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Hydrogeochemistry of the Umm er Radhuma Unconfined Aquifer, Western Desert Iraq- Saudi border

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Abstract

The Umm Er Radhuma unconfined aquifer Hydrogeochemistry in the Saudi – Iraq border desert was studied to identify the main hydrogeochemical processes and rock-water interaction. The measurements were done using standard APHA procedures. The results indicated that Na⁺ and Cl⁻ are the dominant ions in the groundwater. The average contribution of cations in the aquifer is Na⁺ + K⁺ (26 %), Ca²⁺ (14 %), and Mg²⁺ (10%) ; whereas anions contribution is Cl⁻ (24 %) , SO₄²⁻ (20 %), and HCO₃⁻ (6 %). The results reflect that the examined water is hard water of neutral to slightly alkaline, slightly brackish, with mineralized pH conditions. The main conclusion of chemical reactions indicated carbonates, evaporate dissolution, and clay minerals water interaction through ionic exchanging.

Keywords: groundwater rock interaction, Umm Raduma aquifer, Iraq.

هيدروجيوكيميائية خزان ام ارضمة الغير محصور الصحراء الغربية الحدود العراقية – السعودية

وئام حسن كاظم

قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصه

تمت دراسة خزان ام ارضمة الغير محصور في الصحراء الغربية – الحدود العراقية السعودية لتحديد الخصائص الهيدروجيوكيميائية وتفاعل صخر – ماء .تمت القياسات وفقا لاجراءات APHAالقياسية, اشارت النتائج الى ان ايونات الصوديوم والكلورايد هي الايونات السائدة في المياه الجوفية ان معدل مشاركة كل ايون في مياه الخزان هي كالتالي ; (10%) +0 Mg2 ((2 %) + 14%) + 28% ((2 % 6 %) + 4 % حين كانت مشاركة الانيونات كالتالي : 50 Mu AHOO ((2 %) - 504) + 20% ((2 %) - 10 - (6 %)). بينت النتائج ان المياه التي تم فحصها كانت مياه عسرة متعادلة الى قلوية ضعيفة قليلة الملوحة مع ظروف حاصنية معدنية. الاستنتاج الرئيسي من التفاعلات الكيميائية تشير الى وجود الكاربونات المتبخرات الذائبة والمعادن الطينية وان التبادل الايوني يتم من خلال تفاعل ماء مع المعادن.

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Introduction

Accurate estimates of groundwater quality are vital in effectively managing aquifers, especially in regions with very little water. The purpose of groundwater usage depends on its suitability, which has wide variations [1, 2, 3 and 4]. Interaction of groundwater with aquifer mineral species significantly controls the water chemistry [5,6 and 7]. The studied area is located within the Western Desert of Iraq between longitudes $(41^{\circ} 15' 45'' - 45^{\circ} 47' 39'')$ E and latitudes $(29^{\circ} 29' 10'' - 32^{\circ} 6' 17'')$ N (Figure 1). The chosen area is selected near the borders of Iraq and Saudi Arabia, of nearly 60,068 km² of the Western Desert covering the unconfined aquifer of Umm Raduma rocks, Figure 1. Previous works considering the hydrological characteristics and management of umm er Radhuma aquifers within the western desert of Iraq [8,9,10 and 11]. Umm er Radhuma Formation (Paleocene age) contains limestone, marly limestone, and dolomite with intercalations of evaporates. It is considered a vital water resource within the Western Desert of Iraq, particularly in the southern and southeastern parts of Al-Nukhaib and Habbariya vicinities. It also forms an essential aquifer under the Dammam aquifer within the regions west of Nukhaib, Al-Ukhaidir and Rahaliya vicinities [12 and 13]. The thickness of the saturation of the unconfined Umm Raduma aquifer is estimated from 50 m in the west of the southern desert near the international border to 213m in the east, where the unconfined aquifer becomes confined [12 and 14]. Depending on the annual rainfall, it is considered the most vital water input to the aquifer. The rainfall is ranged between 0.0 mm during July and August and 16.1 mm during January, with an average of 9.6 mm, while the annual rainfall is 96.4 mm. The evaporation is ranged between 72.4 mm during December and 487.0 mm during July, with an average of 187.7mm, while the annual evaporation is 2251.8 mm. The Minimum temperature is ranged between 5.8 C° during January, and 29.1 C^o during July, with an average of 17.5 C^o. The maximum temperature is ranged between 15.9 C° during January and 44.5 C° during July, with an average of 30.6 C°. The Relative Humidity (%) is ranged between 20.7 % during July and 66.5 % mm during December, with an average of 39.2 % [5]. The transmissivity is from 2 to 1550 m2/day, permeability is from 0.1 - 21.1 m/day, and well water output is from 2 - 3960 m3/day. The water table static level is of wide range reaching 170.3 m downward from earth's level. The total salt dissolution is from 278 - 6640 mg/l, with various water formulas and maximum sulfate and chloride ions, while Bicarbonatic water is less abundant. Bicarbonate water is mainly found along wadi regions, where water recharge is direct from precipitation [8]. Differences in hydraulic parameters are because of the lithologic and structural characteristics and presence of fractures, fissures; caves and fault zone (Abu Jir Fault Zone) so that leakage of deep oil water occurs through this fault to aquifer water causing high salinity [12, 15 and 16].

