Assessment of groundwater quality for drinking and irrigation purposes, Martubah plain, eastern Libya

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Abstract

The study area is a part of the Martubah plain. It extends from the east of Al Jabal al Akhdar west up to Tamimi Village, 50 km east of Darnah city, in the eastern region of Libya. Groundwater is the main source for water supply and irrigation purposes. In order to evaluate the quality of groundwater in the study area, 22 groundwater samples were collected and analyzed for various parameters. Physical and chemical parameters of the groundwater such as electrical conductivity, p^H, total dissolved solids, Na, K, Ca, Mg, Cl, HCO_3, CO_3, SO_4, and TH were determined. Chemical indexes such as the percentage of sodium, sodium ad sorption ratio, residual of sodium carbonate, permeability index, Magnesium Adsorption Ratio and Chloro-Alkaline Indices were calculated. Based on the analytical results found, groundwater in the area is generally fresh and is hard to very hard. The abundance of the major ions is as follows: Cl > HCO_3 > SO_4 > CO_3 and Na > Mg > Ca > K. The dominant hydrochemical facies of groundwater is of the Na.Mg-Cl, and Na-HCO_3 type. A Gibbs diagram shows that the groundwater samples fall from freshwater to saline water. From the sodium absorption ratio conductivity plot it was found that the groundwater samples fall in the field C_3S_1. Similarly, from a Wilcox diagram the samples fall in the field of good to permissible, permissible to doubtful and doubtful to unsuitable. Most of the groundwater samples show that the groundwater of the study area is unsuitable for drinking purposes and also not suitable for irrigation under ordinary conditions, but may be used occasionally under very special circumstances.
Keywords: Martubah plain, Al Faidiyah formation, Libya groundwater, fossiliferous limestone, physical-chemistry, magnesium adsorption ratio.

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1 Introduction

Water is an essential bio-resource for all life. The freshwater resources account for less than 1% and about 0.01% of all water present on Earth [1]. Therefore, human activities and civilizations were concentrated around these sources of water. These unplanned human activities and increasing economic developments applied huge stresses on groundwater resources. Libya is an arid region and is among those countries in North Africa, which are facing serious shortages in water resources, due to the demands of rapid developments within the country [2]. Therefore, sustaining water resources in this country is a major concern for both decision makers and scientists. Groundwater is considered a major source of water in Libya and particularly the groundwater within the investigated area [3]. Assessment of water is not only used to determine its suitability for human consumption but also in relation to its agricultural, industrial, recreational, commercial uses and its ability to sustain aquatic life. Water quality monitoring is, therefore, a fundamental tool in the management of freshwater resources. The chemical parameters of groundwater play a significant role in assessing water quality, which is suitable for irrigation [4]. However, irrigation with poor quality water may bring undesirable elements into the soil in excessive quantities, affecting its fertility. The quality of groundwater has a definite command over the yield of crops through its effect on the soil environment. Geochemical studies of groundwater provide a better understanding of possible changes in quality as development progresses. Suitability of groundwater for domestic and irrigation purposes is determined by its groundwater geochemistry [5]. This study aimed to identify the ground water quality with some geochemical processes and to understand the ground water characteristics which are very important for ground water management in the study.

2 The study area

The study area is located in the Martubah plain, southeast of Al Jabal al-Akhdar, in northeast Libya (Fig. 1), bounded by 32°09′59″N to 32°43′22″N latitudes and 22°20′15″E to 22°59′10″E longitudes. It occupies an area approximately 2,853 km^2 and the average elevation is 300 m.a.s.l. (Fig. 1). There are no permanent water bodies in the plain except for wadis and springs, which only run during the rainy season. The area has a moderate temperate climate and the air temperature is highest in August (26°C) and lowest in January (8°C) with an annual average of 20°C [6]. The climate of the study area is semi-arid and its average annual rainfall is 154 mm, of which 83% falls during the autumn and winter seasons. The most important economic activity in the area is agriculture, with the chief crops being barley, wheat and some vegetable crops.

