissolution, which release equally charged amounts of (Ca²⁺ + Mg²⁺) and HCO₃⁻, respectively, according to Equations (2) and (3). Accordingly, samples should plot along the 1:1 line if dolomite is the only source of Ca²⁺ and Mg²⁺. According to Figure 7, most of the samples plot above the 1:1 line of (Ca²⁺ + Mg²⁺) against HCO₃⁻, indicating other sources of Ca²⁺ and Mg²⁺ in the groundwater along with dolomite and Calcium carbonate minerals.
Figure 4. Water type distribution for groundwater samples of Umm Er Radhuma aquifer.
Figure 5. Gibbs diagrams, illustrating the main geochemical mechanisms in groundwater.

Figure 6. Laboratory results RAK 05-E. (A) Core sample RAK 05-E. (B) Pie chart showing the results from the X-Ray Diffraction (XRD) Analysis. Core sample RAK 05-E. (C) Low magnification view showing a dolostone sample with abundant replacive dolomite rhomb (DolR), minor anhydrite cement (AnhC) and trace opaque organic matter (Om). (D) High magnification view highlighting abundant fine to medium crystalline, cloudy to clear dolomite rhomb (DolR) with intercrystalline pores (IxlΦ) and intracrystalline pores reflecting leaching of dolomite cores (IcΦ). Minor residual hydrocarbon (Rh) within intercrystalline space observed (MEWA, 2017).
Ca$^{2+}$ + Mg$^{2+}$ against $\text{HCO}_3^-$ relationship, indicating dolomite dissolution as a source of Ca$^{2+}$ and Mg$^{2+}$ along with anhydrite dissolution and reverse cation exchange.

In order to investigate the other sources of Ca$^{2+}$ and Mg$^{2+}$, samples were plotted on Ca$^{2+}$ against $\text{SO}_4^{2-}$ relationship, illustrating the dissolution of anhydrite which would contribute more Ca$^{2+}$ to groundwater if the samples plot along the 1:1 line for the anhydrite dissolution. Based on Figure 8, most of the samples plot along the 1:1 line except for a few samples which plot above and below the 1:1 line. The excess of Ca$^{2+}$ above the 1:1 line suggests another source of Ca$^{2+}$ along with anhydrite dissolution which might be cation exchange, whilst the decrease in Ca$^{2+}$ is probably due to precipitation of calcite and dolomite for some groundwater samples. This has been emphasized by the examination of the saturation indices of carbonate minerals (Figure 9 & Figure 10) which show that nearly most of the samples located in the eastern part of the area are saturated to supersaturated with respect to calcite and dolomite, except for a few samples located in or close to the outcrops where the recharge occurs and the anoxic condition prevails. On the other hand, almost all samples are strongly undersaturated with respect to gypsum and anhydrite (Figure 11, Figure 12 & Table 2).

Due to the abundancy of the organic matter in the middle and eastern parts along with the depletion of oxygen downgradient, sulfate reducing bacteria (SRB) become more active where sulfate are used as an electron acceptor while degrading the organic matter. Accordingly, sulfate becomes very depleted in the groundwater by reduction into hydrogen sulphide (Equation (5)). Hence, the water type Na$^+$-Ca$^{2+}$Cl$^{-}$-SO$_4^{2-}$ dominates in this part of the aquifer. In addition, the released acids and carbon dioxide by the degradation of the organic matter facilitate the dissolution of calcite (Figure 13).

$$\text{Organic matter + SO}_4^{2-} = \text{H}_2\text{S}$$

(5)

According to the result of the saturation indices conducted by phreeqc for the well RAK 05-E (Table 3), the main clay minerals are kaolinite and gibbsite.
Figure 8. Ca$^2+$ against SO$_4^{2-}$ relationship, indicating the dissolution of anhydrite when samples plot along the 1:1 line.

Figure 9. Distribution of the saturation indices of calcite within Umm Er Radhuma aquifer.
Figure 10. Distribution of the saturation indices of dolomite within Umm Er Radhuma aquifer.

Figure 11. Distribution of the saturation indices of anhydrite within Umm Er Radhuma aquifer.
Figure 12. Distribution of the saturation indices of gypsum within Umm Er Radhuma aquifer.