The current work aims to investigate the hydrogeochemistry to high lights the main chemical reactions between water and rocks of the Umm Raduma unconfined aquifer and to reveal the main processes of hydrogeochemistry.

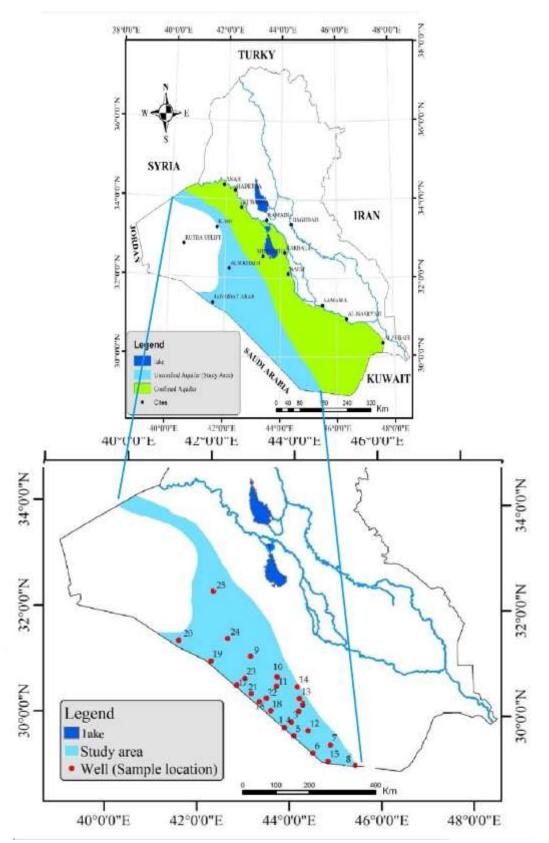


Figure 1: Locations of groundwater wells of the studied Umm Raduma unconfined aquifer [10].

Materials and methods

Twenty-five groundwater samples were collected in October 2009 from Umm Raduma unconfined aquifer in the western desert near the Iraqi-Saudi Arabia borders (Figure 1). The depth of groundwater wells ranges from 100- 300 m, according to Al-Fatlawi, 2021 [16]. The measurements were done using the procedure of APHA, 1998 [17], including hydrogen number (pH), electrical conductivity (E.C.), and TDS using TDS-EC-pH and HANA, type HI 9811. All samples were analyzed for major cations (K⁺, Na⁺, Ca²⁺, and Mg²⁺) and major anions (HCO₃⁻, SO₄²⁻, and Cl⁻). Sodium and K were analyzed using a flame photometer. Calcium, Mg, Cl, CO3, and HCO3 were determined using titration. Sulfate was determined using a spectrophotometer.

The analytical accuracy was calculated according to Hem, 1985 [18] and Al-Hamadani, 2009[19]. Accordingly, the accuracy of the results is accepted.

The hydrochemical formula was computed as the average formula based on the Kurlolov formula, which was referred to in Ivanov et al., 1968 [20].

