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HYDROGEOCHEMISTRY AND QUALITY OF SURFACE WATER AND GROUNDWATER IN THE WADI BU ASH SHAYKH AND ZALLAH AREAS, SIRTE BASIN, NORTH CENTRAL LIBYA

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Abstract: The present study aimed to perform a geochemical evaluation of surface water and groundwater in the Wadi Bu Ash Shaykh and Zallah areas, Sirte Basin, north central Libya. The chemical data include pH, TDS, TH, K, Ca, Na, Mg, Cl, HCO_3, SO_4, NO_3, F, Li, Sr, B, I, and Br. Based on the Piper diagram, the majority of the water samples are of the NaCl Type. Three types of water are identified by the TDS values: brackish, saline, and hypersaline. The LSI indicate that most samples are saturated with $CaCO_3$. The water samples are unfit for human consumption, as evidenced by the drinking water quality indices (PI and WQI). Moreover, the irrigation parameters (pH, TDS, TH, Na, Cl, HCO_3, F, Li, B, Na%, SAR, RSC, MAR, LDP, KR, PI, PS, (Ca+Mg)/(Na+K), and (Ca+Mg)/Na) suggest that the water samples are not appropriate for irrigation.
Keywords: Hydrogeochemistry, Drinking Water Quality, Irrigation Water Quality, Sirte Basin, Libya

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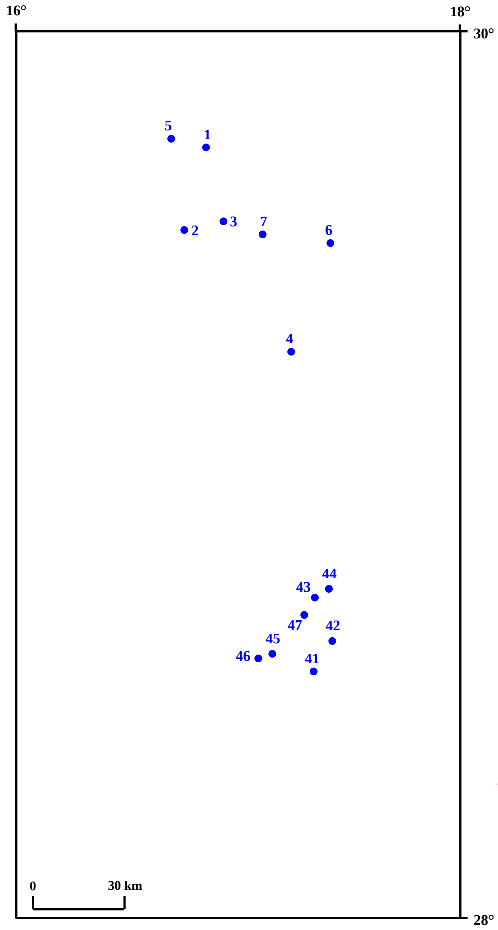
1. Introduction

Water supplies must be evaluated due to the world's population growth, because drinking and irrigation water may include pollutants that are harmful to human health (e.g., Zaidi et al., 2016; Shah et al., 2019; Shaltami et al., 2021; Kamboj and Singh, 2025). Assessing the quality of water is currently one of the most important research that countries are carrying out (Halim et al., 2010; Sudhakar and Narsimha, 2013; Sako et al., 2018; Shaltami and Algomati, 2024). Since the Great Man-Made River supplies water to the majority of Libya's major towns, groundwater is regarded as the primary source of water in the country. Other water sources in Libya include rainfall, seawater desalination, and wells used for home and agricultural purposes. Libyan water has undergone geochemical assessments by a number of authors (e.g., Shaltami et al., 2017; Ahwidy and Elsadq, 2020; Abu Salem et al., 2024). The goal of this work is to advance our understanding of the chemical composition and environmental condition of surface water and groundwater in the Wadi Bu Ash Shaykh and Zallah areas, Sirte Basin, north central Libya (Figure 1). This work determined the following:
(1) The hydrofacies of the water;
(2) The probability for using the water for drinking purposes; and
(3) The possibility of irrigation using the water.