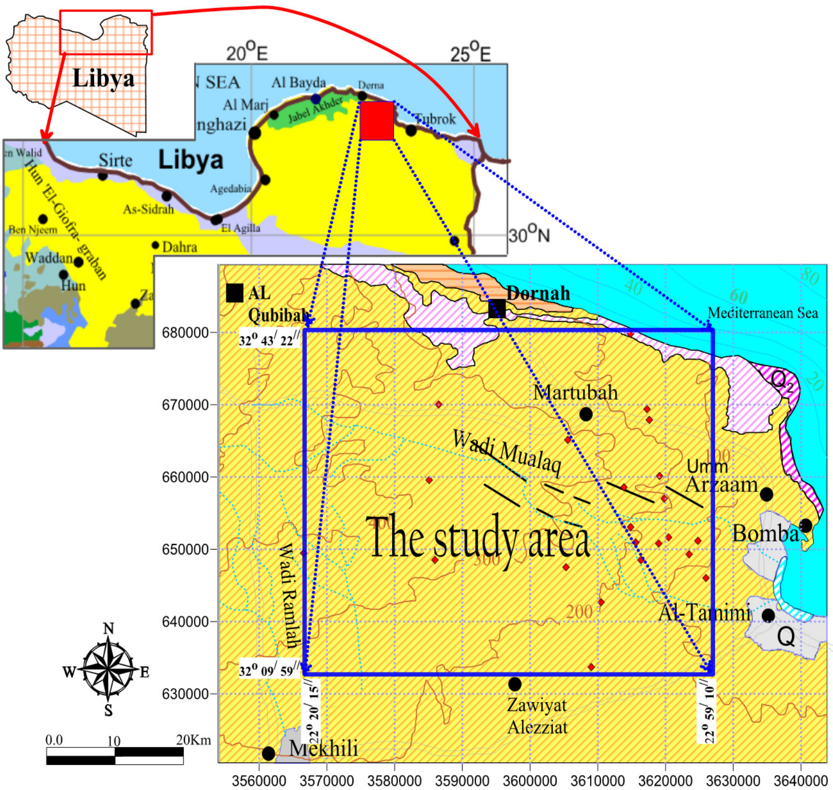

Figure 1: Location of study area.

3 Materials and methods

Groundwater samples were collected from 22 shallow and deep wells and springs of the area. The locations of the sampling points are shown in Fig. 2. The pH and electrical conductivity (EC) were measured using digital conductivity meters immediately after sampling. Water samples collected in the field were analyzed in the laboratory for the major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{-}, SO_4^{2-}, Cl^{-}), using the standard methods as suggested by the American Public Health Association [7]. Sodium (Na^{+}) and Potassium (K^{+}) were determined by flame photometer. Total hardness (TH) as $CaCO_3^{-}$, Calcium (Ca^{2+}), carbonate (CO_3^{+}), bicarbonate (HCO_3^{-}) and chloride (Cl^{-}) were analyzed by volumetric methods. Magnesium (Mg^{2+}) was calculated from TH and Ca^{2+} contents. Sulfates (SO_4^{2-}) were estimated using the colorimetric technique.

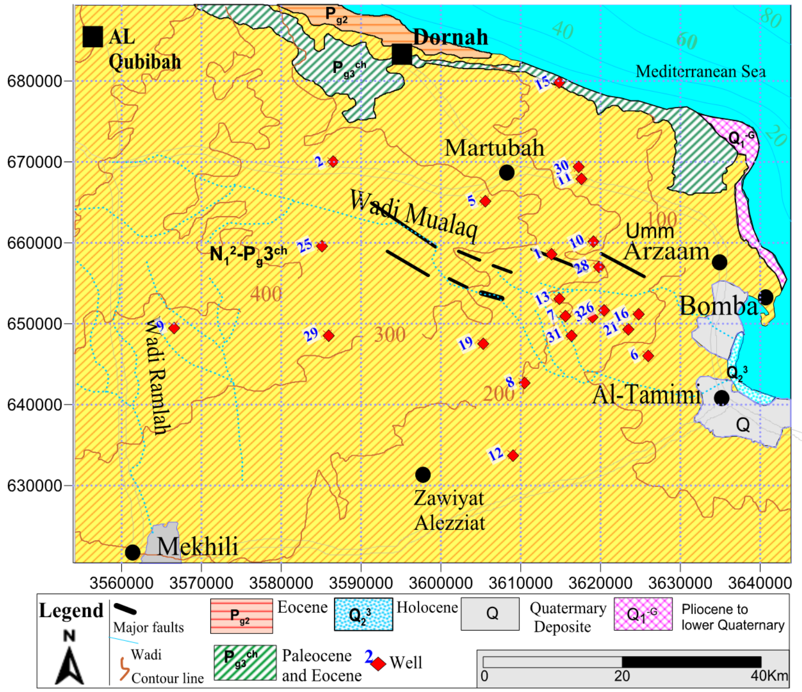

Figure 2: Location and geology map, hydrogeology units and wells position, (after IRC [8]).