Results and discussion

Groundwater is the predominant source of water supply for domestic and other uses. Groundwater abstraction from boreholes for water supply has a long history. There is generally a high rate of abstraction without matching recharge. A general decline in rainfall in the area has led to the over-exploitation of groundwater, and the available groundwater resource is declining. Water levels in boreholes have fallen, and borehole yields have drastically declined.

Properties of Umm Raduma unconfined aquifer Groundwater

A slightly- brackish is the classification of groundwater according to Todd, 2007 [1] as revealed by the results, where the TDS varies from 1410 to 3300 ppm (Table 1). The wide salinity range is due to the various lithology types. The range of E.C. varied from 1774 to 4970 μ s/cm, revealing mineralized water excessively type [21], while it is slightly alkaline to neutral according to Matthess,1982 [22], and the pH ranges between 7.1 to 8.5.

The Na^+ , with a mean of 55.5%, is the dominated cation, while Cl- is the most dominant anions and forms 47.3% on average of the total ions (Figure 2).

The Na ranges from 6.2 to 16.5 epm, while chloride varies between 4.5 and 22.0 epm. Although groundwater in the Umm Raduma unconfined aquifer contains a wide ionic range, it tends to have a uniform water quality, which is with Na-Cl type of water as follows:

2160
$$\frac{Cl(47.3)SO4(41.0)}{Na(55.5) Ca(28.0)Mg(19.5)}$$
 7.7

The access quantity of sodium which is higher than the chloride molar value indicated that it doesn't come from halite and supports that the groundwater originated from a deep fault source to mix the Umm er Radhuma unconfined aquifer meteoric water.

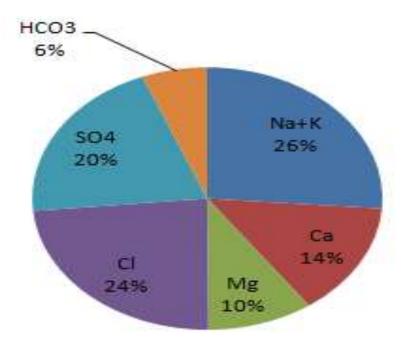


Figure 2: The Umm er Radhuma unconfined aquifer mean ions.

Well	pH	TDS	E.C.	-	_	Ca	Cl	SO4	HCO3
No	-	ppm	µs/cm	epm	epm	epm (%)	epm (%)	epm (%)	epm (%)
				(%)	(%)				
1	8.5	1570	2000	51.8	23.7	24.5	77.9	17.8	4.3
2	8.3	1647	2060	51.3	24.2	24.5	77	18.5	4.5
3	8.1	1498	1835	80.1	9.3	10.6	60.7	37.5	1.8
4	8.5	1437	2130	83.7	6.1	10.2	53.7	44	2.3
5	7.1	2800	4300	37.5	28.7	33.8	34.6	49.4	16
6	7.2	3300	4790	45.2	21.9	32.9	50	38	12
7	8.4	2100	3180	72	12	16	55.2	36	8.8
8	7.2	2420	3510	66.2	14.7	19.1	52.9	37.1	10
9	7.2	3220	4970	52.8	16.9	30.3	40.3	44.8	24.9
10	7.1	2388	3640	71.5	10.7	17.8	57.9	34.7	7.4
11	7.1	3100	4750	53.5	25.5	21	41.1	45.6	13.3
12	7.2	2380	3610	46.1	16.9	37	41.7	42	16.3
13	7.3	1830	2810	40.3	25.9	33.8	36.8	46.4	16.8
14	7.7	1860	2820	43	21	36	37	46.4	16.6
15	7.3	1410	2140	42.2	23.9	33.9	36.6	48.8	14.7
16	7.3	1700	2560	47	18	35	37.4	47.6	15
17	7.7	2020	3040	52	16.2	31.8	40.5	44.8	14.7
18	7.6	2000	3010	47.7	18	34.3	44.8	42.7	12.5
19	7.9	2160	3250	49.6	26.2	24.2	44.6	43.7	11.7
20	7.7	2300	3500	55	16.8	28.2	45.7	43	11.3
21	8.1	3080	4710	42.6	26	31.4	43.3	44.4	12.3
22	8.0	1981	2250	63.1	11.8	25.1	78.0	15.5	6.5
23	7.9	1672	1850	51	18.3	30.8	20.7	68.0	11.3
24	7.8	2539	2900	36.2	30.6	33.3	17.9	64.6	17.5
25	8.1	1580	1774	30.5	25.4	44.1	56.9	23.7	19.5
Min.	7.1	1410	1774	30.5	6.1	10.2	17.9	15.5	1.8
Max.	8.5	3300	4970	83.7	30.6	44.1	78.0	68.0	24.9
Mean	7.7	2160	3096	52.5	19.5	28	47.3	41	12.1