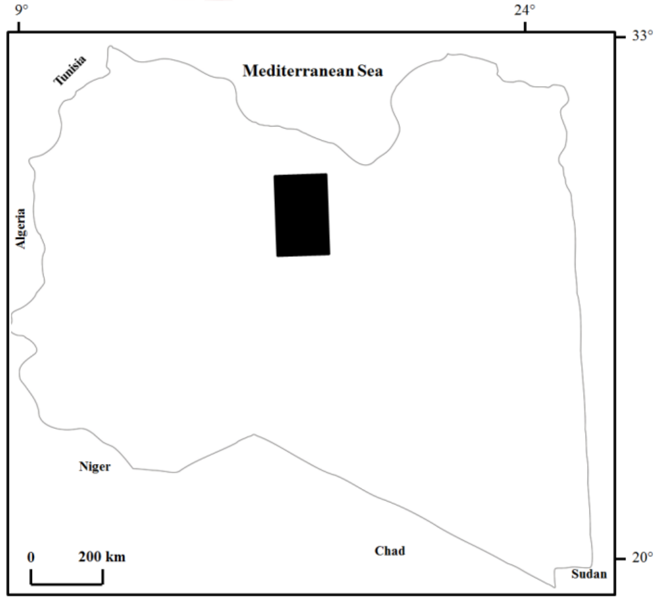


Figure 1. Composite map showing the location of the study area and the location of the studied samples (modified after Jurak, 1985; Vesely, 1985).

The study area is classified as a hydrogeological region with limited prospects (Jones, 1971). Oligocene sediments are the only appropriate aquifer. In the Wadi Bu Ash Shaykh area, the aquifers are sandstones (Jurak, 1985), while sandstones and conglomerates are the main aquifers in the Zallah area (Vesely, 1985).

2. Research Method

The present study used the concentrations of ions reported by Jurak (1985) and Vesely (1985). This study included 14 water samples. The studied water included spring, sabkhas, and groundwater.

3. Results and Discussion

3.1 Hydrogeochemistry

Ions leak out and dissolve in water as rocks and soils condition and water circulates. The main elements affecting the water's geochemistry are the geological formations, the interaction between water and rock, and the relative mobility of ions (Yousef *et al.*, 2009). The influence of rock chemistry on water composition can be inferred from major ions. Marine, terrigenic, and anthropogenic sources are the three primary sources of dissolved solids in water (El-Omla and Aboulela, 2012). Water is divided into four categories based on the TDS concentration: (1) Fresh water (TDS<1000 mg/l); (2) Brackish water (TDS range from 1000 to 10000 mg/l); (3) Saline water (TDS range from 10000 to 35000 mg/l); and (4) Hypersaline (TDS>35000 mg/l). K, Ca, Na, Mg, Cl, HCO_3, SO_4, NO_3, F, Li, Sr, B, I, and Br are among the ions included in the chemical analysis data of the water samples (Table 1). The values of total dissolved solids (TDS) and total hardness (TH) were calculated using the following equations:

$$TDS\ (mg/l) = Cations\ (mg/l) + Anions\ (mg/l)$$
$$TH\ (mg/l\ CaCO_3) = 2.5\ Ca\ (mg/l) + 4.1\ Mg\ (mg/l)$$

Table 1a. Chemical analysis data (concentration in mg/l) of surface water and groundwater in the Wadi Bu Ash Shaykh and Zallah areas (after Jurak, 1985; Vesely, 1985)