4 Results and discussion

4.1 Geological and hydrogeological setting

From a geological point of view, the investigated area is a part of the Martubah plain, which is located to the south east of Al Jabal al Akhdar [8]. Limestone and fossiliferous limestone rocks of different epochs crop out in the study area and range in type from Pliocene to Eocene. Eocene and Miocene sedimentary rocks consist of limestone, chalky limestone and fossiliferous limestone. Oligo-miocene formations in the study area are chiefly comprised of crystalline limestone, and siltstone. The Oligocene formation consists of crystallized limestone and, some fossiliferous limestone [9]. The thickness of this major aquifer increases from the fan deposits in the west towards the middle and south side of plain [10]. Fig. 2 shows the distribution of the outcropping rock formations in the study area. The plane is tectonically active and the most important structure that affects the geology of Martubah plain is the faults system. The exposed lithological units of the Martubah plain range in age from Precambrian to Quaternary and have different hydrogeological characteristics (Fig. 2). The stratigraphic succession of the study area is shown in Table 1 [9]. The units of similar hydrogeological characteristics are summarized in Table 1.

Table 1: Stratigraphic relations of the geologic units in the study area showing hydro-geologic properties.

Age	Formation	Lithology	Hydrogeologic properties
Eocene	Darnah and Apollonia	Chalky limestone,	Permeable
Miocene	Al Faidiyah	Limestone and fossiliferous limestone	Impermeable
Oligocene	Al Abraq Formation outcrops	Calcilutite and limestone, fossiliferous limestone	High permeability
Oligo-miocene	Al Faidiyah	Limestone and fossiliferous limestone	Impermeable

Oligo-Miocene is a water bearing strata, controlled by the lithology, limestone and fossiliferous limestone, surface water infiltrates to the base of the formation, the impermeable layer which is composed of calcareous clay to marl. It is present in the whole of the southern part of the study area, to the south of the Martubah escarpment. However, a very low yield is expected from this formation [10].

The groundwater flow apparently originates from the second plateau in the surroundings of Martubah where water levels are in excess of 300 m.a.s.l, and from here it is directed towards the east, south and west [11]. The natural outlets from the aquifer which seem to control the flow are usually located along wadis where the ground surface intersects the water table and consists of low to very low yield springs which are frequently reduced to just a trickle. This situation is indicative of the small amount of flow involved. The total spring flow from this aquifer does not exceed 10 1/s [11].

4.2 Groundwater chemistry

The chemical composition of groundwater results from the geochemical processes, which occur as water reacts with the geologic materials in which it flows [12]. The water quality analysis included all major anions and cations. The groundwater pH and electrical conductivity (EC) values of the study area range from 6.4 to 8.4 and 738 to 5696 μS/cm, respectively. The total dissolved solids (TDS) in the study area varies between 406 to 3133 mg/l. 64 % of the groundwater in the study area falls under fresh (TDS < 1000 mg/l) types of water [13]. The total hardness (as $CaCO_3$) ranges from 236 to 1200 mg/l. In the study area, the Na and K concentrations in groundwater range from 78 to 920 and 4 to 70 mg/l, respectively. The concentrations of calcium range from 37.9 to 192.5 mg/l, which is derived from calcium rich minerals like feldspars, pyroxenes and amphiboles. The major source of magnesium (Mg) in the groundwater is due to ion exchange of minerals in rocks and soils by water. The concentrations of Mg and HCO_3 ions found in the groundwater samples of the study area range from 34.4 to 1001 and 113 to 347 mg/l respectively. The concentration of chloride ranges from 152 to 1986 mg/l.

Sulfate varies from 29 to 480 mg/l. Fig. 3 shows that Mg, Na and Cl are the dominant cations and anion, respectively. A further illustration of this is shown in Fig. 4 where the mean values of Cl exceed 66% of total anions in milliequivalent units.