Table 2. Saturation indices for the carbonate minerals.

| Well Name | \( \text{O}_2 \) (mg/L) | \( \text{Fe}^{2+} \) (mg/L) | SI Calc. | SI Arag. | SI Dolo. | SI Anhy. | SI Gyp. |
|-----------|--------------------------|-----------------------------|----------|----------|----------|----------|--------|
| GHPH-801  | 0.10                     | 0.05                        | 0.47     | 0.34     | 1.19     | −0.76    | −0.64  |
| OLT D40   | n.d.                     | 0.10                        | 1.39     | 1.27     | 2.88     | −0.81    | −0.75  |
| S-397     | 0.08                     | <0.10                       | 0.42     | 0.28     | 0.88     | −0.24    | −0.09  |
| OLT D13   | 0.13                     | 1.03                        | 1.58     | 1.44     | 3.19     | −0.44    | −0.27  |
| OLT D52   | 0.67                     | 0.03                        | 0.35     | 0.21     | 0.74     | −0.30    | −0.15  |
| OLT D39   | 0.06                     | 0.03                        | 0.48     | 0.35     | 1.01     | −0.78    | −0.75  |
| JZTD2     | 0.58                     | 0.02                        | −0.04    | −0.18    | 0.10     | −0.40    | −0.22  |
| MKSR-801  | 1.02                     | 0.50                        | 0.05     | −0.08    | 0.13     | −0.56    | −0.47  |
| 7-S-11    | 2.13                     | 0.01                        | −0.16    | −0.29    | −0.30    | −1.06    | −0.91  |
| 7-S-25    | 0.30                     | 0.11                        | 1.79     | 1.65     | 3.67     | −0.43    | −0.31  |
| SUHL-801  | n.d.                     | 0.06                        | 0.26     | 0.13     | 0.68     | −0.74    | −0.69  |
Continued

| Phase         | Saturation Index | log IAP | log K (316 K, 1 atm) | (316 K, 1 atm) |
|---------------|------------------|---------|----------------------|----------------|
| Al(OH)$_3$    | −2.26            | 7.43    | 9.69                 | Al(OH)$_3$     |
| Albite        | −1.19            | −18.11  | −16.92               | NaAlSi$_2$O$_5$ |

Table 3. Result of the saturation indices for the Well RAK 05-E.
Continued

| Compound         | Density | Entropy | Energy | Formula                      |
|------------------|---------|---------|--------|------------------------------|
| Alunite          | −3.81   | −7.31   | −3.50  | KAl₃(SO₄)₂(OH)₆             |
| Anhydrite        | −0.58   | −5.07   | −4.49  | CaSO₄                        |
| Anorthite        | −2.59   | −21.82  | −19.23 | CaAl₂Si₂O₈                   |
| Aragonite        | 0.20    | −8.27   | −8.47  | CaCO₃                        |
| Ca-Montmorillonite| 1.67    | −40.92  | −42.59 | Ca₉₆Al₃₃Si₃₃O₆₃(OH)₉         |
| Calcite          | 0.33    | −8.27   | −8.60  | CaCO₃                        |
| Chalcedony       | 0.25    | −3.10   | −3.35  | SiO₂                         |
| Chlorite         | −1.29   | 60.77   | 62.06  | Mg₅Al₂Si₃O₁₀(OH)₈             |
| Chrysotile       | −3.17   | 26.92   | 30.09  | Mg₃Si₂O₅(OH)₄                |
| CO₂ (gas)        | −1.47   | −3.12   | −1.65  | CO₂                          |
| Dolomite         | 0.64    | −16.84  | −17.48 | CaMg(CO₃)₂                   |
| Fe(OH)₃ (aqueous)| 1.02    | 5.91    | 4.89   | Fe(OH)₃                      |
| FeS              | −0.53   | −4.44   | −3.92  | FeS                          |
| Gibbsite         | 0.27    | 7.43    | 7.16   | Al(OH)₃                      |
| Goethite         | 7.51    | 5.91    | −1.60  | FeOOH                        |
| Gypsum           | −0.47   | −5.07   | −4.60  | CaSO₄·2H₂O                   |
| H₂ (gas)         | −21.99  | −25.12  | −3.13  | H₂                           |
| H₂O              | −1.07   | −0.00   | 1.07   | H₂O                          |
| H₂S              | −4.06   | −12.02  | −7.96  | H₂S                          |
| Halite           | −6.11   | −4.53   | 1.58   | NaCl                         |
| Hematite         | 17.12   | 11.82   | −5.30  | Fe₂O₃                        |
| Illite           | 0.82    | −37.17  | −37.98 | K₁₀₂Mg₈₂₃Al₃₃Si₃₃O₆₃(OH)₂     |
| Jarosite-K       | −1.36   | −11.87  | −10.52 | KFe₃(SO₄)₂(OH)₆             |
| K-feldspar       | −0.28   | −19.57  | −19.29 | KAlSi₃O₆                   |
| K-mica           | 5.98    | 16.21   | 10.23  | KAl₃Si₃O₁₉(OH)₉             |
| Kaolinite        | 2.70    | 8.66    | 5.96   | Al₂Si₂O₅(OH)₄                |
| Mackinawite      | 0.20    | −4.44   | −4.65  | FeS                          |
| Melanterite      | −6.82   | −8.84   | −2.02  | FeSO₄·7H₂O                   |
| O₃ (gas)         | −33.66  | −36.66  | −3.00  | O₃                          |
| Pyrite           | 23.44   | 5.43    | −18.01 | FeS₂                        |
| Quartz           | 0.63    | −3.10   | −3.73  | SiO₂                         |
| Sepiolite        | −2.54   | 12.77   | 15.31  | Mg₂SIO₃·OH·3H₂O             |
| Sepiolite        | −5.89   | 12.77   | 18.66  | Mg₂SIO₃·OH·3H₂O             |
| Siderite         | −1.05   | −12.04  | −10.99 | FeCO₃                        |
| SiO₂             | −0.53   | −3.10   | −2.57  | SiO₂                         |
| Sulfur           | 12.14   | 16.62   | 4.49   | S                           |
| Sylvite          | −6.97   | −5.98   | 0.98   | KCl                          |
| Talc             | 1.25    | 20.71   | 19.46  | Mg₂SIO₃·OH·3H₂O             |
which have major effect on the cation exchange process taking place in the aquifer.