The interaction of Umm Raduma Groundwater and the rocks of the aquifer

The data on groundwater quality give important clues to the geological history of the rocks and indications of groundwater recharges, discharges, movement, and storage.

The mathematical ratios between ions (Hydrochemical functions) are used to identify the groundwater properties and to conclude the interaction of Umm Raduma groundwater and the rocks of the aquifer [6 and 23].

The Na (epm) / Cl (epm) show (1.2) mean amount of rNa^+/rCl^- reflect the occurrence of other input of Na which is not as halite rocks but could be the partial leaching of terrestrial minerals (Table 2). The average ratio of rCa^{2+}/rMg^{2+} (1.5) that is ten times greater than of seawater (actually, this ratio in seawater is 0.14) and five times less than of the rainwater (actually, this ratio in rainwater is 7.14) [24]. These results indicated the interaction of Umm er Radhuma Groundwater and the rocks of the aquifer by limestone and dolomite rocks leaching under the pH of rainwater (relatively acidic pH). In contrast, the leaching of the sulfate rocks in the Umm Raduma aquifer is shown by the high average value of rSO_4^{2-}/rCl^- ratio (1.1) in groundwater.

The $Ca^{2+} + Mg^{2+}$ and $SO_4^{2-} + HCO_3^{-}$ values reflect an ion exchange due to $SO_4^{2-} + HCO_3^{-}$ excessing as in the case of Umm er Radhuma groundwater that is ordinarily close to the 1:1 line (Figure 3) [25 and 26]. The results indicate that most of the groundwater samples of the Umm Raduma unconfined aquifer are shifted to the right, indicating cation exchange with clay minerals resulting from gypsum dissolution (Figure 3).

S. No.	Ca/ Mg	SO4/ Cl	Ca+Mg	SO ₄ + HCO ₃	Cl	Na+K	Na/ Cl	Na	Cl /(Cl +HCO ₃)	Na/(Na +Ca)
1	1.0	0.23	9.5	4.4	15.5	10.2	0.65	10	0.95	0.68
2	1.0	0.23	9.9	4.7	15.9	10.4	0.64	10.1	0.95	0.68
3	1.2	0.62	4.3	8.5	13.1	17.3	1.3	17	0.97	0.88
4	1.6	0.81	3.1	8.7	10.2	15.7	1.5	15.2	0.96	0.89
5	1.2	1.43	25.5	26.6	14.0	15.3	1.1	15.2	0.68	0.53
6	1.5	0.77	20.0	22.3	22.0	16.5	0.73	16.1	0.8	0.58
7	1.3	0.65	8.2	13.2	16.3	21.3	1.3	21	0.86	0.82
8	1.3	0.7	11.5	16.1	18.1	22.6	1.2	21.1	0.84	0.78
9	1.8	1.1	23.0	28.1	19.0	25.7	1.3	25.2	0.88	0.63
10	1.7	0.6	9.6	14.3	19.6	24.2	1.2	24	0.75	0.8
11	0.8	1.1	19.9	25.4	17.8	23.0	1.3	22.7	0.68	0.72
12	2.2	1.0	17.5	18.9	13.5	15.0	1.1	14.8	0.61	0.56
13	1.3	1.2	15.2	15.8	9.2	10.3	1.1	10	0.39	0.54
14	1.7	1.25	15.0	16.8	9.9	11.3	1.1	11	0.55	0.47
15	1.4	1.3	11.9	13.0	7.5	8.7	1.1	8.2	0.56	0.55
16	2.0	1.3	12.1	14.2	8.5	10.7	1.2	10.2	0.59	0.57
17	2.0	1.1	13.3	16.6	11.3	14.5	1.2	14	0.79	0.62
18	1.9	0.96	14.3	15.1	12.2	13.0	1.1	12.9	1.16	0.58
19	0.9	1.0	14.7	16.4	13.1	14.5	1.1	14.2	1.1	0.67
20	1.7	0.9	14.9	18.1	15.2	18.3	1.2	18	0.8	0.66
21	1.2	1.0	25.6	25.5	19.5	19	1.0	18.8	0.78	0.58
22	2.2	0.2	4.8	5.8	20.7	16.8	0.8	16.3	0.9	0.71
23	1.7	3.3	10.7	17.3	4.5	11.2	2.4	11	0.64	0.63
24	1.1	3.6	22.5	29.0	6.3	12.8	1.9	12.2	0.5	0.52
25	1.7	0.4	14.2	8.6	11.4	6.2	0.5	6	0.74	0.4
Aver.	1.5	1.1	14.1				1.2			