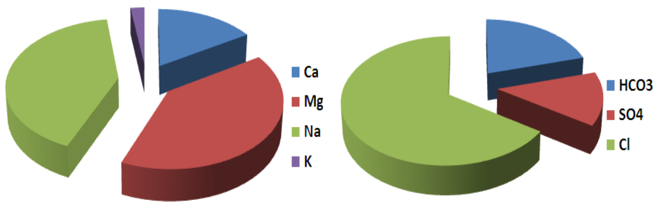

Figure 3: Pie diagrams of the median values of major ions.

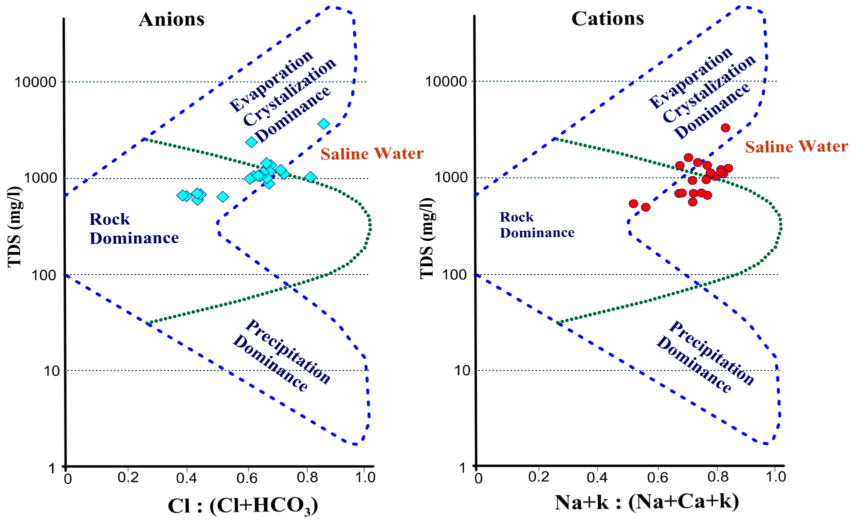

Figure 4: Mechanisms governing groundwater chemistry (after Gibbs [14]).

The abundance of the major ions in the groundwater is in the following order: Na > Mg > Ca > K and Cl > HCO_3 > SO_4 > CO_3. The minimum, maximum and average values of physical and chemical parameters of the groundwater samples are presented in Table 3. The concentration of dissolved ions in groundwater samples are generally governed by lithology, the nature of geochemical reactions and solubility of interaction rocks. The functional sources of dissolved ions can be broadly assessed by plotting the samples, according to the variation in the ratio of (Na+K)/(Na+Ca+K) and Cl/(Cl+HCO_3) as a function of TDS [14]. The Gibbs plot of data from study area Fig. 4 indicates the interaction between the rock chemistry and the chemistry of the percolation waters under the subsurface. The groundwater samples range from freshwater to saline water.

Table 2: Minimum, maximum average and SD values of the physical and chemical parameters of groundwater samples.

Parameters	Minimum	Maximum	Average	SD
pH	6.4	8.4	7.81	0.45
EC µs/cm	738	5696	1656.54	1062.2
TDS mg/l	405.9	3132.8	921.8	578.2
Na mg/l	78	920	208.7	173.8
K mg/l	4	70	19.51	17.7
Ca mg/l	37.9	192.5	71.02	33.1
Mg mg/l	34.4	1001	105.32	202.1
Cl mg/l	152	1986	403.55	375.9
HCO_3 mg/l	113	347	220.7	15.1
CO_3 mg/l	0.1	0.15	0.1	0.01
SO_4 mg/l	29	480	115.2	109.1
TH mg/l	236	1200	447.72	205.6
SAR	2.11	16.3	5.7	3.16
NA%	10.3	62.5	42.6	12.6
RSC	-18.5	-1.55	-8.7	-
MH%	60	93.7	61.7	6.69

EC: Electrical conductivity, TDS: Total dissolved solids, SAR: Sodium adsorption ratio, TH: Total hardness, SD: Standard deviation, RSC: Residual sodium carbonate, MH: Magnesium Adsorption Ratio.

Table 3: Groundwater samples of the study area exceeding the permissible limits prescribed by WHO for drinking purposes.