Area	Type	Sample No.	pH	TDS*	TH*	K	Ca	Na	Mg	Cl	HCO_3
Wadi Bu Ash Shaykh	Drilled well	1	7.9	4274	2128.5	24	507	600	210	1215	198
	Artesian well	2	7.2	4341	845	23	42.8	900	180	1335	214
	Dug well	3	7.2	4926	1980	31	464	900	200	1400	180
	Spring	4	7.1	20869	6912	72.2	846	4800	1170	8000	818
	Sabkha	5	7.6	38977	8004	360	676	8700	1540	18800	70
	Sabkha	6	6.8	168013	32395	970	1232	52000	7150	99000	52
	Sabkha	7	6.9	320330	54063	2340	18427	99000	1950	175000	116
Zallah	Drilled well	41	7.3	1549	582.5	13.8	151	270	50	348	186
	Drilled well	42	7.4	1666	520	15.3	126	330	50	325	241
	Dug well	43	7.2	2696	899.5	18.6	245	550	70	810	323
	Catcher trench	44	7.4	30298	6041.5	320	957	8600	890	12900	128
	Artesian well	45	6.8	34227	4126	126	1142	11400	310	19300	305
	Artesian well	46	7.1	34649	4541.5	132	1341	11400	290	19300	244
	Sabkha	47	7.5	72219	16397	770	589	20500	3640	37000	342

Table 1b. Chemical analysis data (concentration in mg/l) of surface water and groundwater in the Wadi Bu Ash Shaykh and Zallah areas (after Jurak, 1985; Vesely, 1985)

Area	Type	Sample No.	SO_4	NO_3	F	Li	Sr	B	I	Br
Wadi Bu Ash Shaykh	Drilled well	1	1506	-	1.7	0.12	9.9	0.99	0.03	1.34
	Artesian well	2	1457	176	1.2	0.1	9.6	0.73	0.03	1.45
	Dug well	3	1737	-	1.3	0.13	9.7	1	0.03	1.44
	Spring	4	5100	-	6.9	0.53	43.8	5.03	0.05	6.75
	Sabkha	5	8775	-	-	0.83	31.2	12.9	0.05	11.5
	Sabkha	6	7516	-	-	1.18	44.9	7.45	0.64	38.6
	Sabkha	7	23371	-	-	1.32	18.7	5.54	2.05	98
Zallah	Drilled well	41	473.3	51.5	1.3	0.05	2.4	0.35	<0.03	1.5
	Drilled well	42	543.3	30	1.6	0.07	1.9	0.49	<0.03	1.29
	Dug well	43	650	21	1.4	0.09	4.3	0.76	<0.03	1.91
	Catcher trench	44	6454	-	-	0.52	27.6	5	0.04	15.8
	Artesian well	45	1535	-	-	3.14	50.7	12.3	0.3	42.5
	Artesian well	46	1828	-	-	3.14	54.7	12.5	0.28	43.3
	Sabkha	47	9302	-	-	1.35	41.2	7.27	0.22	25.6

Using the Piper diagram (Figure 2), the hydrofacies of the water samples were evaluated. Sample 1 is categorized as CaCl Type, while samples 3 and 41 fall into the NaCl Type and CaMgCl Type categories. The remaining samples are classed as NaCl Type. Moreover, the TDS concentration divides the water samples into three categories (Figure 3): (1) Samples 1, 2, 3, 41, 42, and 43 are categorized as brackish water; (2) Samples 4, 44, 45, and 46 belong to saline water; and (3) Samples 5, 6, 7, and 47 are included in hypersaline.