In order to investigate the influence of the cation exchange taking place on the clay minerals in the aquifer, the ratio of \([\text{Ca}^{2+} + \text{Mg}^{2+}] - (\text{SO}_4^{2-} + \text{HCO}_3^-)\) against \((\text{Na}^+ - \text{Cl}^-)\) has been applied. Based on Figure 14, most of groundwater samples plot close to 1:1 line, indicating that cation exchange is affecting the hydrochemical composition of the groundwater. Cation exchange can also be quantified by the Chloro-Alkaline indices (CAI) suggested by Schoeller (1977), to indicate ion exchange between the groundwater and its host environment during residence or travel. The value of these indices can be positive or negative. If the value is positive then it explains that the exchange of Na\(^+\) and K\(^+\) ions are from water with Mg\(^{2+}\) and Ca\(^{2+}\) ions of the rocks. This indicates a direct base
Figure 14. \[ (\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_{4}^{2-} + \text{HCO}_{3}^-) \] against \((\text{Na}^+ - \text{Cl}^-)\), showing that the effect of cation exchange is active on the hydrochemistry of the groundwater.

Figure 15. (CAI) or \([\text{Cl}^- - (\text{Na}^+ + \text{K}^+)]/\text{Cl}^-\) (in meq/L), the positive values indicate reverse cation exchange, while the negative values indicate cation exchange.

(cation-anion) exchange reaction. In contrast, if the value is negative then it means that there is an exchange \(\text{Mg}^{2+}\) and \(\text{Ca}^{2+}\) of the water with \(\text{Na}^+\) and \(\text{K}^+\) ions from rocks, so the exchange is in indirect base indicating chloro-alkaline disequilibrium. These reactions are known as cation-anion exchange reaction. The Chloro-Alkaline index (CAI) is defined by the ratio of \([\text{Cl}^- - (\text{Na}^+ + \text{K}^+)])/\text{Cl}^-\) (in meq/L). Most of groundwater samples have values greater than zero which indicate reverse cation exchange, where \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) are being released from the aquifer matrix to groundwater (Figure 15).

The most plausible source of \(\text{Na}^+\) and \(\text{Cl}^-\) is halite dissolution which releases equal molar amounts of \(\text{Na}^+\) and \(\text{Cl}^-\) into groundwater (Equation (6)) Accordingly, samples should plot on the 1:1 line of halite dissolution on the \(\text{Na}^+\) against \(\text{Cl}^-\) plot. According to Figure 16, most of the groundwater samples plot along the 1:1 halite dissolution whilst a few samples plot below the line, which is attributed mostly to reverse cation exchange.
5. Conclusion

Groundwater salinity increased from west to east, reaching a TDS of more than 27,000 mg/L near the border with the United Arab Emirates with a dominating Na⁺-Ca²⁺Cl⁻-SO₄²⁻ water type. The dissolution/precipitation of carbonates and evaporation and precipitation of minerals, especially anhydrite, gypsum, and halite account mainly for the solutes and salinity in groundwater. In addition, other sources of Ca²⁺ and Mg²⁺ in the groundwater along with dolomite and calcium carbonate minerals. Whilst the dissolution of anhydrite contributed more Ca²⁺ to groundwater. On the other hand, the main clay minerals are kaolinite and gibbsite which affected the cation exchange process as illustrated by the Chloro-Alkaline index (CAI), where most of the groundwater samples had positive values, indicating the effect of ion exchange on groundwater chemistry. In the eastern part of the aquifer, the Na⁺-Ca²⁺Cl⁻-SO₄²⁻ water type dominated as the anaerobic conditions prevailed and the reduction of sulphate took place.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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