Water quality parameter	WHO (2004, 2011)		Number of samples exceeding PL	Samples exceeding PL %	Undesirable effects
	Desirable Limit (DL)	Maximum permissible limit (PL)			
pH	7–8.5	9	-	-	Taste
CE (µS/cm)	500	1,500	11	50	Gastrointestinal irritation
TDS mg/l	500	1,500	-	-	Gastrointestinal irritation
Na mg/l	-	200	11	50	Scale formation
K mg/l	-	12	13	59	Bitter taste
Ca mg/l	75	200	-	-	Encrustations in water structure
Mg mg/l	50	150	2	9	Scale formation
Cl mg/l	200	600	1	4.5	Salty taste
HCO_3 mg/l	-	240	4	18	-
CO_3 mg/l	-	-	-	-	-
SO_4 mg/l	200	400	1	4.5	Laxative effects
TH mg/l	100	500	4	18	Scale formation

4.3 Hydrogeochemical facies

The values obtained from the groundwater samples analysis, and their plot on the Piper's diagrams [15] reveal that the dominant cations are Na, Mg and the anion is Cl. In the study area, the major groundwater type is Na-Cl and mixed Ca-Mg-Cl (Fig. 5); Chadha [16] has proposed a new diagram for geochemical data presentations. The proposed diagram is a modification of the Piper diagram with a view to extending its applicability in representing water analysis in the simplest way possible. Results of the analysis were plotted on the proposed diagram to test its applicability for geochemical classification of groundwater and to study the hydrochemical processes (Fig. 6). The plot shows that all of the groundwater samples fall under the subdivision of alkaline earths exceed alkali metals and weak acidic anions exceed strong acidic anions (Ca-Mg-Cl water type and Na- Cl water type).

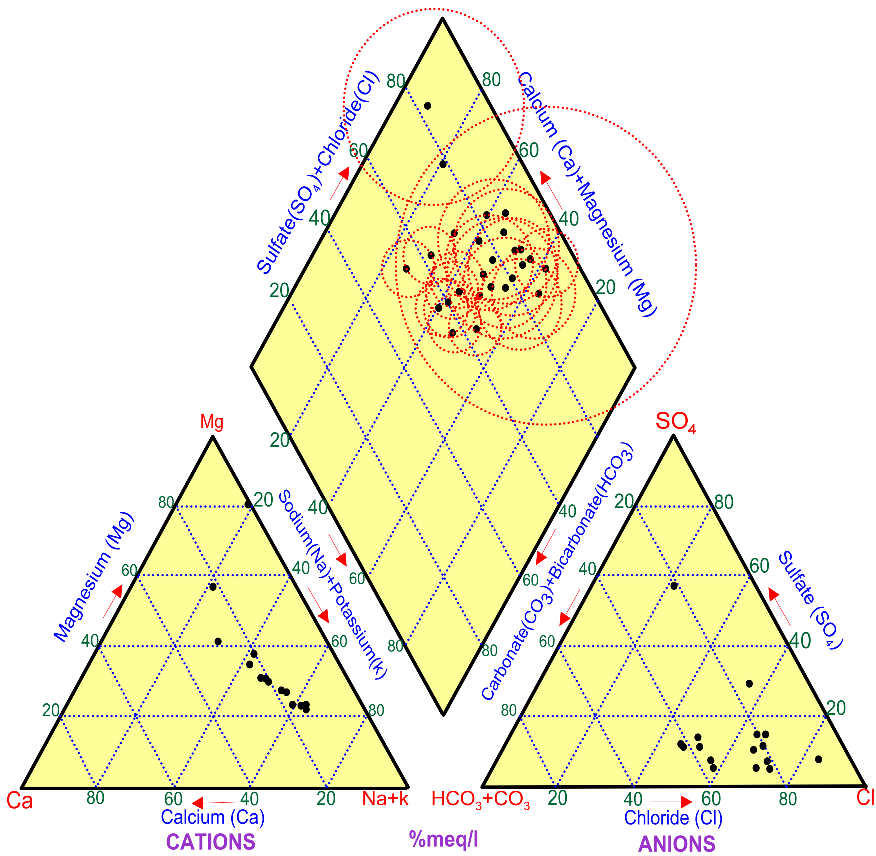

Figure 5: Piper diagram representing hydrochemical types [15].