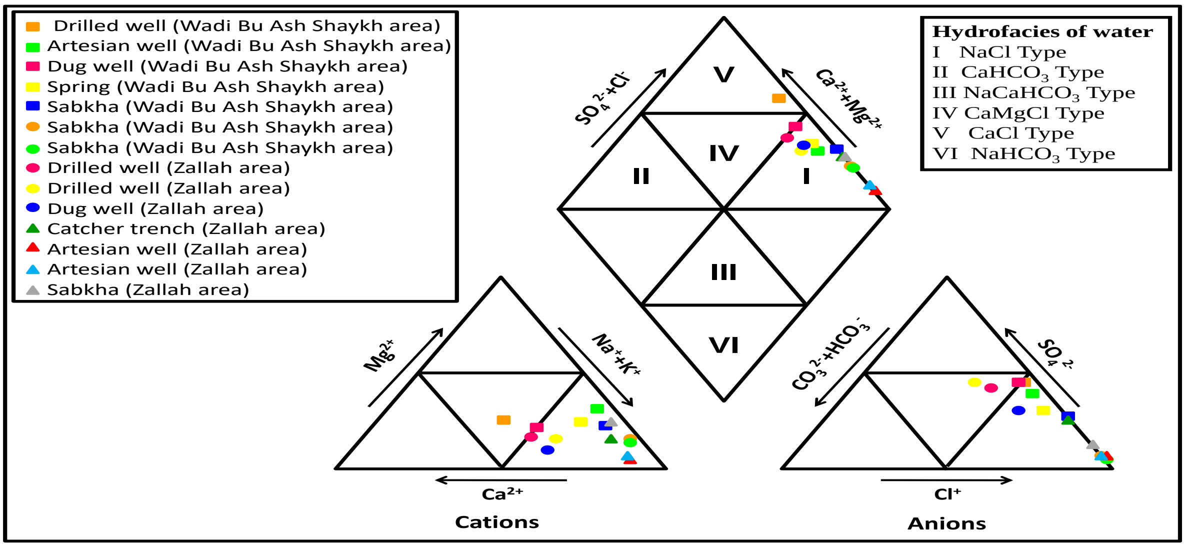


Figure 2. Piper diagram showing the hydrochemical facies of the water samples (fields after Tweed et al., 2005).

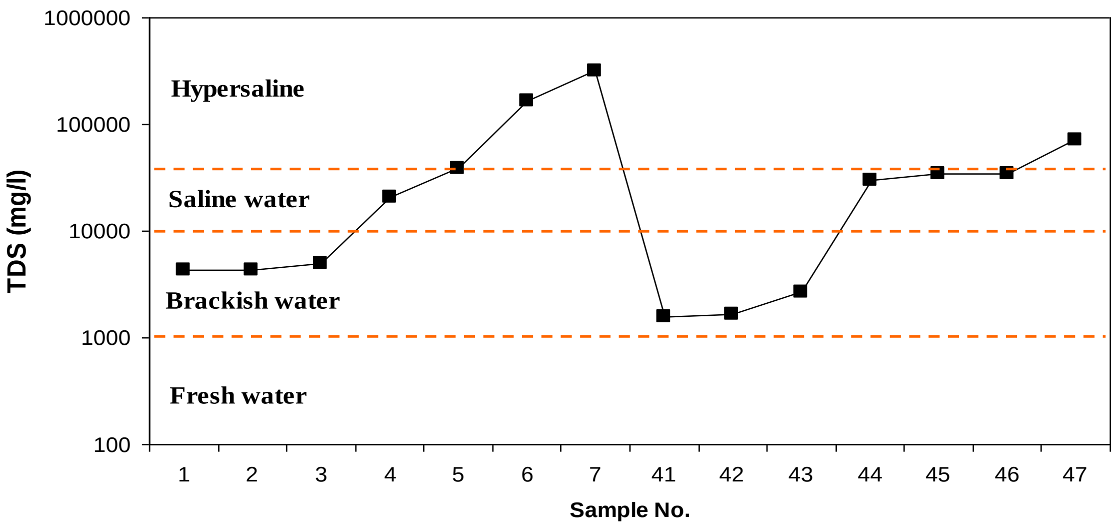


Figure 3. Binary plot showing the classification of the water samples based on the TDS concentration

In the water samples, there is a noticeable influence of evaporation since the total amounts of Cl and SO_4 (33213 mg/l, in average) are higher than the HCO_3 concentration 244.1 mg/l, in average). Moreover, the average seawater ratio (0.004) is lower than the average HCO_3/Cl ratio (0.16) in the water samples. The weathering of rocks is most likely the cause of the high ratio. The above assumptions are supported by the binary plots of $Cl/(Cl+HCO_3)$ versus TDS (Figure 4) and Cl versus B (Figure 5).

