Hydrochemical Investigation and Quality Assessment of Groundwater in WadiJarif, Sirte City, Libya

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Abstract:

Hydrochemistry of groundwater in WadiJarif, Sirte City, Libya was used to assess the quality of groundwater for determining its suitability for drinking, domestic and agricultural purposes. A total of 30 groundwater samples were collected randomly from WadiJarif, boring and analyzed for major ion chemistry to understand the operating mechanism of geochemical processes for ground water quality. The quality analysis is performed through the estimation of pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, HCO_3^{-}*. The results of chemical analyses indicate that the groundwater chemistry of the Wadi Jarif* *aquifers is highly influenced by their bearing facies and sea water intrusion. The water salinity is moderately saline classes, where the (TDS) ranges from 3311 to 8187ppm. The dominant water types are* Na_2SO_4 *of meteoric genesis and NaCl of marine genesis. Assessment of groundwater of WadiJarif for different uses indicates that the groundwater are classed as unsuitable for drinking (all studied samples TDS more than 1500), also, this groundwater can't be used for domestic purposes for its high TDS and TH. Moreover most of the groundwater of the study area is not recommended for irrigation under normal conditions. However, it is suitable for the salt tolerant crops and high permeable soils under good irrigation management.*

Key words: *Sirte City, WadiJarif, Hydrochemistry of Groundwater, chemical analysis.*

1. Introduction

Sirte is a city that lies on the coast of the Mediterranean Sea (Fig. 1) being overwhelmed by the arid or the semi-arid climate. Across the extension of this city, there are several valleys descending from south to the north to be pouring into marshes across the long coast [1].

WadiJarif area is selected for this study, because the previous studies did not address the hydrological, hydrogeological and hydrogeochemical in this area in details. In addtion to its large shortage in good quality water resources. The present work aims to define and evaluate the hydrochemical conditions of the groundwater of WadiJarif through the available data of thirty water points collected during field work.

The study area, as shown in the Figure (1), is located in WadiJarif and extends from longitude “16º 12' 00" to 16º 30' 00" E. and latitude 30º 12' 00" to 31º 15' 00" N. lies about 389 km east-southeast of Tripoli, capital of Libya. The length of this valley is approximately (31 km) with stream tube tightens at the heights of the valley and increases in width at the bottom of the valley. This valley is flowing down into marshes.

The Sirte area includes a narrow coastal plain which extends inland of 3-4 km from the present shoreline. Along the shore is a belt of low lying sand dunes, and just inland from these is a series of salt flats or " Sabkha" that lie at or near sea level and are subject to flooding during the rainy season. South of the coastal plain the land surface rises gradually in a gently undulating plateau which is about 70-80 m above sea level at south of the study area. The main stream in the area is the WadiJarif, which drains north into the sea. This stream and its tributaries, which slightly incise the plateau, are all ephemeral and carry runoff only after heavy or prolonged rain storms.

The climate of the Sirte area includes mild winters and hot dry summers; it is typical of the Mediterranean region. The bulk of the annual rain falls during the fall and winter months that is, from October to March. Rainfall during the remainder of the year is generally insignificant. The average annual precipitation decreases from about 170 mm (millimeters) in north to about 40 mm in south with the distance away from the coast **(Fig. 2).** Rainfall has been very seldom and the rate is nearly 60 mm/year, usually runoff in WadiJarif occurrence event each 25 to 30 years. The temperature is approximately 40˚C in the summer and decrease on the other seasons [2].