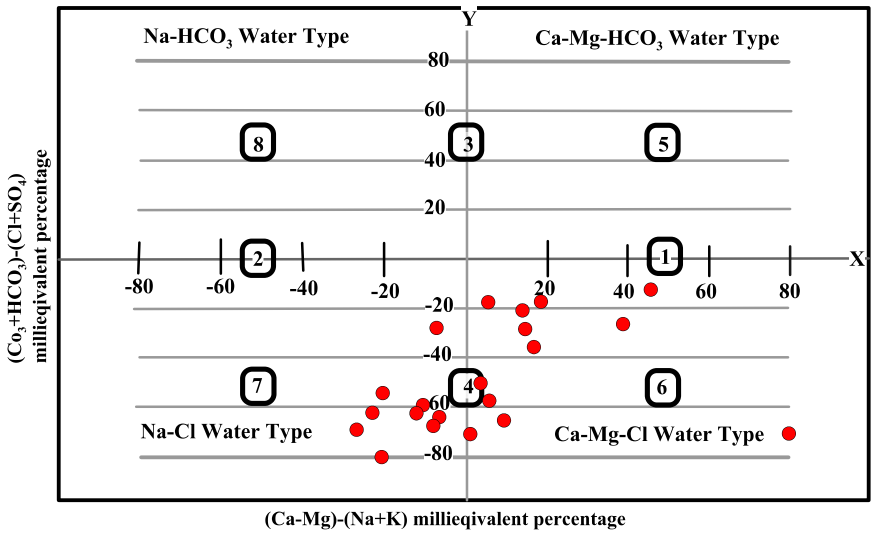

Figure 6: Diagram showing geochemical classification and hydrochemical parameters of groundwater (after Chadha [16]).

4.4 Drinking and irrigation water quality

The analytical results have been evaluated to ascertain the suitability of groundwater in the study area for drinking and agricultural uses. The drinking water quality is evaluated by comparing it with the specifications of TH and TDS set by the World Health Organization (WHO) [17, 18]. According to the WHO specification, a TDS amount of up to 500 mg/l is the highest desirable and up to 1500 mg/l is the maximum permissible (Table 4). Based on this classification, 82% of samples belong within the highest desirable category and the remaining samples belong to the maximum permissible category. The hardness values range from 236 to 1200 mg/l. The classification of groundwater is based on total hardness [19]. Table 5 shows that 86.4% of the groundwater samples fall in the very hard water category, and remaining samples fall in the hard category. The maximum allowable limit of TH for drinking is 500 mg/l and the most desirable limit is 100 mg/l as per the WHO international standard. Based on this classification it indicates that 18% of the groundwater samples exceed the maximum allowable limits.

Table 4: Groundwater classification based on TH [19].

Total hardness as CaCO3(mg/l)	Water class	Number of samples	Percentage of samples
< 75	Soft	-	-
75-150	Moderately hard	-	-
150-300	Hard	3	13.6
>300	Very hard	19	86.4

Table 5: Classification of groundwater for irrigation based on EC.

Salinity Hazard (Class)	EC (μS/cm)	Representing Wells
Excellent (C_1)	<250	Nil
Good (C_2)	250–750	Nil
Doubtful (C_3)	750–2250	1–3, 5–8, 10–13, 16, 19, 21, 25, 26, 28–31
Unsuitable (C_4)	>2,250	99, 15, 29

Table 6: Sodium hazard classes based on USSL classification.

Categories	SAR	Representing Wells
Excellent (S_1)	< 10	1–3, 5–13, 15, 16, 19, 21, 25, 26, 28, 30, 31
Good (S_2)	10–18	29
Doubtful (S_3)	18–26	Nil
Unsuitable (S_4)	> 26	Nil

Salinity and indices such as the sodium absorption ratio (SAR), sodium percentage (Na %), residual sodium carbonate (RSC), and permeability index (PI) are important parameters for determining the suitability of groundwater for agricultural uses [20]. Electrical conductivity is a good measure of salinity hazard to crops as it reflects the TDS in groundwater. The US Salinity Laboratory [22] classified ground waters on the basis of electrical conductivity (Tables 5 and 6). Based on this classification, 16% of samples belong in the doubtful category and 84% in the good category. SAR is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops [21]. SAR is defined by Karanth [23] as eqn. (1),

$$SAR = Na / \sqrt{(Ca + Mg) / 2} \qquad (1)$$

where all ionic concentrations are expressed in meq/l. The SAR values range from 2.12 to 16.2 and according to the Richards [24] the classification is based on SAR values (Table 6). 95% of the groundwater samples belong to the excellent category. SAR can indicate the degree to which irrigation water tends to enter into cation exchange reactions in soil. Sodium replacing adsorbed calcium and magnesium is a hazard as it causes damage to the soil structure and becomes compact and impervious [24]. The analytical data plotted on the US salinity diagram [22] illustrates that 45% of the groundwater samples fall within the field of C_3S_1, indicating high salinity and low sodium water, which can be used for almost all types of soil with little danger of exchangeable sodium, and 50% of the groundwater samples fall in the field of C_3S_2, and only 4.5% of the groundwater samples (one sample) falls in the high hazard water type (C_4S_4) (Fig. 7).