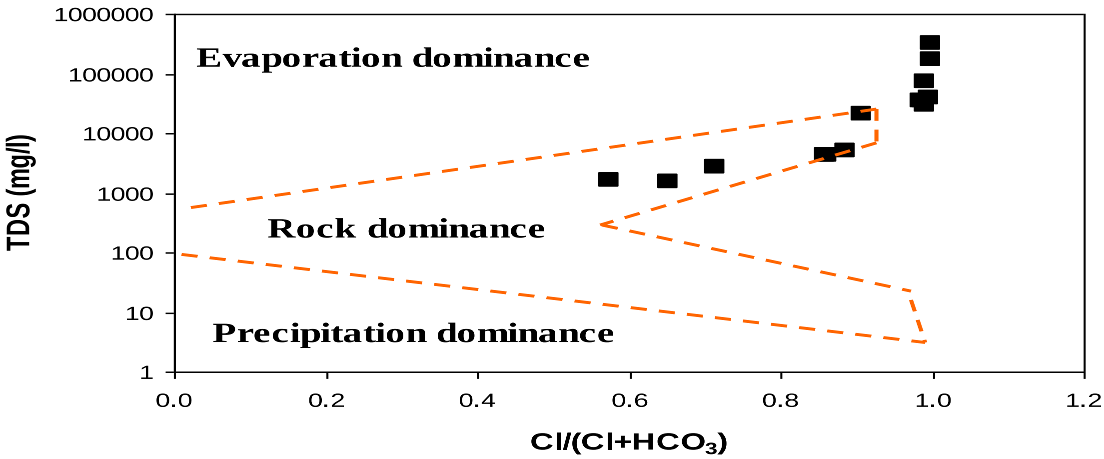


Figure 4. Binary plot of Cl/(Cl+HCO$_3$) vs. TDS showing the sources of dissolved solids in the water samples (fields after Gibbs, 1970)