Table 2: Hydrochemical function (epm) of groundwater in the Umm Raduma unconfined aquifer.

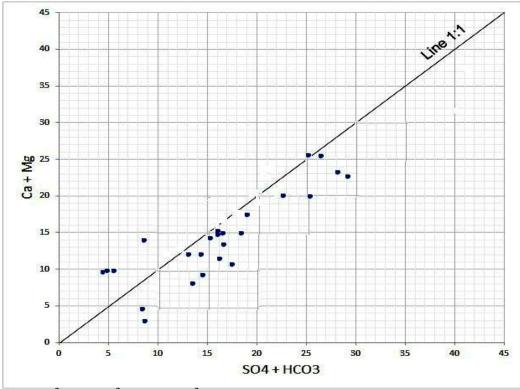


Figure 3: $Ca^{2+} + Mg^{2+}$ and $SO_4^{2-} + HCO_3^{-}$ ratio in groundwater of the Umm Raduma unconfined aquifer.

Maya and Loucks,1995 [27] concluded that the ratio Ca/Mg equal to 1.0 indicates dissolution of dolomite, but a higher ratio reflects a more significant calcite contribution. In this research, the average ratio of Ca/Mg is 1.5. Moreover, the high $Ca^{2+} + Mg^{2+}$ molar amounts (higher than 5.0 to lower than 21.0 epm) indicate Ca and Mg's contribution to groundwater due to the dissolution of calcite, dolomite and gypsum (Figure 4).

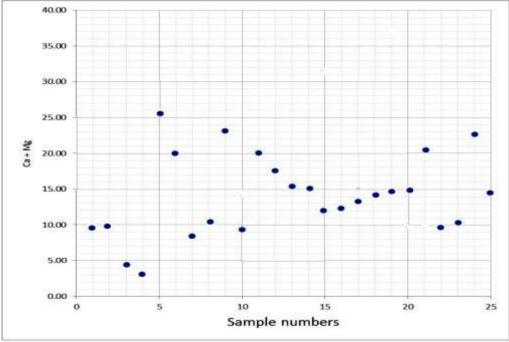


Figure 4: $Ca^{2+} + Mg^{2+}$ molar values in the Umm er Radhuma unconfined aquifer water.

Carbonates of the Dammam and Umm er Radhuma Formations and gypsiferous claystone and sulfate rocks of the Zahra and Rus Formations, respectively, were affected by leaching (Figure 5) [28].

The groundwater points are drawn with the $Na^+ + K^+$ and $\frac{1}{2}$ total cations (Figure 6) [24]. It refers to the weathering of silicate and halite rocks leaching.

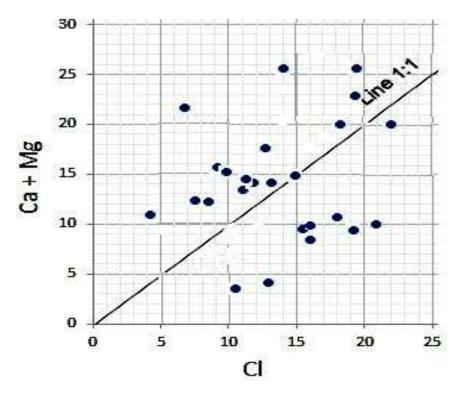


Figure 5: (Ca + Mg) and Cl (epm) ratio in the Umm Raduma aquifer.