Wilcox [25] used sodium percentage and electrical conductance in evaluating the suitability of groundwater for irrigation. The percentage of Sodium (Na%) is computed with respect to the relative proportions of cations present in water, where the concentrations of ions are expressed in meq/l. Na% is obtained using eqn. (2).

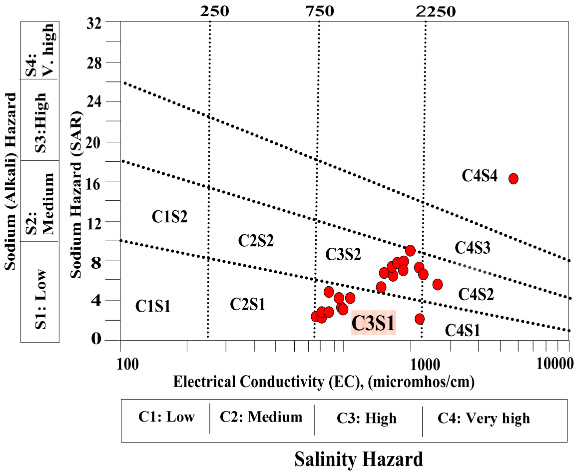

Figure 7: Rating of groundwater samples in relation to salinity and sodium hazard.

$$Na\% = (Na + K) / (Ca + Mg + K) \times 100 \qquad (2)$$

Wilcox plots SAR vs EC to develop the suitability of water for irrigation purpose. In the study area, nearly 22% groundwater samples fall in the field of good to permissible, 50% of the groundwater samples fall in the field of permissible to doubtful and 18 % of the groundwater samples fall in the field of doubtful to unsuitable for irrigation, indicating low to medium SAR and high to very high salinity (Fig. 8). It is moderately suitable for irrigation purposes.

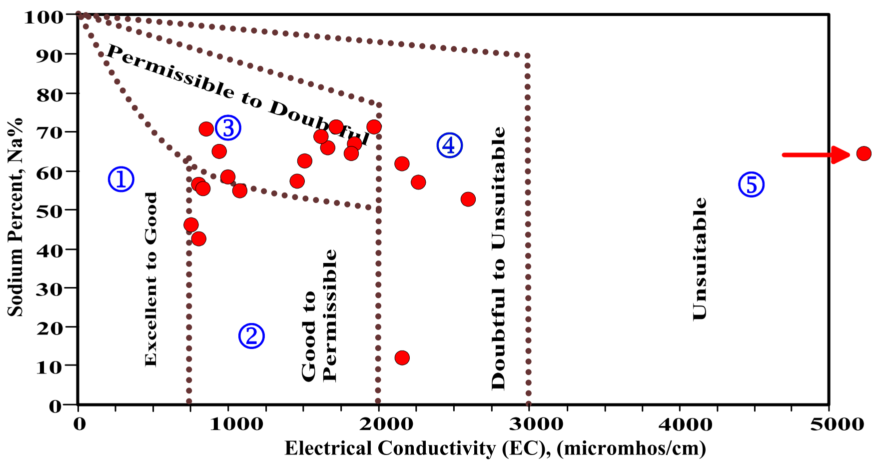

Figure 8: Rating of groundwater samples on the basis of electrical conductivity and percent sodium (after Wilcox [25]).

Residual sodium carbonate (RSC) has been calculated to determine the hazardous effects of carbonate and bicarbonate on the quality of water for agricultural purpose and has been determined by eqn. (3),

$$RSC = (CO_3 + HCO_3) - (Ca + Mg) \tag{3}$$

where all ionic concentrations are expressed in meq/l [26]. The classification of irrigation water according to RSC values is that waters containing more than 2.5 meq/l of RSC are not suitable for irrigation, while those having 2.93 to 2.3meq/l are doubtful and those with less than 1.25 meq/l are good for irrigation. Based on this classification, all of the groundwater samples belong to the good category.