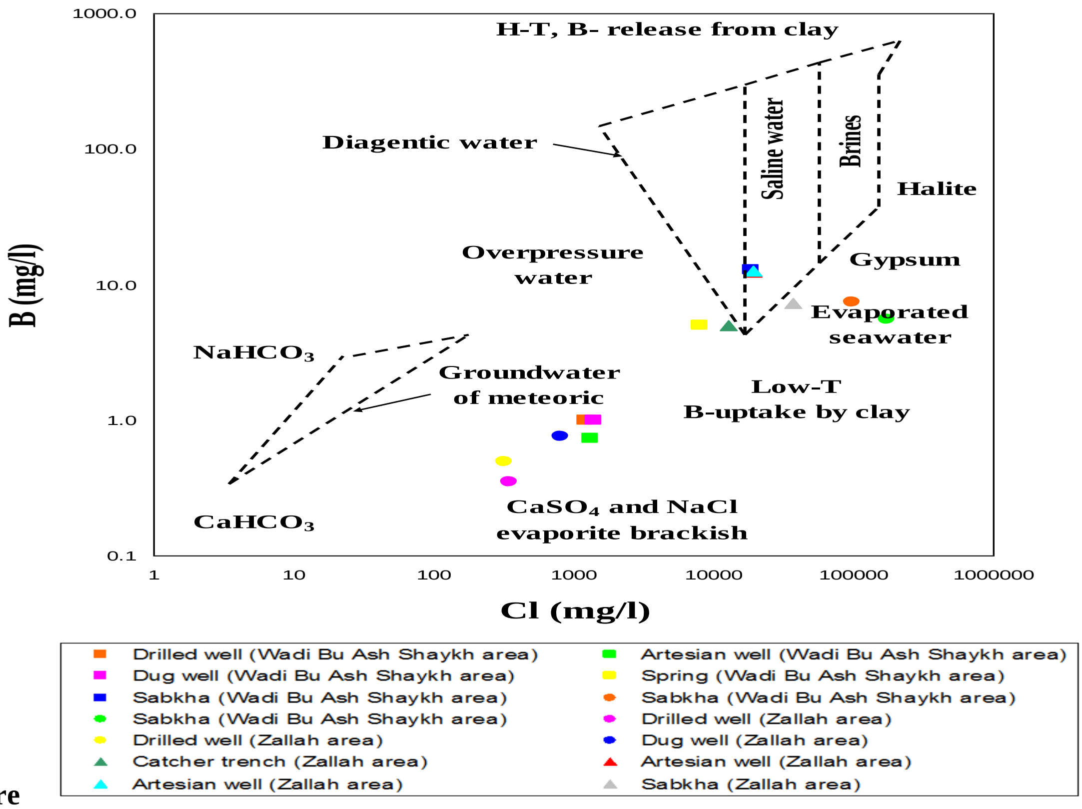


Figure 5. Binary plot of Cl vs. B showing the sources of dissolved solids in the water samples (fields after Boschetti et al., 2011).

It is possible to predict how much calcite will precipitate or dissolve in water by using the Langelier Saturation Index (LSI, Langelier, 1936). The following values illustrate the suggestions for the LSI: (1) LSI<0 (water's saturation level with $CaCO_3$ is low); (2) LSI=0 (water is seen as neutral); and (3) LSI>0 (considering $CaCO_3$, water is supersaturated). The enhancement of the LSI proposed by Carrier Air Conditioning Company (1965) is as follows: (1) **Class I:** Serious corrosion (–2<LSI<–0.5); (2)

Class II: Slightly corrosion but non-scale forming (–0.5<LSI<0); (3) **Class III:** Balanced but pitting corrosion possible (LSI=0); (4) **Class IV:** Slightly scale forming and corrosive (0<LSI<0.5); and (5) **Class V:** Scale forming but non corrosive (0.5<LSI<2). LSI values of the water samples were calculated using PHREEQC software (Table 2). Samples 2, 5, and 45 are obviously undersaturated in terms of $CaCO_3$, while $CaCO_3$ saturation is evident in the remaining samples. Furthermore, the samples are classified into four different classes: (1) Class I includes samples 2 and 6; (2) Samples 5 and 45 belong to class II; (3) Samples 1 and 4 are included in class V; and (4) Class IV comprises the remaining samples.

Table 2. LSI values of the water samples

Area	Type	Sample No.	WQI
Wadi Bu Ash Shaykh	Drilled well	1	0.90
	Artesian well	2	-0.75
	Dug well	3	0.18
	Spring	4	0.6
	Sabkha	5	-0.26
	Sabkha	6	-1.4
	Sabkha	7	0.09
Zallah	Drilled well	41	0.05
	Drilled well	42	0.17
	Dug well	43	0.29
	Catcher trench	44	0.03
	Artesian well	45	-0.15
	Artesian well	46	0.12
	Sabkha	47	0.08

3.2 Drinking Water Quality

The acceptable limits (Table 3) were used in this study to evaluate the drinking water quality. Below is a comparison between the concentration of the analyzed parameters and the acceptable limits:
(1) The pH values are within the acceptable limits.
(2) The values of TDS, TH, K, Na, and Li are higher than the permissible limits.
(3) Except for samples 2, 41, and 42, the Ca concentrations exceed the allowable limits.
(4) The Mg values surpass the acceptable limits, with the exception of samples 41, 42, and 43.
(5) The concentrations of Cl, SO_4, and Sr are greater than the permitted limits, except for samples 41 and 42.
(6) Except for sample 4, the HCO_3 values are below the allowable limits.
(7) The NO_3 concentrations exceed the acceptable limits, with the exception of samples 42 and 43.
(8) The F values surpass the permissible limits, except for samples 41and 43.
(9) There is a variation in the values of B and Br; some values are lower than the allowable limits (samples 1, 2, 3, 41, 42, and 43), while others are greater (samples 4, 5, 6, 7, 44, 45, 46, and 47).
(10) All samples (except for samples 6, 7, 45, and 46) have I values below the permitted limits.