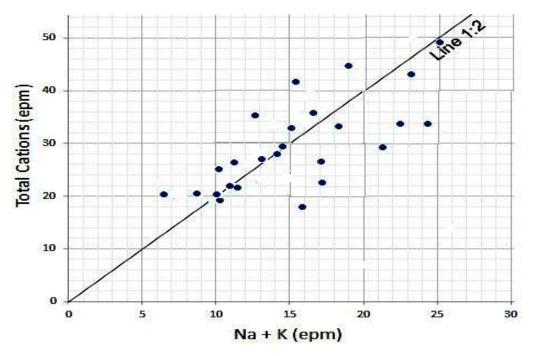


Figure 6: (Na + K) and total cations (epm) ratio in groundwater of the Umm Raduma unconfined aquifer.

The active chemical processes

The sources of heavy metals in soil are mainly natural, including geologic sources such as rock formations and soils [23]. The evaporation has affected the system of groundwater and salinity [6, 13 and 29]. The plot relation of Na/Cl versus EC. was applied to understand the active chemical processes in Umm Raduma unconfined aquifer. Mayback,1987[27] stated that the molar ratio of Na/Cl is approximately close to 1.0, showing the dissolution of halite, while over 1.0 indicates the release of Na ion from weathering of silica. Accordingly, in this research, the Na/Cl ratio of 19 out of 25 samples is greater than 1.0, with an average of 1.2, which indicates halite or silica (clay minerals) dissolution (Table 2 and Figure 7). 76% of the samples are higher than the 1:1 ratio showing the direct relation of Cl with Na that attributed exchange to the ions in clay minerals and silicate weathering (Figure 8) [18].

According to Gibbs [30] diagram, it is noticed that the weathering processes are the active chemical processes without dilution process of annual rainfall that recharges and feeds the Umm er Radhuma unconfined aquifer (Figure 9 A-B).

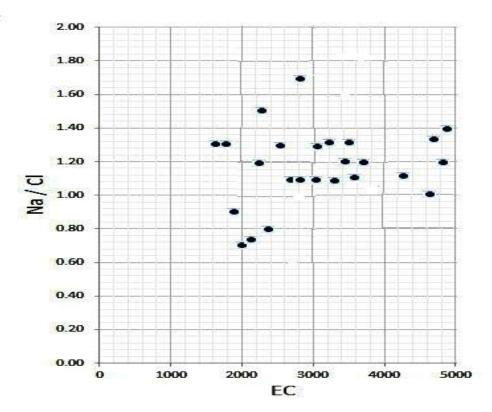


Figure 7: The relation of (Na / Cl) versus E.C. in the Umm Raduma groundwater aquifer.

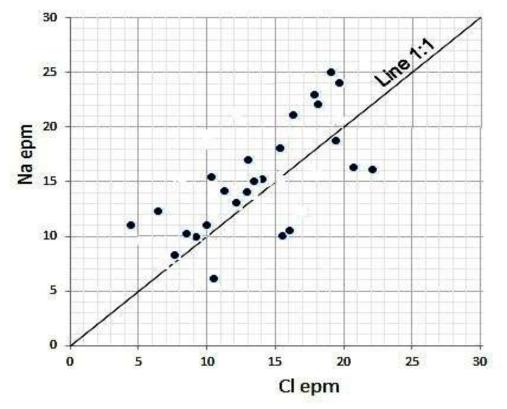
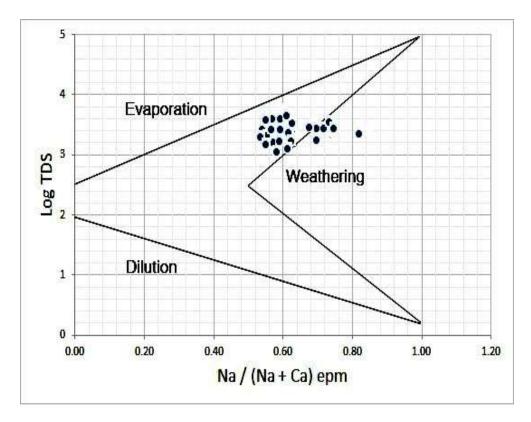


Figure 8: The relation of Na and Cl in the Umm Raduma groundwater aquifer.