PI are important parameters for determining the suitability of ground water for irrigation uses [27]. It is defined as eqn. 4.

WHO [28] uses a criterion for assessing the suitability of water for irrigation which is based on its PI. The PI ranges from 12% to 72% and the average value is about 59%. According to PI values, 95% of the groundwater in the study area can be designated as class II (25–75%) this shows that the groundwater in study area is suitable for irrigation purposes.

Magnesium hazard (MH); in general Ca^+ and Mg^+ maintain a state of equilibrium in groundwater. If more Mg^+ is present in the water the quality of the soil is affected, converting it to alkaline and decreasing the crop yield [29]. The proposed MH value for irrigation water is given by the following formula (where the concentrations are expressed in meq/l):

$$MH = 100 \times Mg^{+2} / (Ca^{2+} + Mg^{+2}) \tag{4}$$

MH values >50 are considered harmful and unsuitable for irrigation purposes. In the analyzed groundwater samples, the MH ranges from 60% to 93.7% with an average of 61.7%. Based on this classification, the groundwater in the study area is unsuitable for irrigation purposes.

4.5 Chloro-Alkaline Indices (CAI)

Schoeller [30] has evolved a formula, Chloro-Alkaline Indices (CAI), to find the ion exchange between the ground water and its surroundings when resident or travelling in the aquifer.

The CAI-I can be determined by eqn. (5).

$$CAI - \mathrm{I} = Cl - \left(Na + K\right) / Cl \tag{5}$$

where all ionic concentrations are expressed in terms of meq/l. The negative value of CAI indicates that there is exchange between sodium and potassium (Na^++K^+) in water with calcium and magnesium (Ca^{+2}+Mg^{+2}) in the rocks by a type of base-exchange reactions. The positive value of CAI represents the absence of base-exchange reactions and the existence of cation-anion exchange type reactions [29]. In the study area, four samples have the negative value of CAI-I proving the base-exchange reactions, while 18 samples indicate the cation-anion exchange reactions as summarized in Table 7.

Table 7: The negative and positive values of CAI-I.

ID	1	2	3	5	6	7	8	9	10	11	12
CAI- I	0.17	0.11	0.29	0.14	0.04	-0.16	0.19	0.03	0.06	0.03	-0.26

ID	13	15	16	19	21	25	26	28	29	30	31
CAI- I	-0.04	0.28	0.38	0.27	0.23	-0.01	0.11	0.22	0.28	0.22	0.22

5 Conclusion

A baseline study of the hydrogeochemical parameters of natural influences on groundwater quality for drinking and agricultural uses in Martubah plain, southeast of Al Jabal al-Akhdar.

Ninety-one percent of the groundwater samples were slightly alkaline (7.4–8.4) and within the WHO (2004) standard for drinking water. More than 50% of the ions of the groundwater sources were out of the WHO (2004) guideline values for drinking water. Sodium (Na^+) was the dominant cation, while Cl^- was the dominant anion for all the groundwater sources. The relative abundance of cations and anions in the ground-water sources were as follows: Na >Mg > Ca > K and Cl > HCO_3 > SO_4 > CO_3, respectively. The groundwater sources were fresh water with a relatively low mineralisation of 406–3133 mg/l TDS. The main sources of ions were from sediments and clay units which constitute the geology of the area.

The water types in the area were: Ca-Mg-Cl (54%), Na-Cl (36%) and Ca-Cl (9%). The main hydrogeochemical processes that influenced the chemical composition of the water sources were incongruent silicate dissolution and cation exchange. Based on EC, SAR, Na%, RSC and PI, 50% of the groundwater sources were considered unsuitable for agricultural purposes. Thus the groundwater must be used only for salt tolerant crop, permeable soil with careful soil and water management. However, according to MH classification, the groundwater in the study area is unsuitable for irrigation purposes.

Interpretation of hydrochemical analysis reveals that the groundwater in study area is fresh, hard to very hard. The sequence of the abundance of the major ions is in the following order: Na > Mg > Ca> K and Cl > HCO_3 > SO_4 > CO_3. Alkali earths slightly exceed alkalis. Falling of water samples in the rock dominance area in the Gibbs plot indicate the interaction between rock chemistry and the chemistry of the percolating precipitation waters in the subsurface.

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