Table 3. The acceptable limits for drinking water (concentration in mg/l)

Ion	PI	Reference
pH	6.5-8.5	WHO (1997)
TDS	500	WHO (1997)
TH	500	WHO (2011)
K	12	WHO (1997)
Ca	200	WHO (1997)
Na	200	WHO (1997)
Mg	150	WHO (1997)
CI	600	WHO (1997)
HCO_3	600	WHO (1997)
SO_4	600	WHO (1997)
NO_3	50	WHO (2017)
F	1.5	WHO (2004)
Li	0.06	US EPA (2023)
Sr	4	ATSDR (2004)
B	2.4	WHO (2009)
I	0.24	Health Canada (2022)
Br	6	WHO (2009)

Two different kinds of drinking water quality indices (pollution index (PI) and water quality index (WQI)) were used in order to assess the water samples more precisely. Here is how to calculate these indices:

$PI = ((C_{max}/MAC)^2+(C_{min}/MAC)^2)^{1/2}/2$ (Caerio et al., 2005)
$WQI = 100-((F_1^2+F_2^2+F_3^2)^{1/2}/1.732)$ (CCME, 2001)

Where, C (mg/l) and MAC (mg/l) are the metal value and the acceptable limit, respectively. F1 shows the degree of non-compliance with water quality standards throughout the pertinent time period. F2 represents the percentage of individual tests that fall short of the goals. F3 shows the proportion of test values that fail and fall short of the intended outcomes. Several classes of drinking water quality are distinguished by the drinking water quality indices (Tables 4 and 5). The PI values (Table 6) indicate that the water samples are no effect by HCO_3, slightly affected by NO_3, moderately affected by F and B, strongly affected by I, and seriously affected by K, Ca, Na, Mg, Cl, SO_4, Li, Sr, and Br. Furthermore, the WQI values (Table 7) show that the water samples have poor quality. From the foregoing, we can infer that the water samples are unfit for human consumption.

Table 4. Classification of drinking water quality based on the pollution index (after Caerio et al., 2005)

Class	PI
No effect	< 1
Slightly affected	1-2
Moderately affected	2-3
Strongly affected	3-5
Seriously affected	>5

Table 5. Classification of drinking water quality based on the water quality index (after CCME, 2001)

Class	WQI
Poor	0-44
Marginal	45-64
Fair	65-79
Good	80-88
Very good	89-94
Excellent	95-100

Table 6. Pollution index values of the water samples

Ion	PI
K	97.5
Ca	53.2
Na	247.5
Mg	23.8
CI	145.8
HCO_3	0.7
SO_4	19.5
NO_3	1.8
F	2.3
Li	25.8
Sr	6.8
B	2.7
I	4.3
Br	8.2

3.3 Irrigation Water Quality

The viability of using the water samples for irrigation purposes was evaluated using pH, TDS, TH, Na, Cl, HCO_3, F, Li, B, sodium percent (Na%), sodium adsorption ratio (SAR), residue sodium carbonate (RSC), magnesium adsorption ratio (MAR), lime deposition potential (LDP), Kelley's ratio (KR), permeability index (PI), potential salinity (PS) as well as the Neiggebauer classification (Table 8). Tables (9 and 10) show how water is evaluated for irrigation purposes based on the above-mentioned parameters. The irrigation parameters are computed as follows:

Na% = (Na*100)/(Ca+Mg+Na+K)
SAR = Na/√(Ca+Mg)/2
RSC = (HCO_3+CO_3))–(Ca+Mg)
MAR = (Mg/(Mg+Ca))100
LDP = Ca+ Mg
KR = Na/(Ca+Mg)
PI = ((Na+HCO_3)/(Ca+Mg+Na))100
PS = Cl+(SO_4/2)
(To represent all concentrations, meq/l is utilized)

The water samples have values of pH, TDS, TH, Na, Cl, HCO_3, F, Li, B, Na%, SAR, RSC, MAR, LDP, KR, PI, PS, (Ca+Mg)/(Na+K), and (Ca+Mg)/Na ranging from 6.8 to 7.9, 1549 to 320330 mg/l, 520 to 54063 mg/l, 11.7 to 4304.3 meq/l, 9.3 to 5000 meq/l, 0.9 to 13.4 meq/l, 1.2 to 6.9 mg/l, 0.1 to 3.1 mg/1, 0.4 to 12.9 mg/l, 37.5 to 85.2, 4.9 to 184.9, –1081.9 to –6.5, 15 to 91.2, 10.5 to 1083.9, 0.6 to 6, 42.6 to 86.5, 14.9 to 5243.4, 0.2 to 1.6, and 0.2 to 1.6, respectively. Generally, these values suggest that the water samples are unfit for irrigation.

Table 7. Water quality index values of the water samples

Area	Type	Sample No.	WQI
Wadi Bu Ash Shaykh	Drilled well	1	18.33
	Artesian well	2	24.33
	Dug well	3	10.27
	Spring	4	13.81
	Sabkha	5	12.88
	Sabkha	6	9.20
	Sabkha	7	9.60
Zallah	Drilled well	41	6.72
	Drilled well	42	14.20
	Dug well	43	18.49
	Catcher trench	44	10.83
	Artesian well	45	10.83
	Artesian well	46	12.09
	Sabkha	47	4.66

Table 8. Neiggebauer classification of irrigation water (after Bajraktari et al., 2022)

Description of water	Class of water	Quantity of dry matter (mg/l)	Ion concentration (meq/l)
Water without remark	I_a	<700	(Ca+Mg)/(Na+K)>3
	I_b	<700	(Ca+Mg)/Na>3
Good water	II	<700	(Ca+Mg)/Na>1
Water to be analyzed	III_a	700-3000	(Ca+Mg)/Na>3
	III_b	700-3000	(Ca+Mg)/Na>1
Unsuitable water for irrigation	IV_a	<700	(Ca+Mg)/Na<1
	IV_b	700-3000	(Ca+Mg)/Na<1
	$IV_{c,d,e}$	>3000	Regardless of the ion concentration

Table 9. Water evaluation for irrigation purposes based on irrigation parameters (after California Plant Health Association, 2002)

Parameter	Suitable	Unsuitable
pH	<7	>8
TDS (mg/l)	<500	>2000
TH (mg/l)	<150	>300
Na (meq/l)	<3	>9
CI (meq/l)	<4	>10
HCO_3 (meq/l)	<1.5	>8.5
RSC	<1.25	>2.5

Na%	<25	>60
SAR	<10	>18
MAR	<50	>65
PI	<75	>50
KR	<1	>2
LDP	<1	>2
PS	<10	>10

Table 10. The acceptable limits for irrigation water (after Rowe and Abdel-Magid, 1995)

Constituent	Long-term use (mg/l)	Short-term use (mg/l)
F	1	15
Li	2.5	2.5
B	0.75	3

4. Conclusion

The following is a summary of this work's conclusions:
(1) NaCl Type is the dominant hydrofacies in most water samples.
(2) There are three types of water: brackish, saline, and hypersaline.
(3) $CaCO_3$ saturation is evident in most samples.
(4) The studied water should not be used for drinking and irrigation purposes.

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