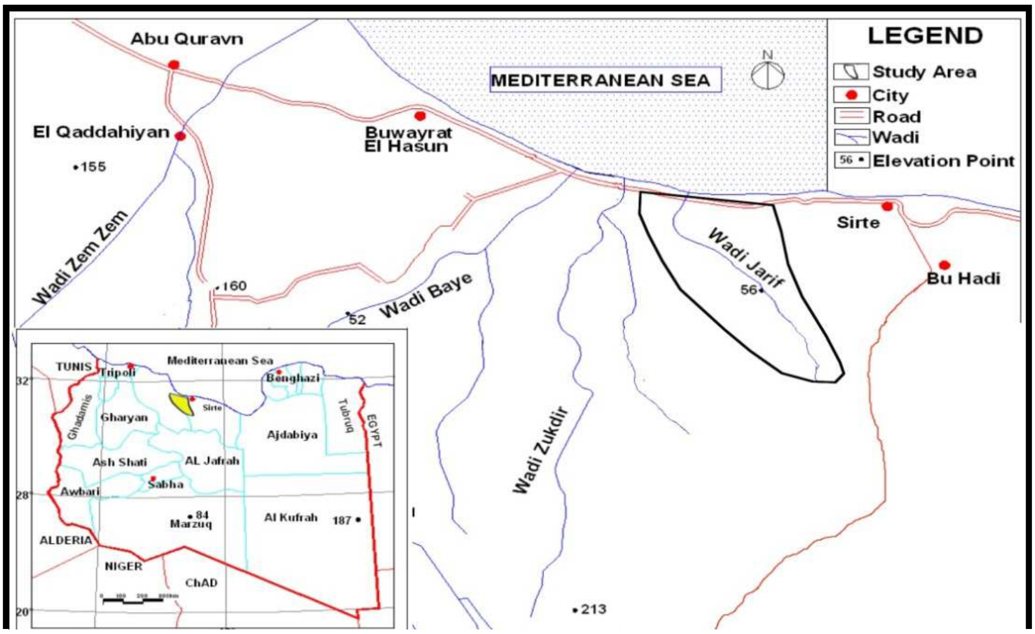

Figure 1. Location map of Sirte showing WadiJarif

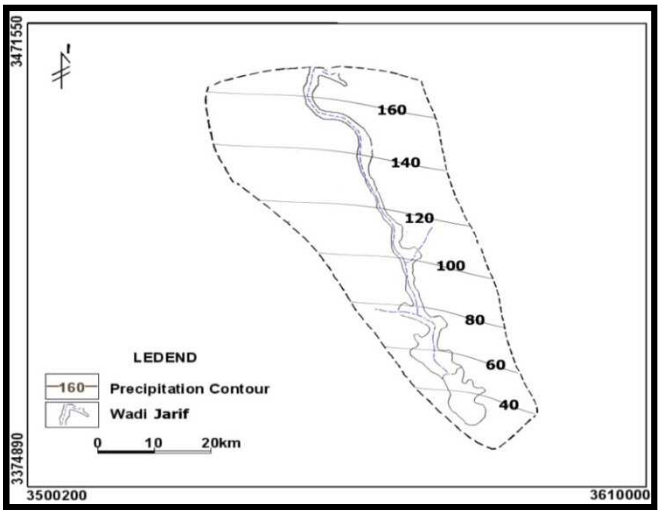

Figure 2. Distribution of average annual precipitation in the study area

2. Geological setting

2.1. ***Stratigraphy;*** the exposed rock units in the study area are belonging to the Tertiary and Quaternary times from base to top respectively. The Quaternary deposits cover the coastal strip and WadiJarif, while The Tertiary deposits are outcropping in the rest parts of the region [3, 4, 5].The following rock units were distinguished in the study area from base to top (Table 1 & Fig. 3):-

The Eocene deposits; which are represented by***Bishimah Formation***.The formation has been divided into three members, the *Khayir Member;* which consist of chalky and gypsiferous marl with thin dolomitic limestone. The *WadiZakim Member*; is made up of dolomite, dolomitic micrite and chalky limestone. *The Rawaghah Member* forms the upper unit of the Bishimah Formation. It is consists of Hard and massive dolomite and contains numerous chert nodules and lenses of silicified dolomite. ***Al Jir Formation*** included two members. The lower unit *Bin Isa Member;* which consist of hard, compact chalk and chalky limestone containing chert nodules and thin stringers of gypsum. The upper unit was named the *Bi'rZaydan Member*. It is composed of compact white limestones. ***WadiThamat Formation*** is subdiveded into three members. *The Al Gata Member* consists of a series of marls, dolomitic limestones and micriticlimestones containing oyster-rich coquinas. The *Thmed al Qusur Member*; which mainly represented by white chalk and chalky limestone with chert nodules.The *Qararat al Jifah Member* is composed of fossiliferous and coquinoid limestone, dolomitic limestone with traces of gypsum, and greenish marl.

The Oligocene is represented by ***Umm ad Dahiy Formation*** which consists of Chalky, oolitic and coquinoid limestone interbedded with dolomitic marls and clays.***Bu Hashish Formation;*** in the type area it comprises 40m of soft chalky marls, vuggy dolomites, chalky limestones and chalk.

The Miocene deposits; represented mainly by***Marada Formation*** which divided into two members. These are *QaratJahannam Member*, it comprises 123 m of stacked clastic sequences of cross-bedded fluvial sandstones, grading into siltstones and siltyclaystones with traces of gypsum. *The ArRahlah Member* was defined from outcrops to the east of Maradah. At the type locality 120 m of calcarenites, calcareous sandstones and sandy limestones overlie the QaratJahannam Member.***Al Khums Formation*** is subdivided into two superimposed members. The lower unit the *WadiYunis Member* is represented by 60 m of skeletal, chalky, dolomitic and gypsiferouslimestones, with occasional siltstones, marls and bedded gypsum. The *Quwayrat al Jibs Member* comprises about 15 m of marls, bedded gypsum, calcarenites and sandstones.

The Pliocene deposits; represented mainly by Al Hishah Formation, which composed of calcarenite and sandstone with gypsum, which reaches a thickness of 20 m in the Al Qaddahiyah area. Similar deposits have been found at Al Aqaylah, Maradah, Bi'rZaltan and SabkhatGhuzayil which have also been referred to the Al Hishah Formation.