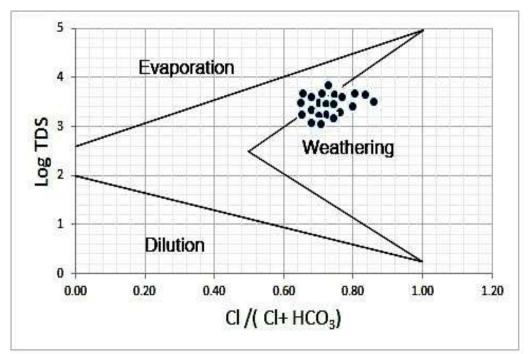


Figure 9: classification of A and B Gibbs diagrams in the Umm Raduma groundwater aquifer.

The groundwater origin and Ions sources

Because of the geological nature of the study area, it is characterized by distinguished hydrogeology through the presence of the Abu Jir, Schbicha, Athamin – Um Zulaim and Safawi- Samawa fault systems. The hydrogeology situation depends on the nature of the structural, geological, type of formations, and nature of the water-bearing rocks and cavities. The relationship between ions is used to determine the origin of the water. Sullin, 1946 [31] used the (rNa / rCl) to indicate the marine origin (rNa / rCl \leq 1) or continental origin (rNa / rCl \geq 1) of groundwater. The groundwater environment in geological formations leads to the variation in ion concentration ratios (dilution or concentration), so two classes could be distinguished for both origins depending on the appearance of hypothetical salts. It is possible to find the dilution or concentration ratios by comparing them with the concentration of

seawater or continental water [32]. Accordingly, the results show that 20 well samples out of 25 are of continental origin and that the hypothetical salt is sodium sulfate (Na_2SO_4) since most of these groundwater samples are located in the recharge zone area (Figure 10, Table 3). This finding follows the ratio of Na/(Na+Cl) that reflects marine origin groundwater suffering changes in its ions concentration after deposition as a result of mixing with rain water penetrating from the surface to the groundwater through the faults and fractures in the area in 72% wells, where the values of this ratio are more than 0.5.

To describe source ions and rocks (type of lithology) affected groundwater chemistry according to Hounslow, 1995[33]. The chemical functions are calculated (Table 3) and used. The results indicated that the Mg/ (Ca+Mg) is lower than 0.5, reflecting carbonate rocks' leaching as the main operation, but over 0.5 shows calcite precipitation and dolomite dissolution. As well as, the ratio of Ca/ (Ca+SO₄) is minor from 0.5, getting rid of Ca by ion exchange or calcite deposition. While the amounts of Mg/ (Ca+SO₄) are lower than 0.5 in the Umm er Radhuma groundwater aquifer, reflecting that the calcite and gypsum have more contribution than dolomite. The result of the (Ca+Mg)/SO₄ ratio indicates dedolomitization operation by about 56 % of the calculated ratios of this function. The ratio of (Ca+Mg)/SO₄ is within 0.8-1.2, reflecting dedolomitization. The TDS values reveal carbonate weathering that is higher than 500ppm, but if it is lower than 500 ppm, indicating weathering of silicate

minerals. According to the ratio of Cl / Σ anions, the rock weathering is the active operation in Umm Raduma unconfined aquifer, indicated by the lower ratios than 0.8. While the computed amounts of HCO₃/ Σ anions ratio is lower than 0.8, reflecting the brine water of Abu Jir Fault deep aquifers.

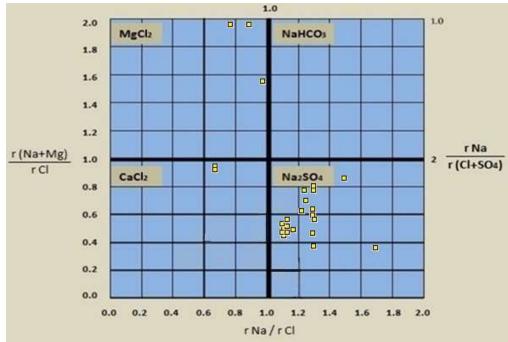


Figure 10: The origin and development of the water samples of the Umm er Radhuma unconfined aquifer [32].

S.	Na/	- Mg/	Ca/	Mg/	$\frac{(Ca+Mg)}{}$	-	HCO ₃ /	- (Na+	Na/
No	(Na+Cl)	(Ca+Mg)	(Ca+SO ₄)	$(Ca+SO_4)$	SO ₄	∑Anions	∑Anions	Mg)/Cl	(Cl+SO ₄)
1	0.4	0.5	0.58	0.57	2.7	0.78	0.04	0.96	0.54
2	0.4	0.5	0.57	0.56	2.6	0.77	0.04	0.97	0.53
3	0.57	0.47	0.22	0.19	0.53	0.6	0.02	1.47	0.81
4	0.6	0.39	0.19	0.12	0.37	0.54	0.02	1.66	0.85
5	0.5	0.46	0.40	0.35	1.27	0.35	0.16	1.92	0.45
6	0.4	0.4	0.42	0.28	1.2	0.5	0.12	1.74	0.53
7	0.57	0.43	0.31	0.23	0.77	0.55	0.09	1.52	0.79
8	0.56	0.43	0.24	0.26	0.9	0.53	0.1	1.53	0.73
9	0.57	0.36	0.41	0.23	1.1	0.4	0.15	1.78	0.64
10	0.55	0.38	0.34	0.2	0.8	0.58	0.07	1.42	0.77
11	0.56	0.55	0.31	0.38	1.1	0.41	0.13	1.91	0.61
12	0.53	0.3	0.47	0.2	1.3	0.42	0.16	1.52	0.55
13	0.53	0.4	0.43	0.33	1.3	0.37	0.17	1.84	0.5
14	0.53	0.37	0.39	0.25	1.2	0.37	0.16	1.7	0.51
15	0.54	0.4	0.41	0.29	1.2	0.37	0.15	1.82	0.5
15	0.56	0.34	0.43	0.22	1.1	0.37	0.15	1.74	0.55
17	0.56	0.34	0.41	0.21	1.1	0.4	0.15	1.68	0.61
18	0.52	0.34	0.45	0.25	1.2	0.45	0.12	1.47	0.55
19	0.53	0.5	0.35	0.33	1.14	0.44	0.12	1.68	0.56
20	0.55	0.38	0.39	0.16	1.0	0.46	0.11	1.57	0.62
21	0.49	0.45	0.41	0.34	1.3	0.43	0.12	1.57	0.48
22	0.45	0.32	0.6	0.29	2.4	0.8	0.06	2.38	0.13
23	0.7	0.37	0.3	0.19	0.7	0.2	0.11	2.38	0.21
24	0.67	0.48	0.34	0.31	1.0	0.18	0.18	3.81	0.37
25	0.35	0.37	0.66	0.38	3.0	0.57	0.19	2.41	0.39

Table 3: Calculated functions for interpretation of the source rock.

Conclusions

1. Groundwater studies are hard water, slightly alkaline, slightly brackish and mineralized. The dominated type of water is Na-Cl with 52% and Na-SO₄ with 48 %, where groundwater constituent is ordered as: Na>Ca>Mg (88%); Na> Mg > Ca (8%); Ca > Na > Mg (4%); Cl>SO₄>HCO₃ (52%); SO₄>Cl>HCO₃ (48%).

2. 68% of groundwater wells are alkali groundwater with Na, chloride and sulfates, but the remnant (32%) represents the amount of earth alkali water saturated with Mg and Ca.

3. The groundwater chemistry of the study area was affected by multi-chemical processes; these are silicate weathering indicated by the ionic exchange and dissolution of calcite, dolomite, gypsum, and halite.

4. The source of ions supplied by calcite and gypsum is higher than dolomite as a rock-water interaction in the Umm Raduma unconfined aquifer, and the dedolomitization did not occur.

5. The main source of sulfate is the dissolving of gypsum; the evaporation and oxidationreduction are ineffective in the Umm er Radhuma unconfined aquifer.

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