The Pleistocene formations include ***QaratWeddah Formation*** which consists of aeolian sands, with intervals of lacustrine clays and marls with traces of gypsum. ***Gargaresh Formation*** formed of oolitic and ooskeletalcalcarenite and calcareous sandstone that the grains of which were derived from reworking of marine sediments of older deposits. ***Old Sabkha Sediments*** consist of intercalations of greenish siltstones, claystones and evaporites consisting of coarsely crystalline gypsum, gypsarenite and halite.

The Holocene deposits include ***recentwadi deposits***; these deposits occur along the courses of WadiJarif, and consist of non-cemented, fine to coarse grained sand and some gravel varying in thickness from 1 to 5

m. ***Beach sand*** occurs along the present coast line only, and consists mostly of light-gray sand, produced by the weathering of the Gargaresh Formation, with highly abundant shell fragments. ***Fluvio-Eolian Deposits*** are represented by fine-grain sand, silt with thin intercalations of gravels of variable degree of roundness. The thickness of these deposits various from 1 to 10 m. Eolian deposits (sand dunes) are represented by pinky and light over dark sand that's the grain diameter is 0.1-0.2 mm around, well sorted. Most of the grains are carbonate with plenty of quartz. The thickness of the deposits is usually less than 1 m. ***The coastal dunes*** consist of shell fragments with small amount of silica sands. It is worth mentioning that the eolian material composing both field dunes and coastal dunes contains a large amount of grains of gypsum. **S*abkha sediments*** occupy the depression along the Sabkha Al Kabirah controlled on the western side by a structural lineament that influence the location of thermal springs and associated mineralization. The sabkha deposits attain a maximum thickness of 10 m and consist of reddish silt and sand which are mainly of eolian origin and evaporite precipitated minerals such as gypsum and halite.

2.2 Tectonic: there are three structural units in the study area: the eastern Sirte Basin, western Al Hamada al Hamra Basin and southern Hun Graben, which determine the structure of the whole region. In the northern part of the study area, the landform is wide coastal plain, and the distribution of the stratum is horizontal or sub-horizontal. The sediments are undisturbed and no fold-type structures were formed except some faults. In the southern part of the study area, the stratums have fluctuation, but the hypsography doesn't exceed 1-2 m. The fold has not developed there. However, there are obvious north-west toward faults due to the influence of the Hun Graben structure [4].

Table 1.Lithostratigraphy of the study area (adopted from Gefli [3])

<table>
<tr><th>Period</th><th>Epoch</th><th>Age</th><th>Fm.</th><th>Mb.</th><th>Lithology</th></tr>
<tr><td rowspan="17">Tertiary</td><td rowspan="9">Eocene</td><td rowspan="3">Ypresian</td><td rowspan="3">Bishimah</td><td>Khayir</td><td>Chalky and gypsiferous marl with thin dolomitic limestone.</td></tr>
<tr><td>WadiZakir</td><td>Dolomite, dolomitic micrite and chalky limestone.</td></tr>
<tr><td>Rawaghah</td><td>Hard and massive dolomite and contains numerous chert nodules and lenses of silicified dolomite.</td></tr>
<tr><td rowspan="2">Lutetian</td><td rowspan="2">Al Jir</td><td>Bin Isa</td><td>Hard, compact chalk and chalky limestone containing chert nodules and thin stringers of gypsum.</td></tr>
<tr><td>BirZayden</td><td>Compact white limestone.</td></tr>
<tr><td>Lutetian</td><td rowspan="3">WadiThamat</td><td>Al Gata</td><td>Marls, dolomitic limestone and micritic limestone.</td></tr>
<tr><td>Priabonian</td><td>Thmed al Qusur</td><td>White chalk and chalky limestone with chert nodules.</td></tr>
<tr><td>Priabonian-Bartonian</td><td>Qararat al Jifah</td><td>Fossiliferous and coquinoid limestone, dolomitic limestone with traces of gypsum.</td></tr>
<tr><td colspan="4" style="display:none"></td></tr>
<tr><td rowspan="2">Oligocene</td><td>Rupelian</td><td>Umm ad Dahiy</td><td></td><td>Chalky, oolitic and coquinoid limestone interbedded with dolomitic marls and clays.</td></tr>
<tr><td>Chatian</td><td>Bu Hashish</td><td></td><td>Soft chalky marls, vuggy dolomites, chalky limestone and chalk.</td></tr>
<tr><td rowspan="4">Miocene</td><td>Aquitanian-Burdigalian</td><td rowspan="2">Marada</td><td>QaratJahannam</td><td>Cross-bedded fluvial sandstones, grading into siltstones and siltyclaystones with traces of gypsum.</td></tr>
<tr><td>Burdigalian Serravallian</td><td>ArRahlah</td><td>Calcarenites, calcareous sandstones and sandy limestone.</td></tr>
<tr><td>Tortonian</td><td rowspan="2">Al Khums</td><td>WadiYunis</td><td>Skeletal, chalky, dolomitic and gypsiferouslimestones, with occasional siltstones, marls and bedded gypsum.</td></tr>
<tr><td>Tortonian - Messinian</td><td>Quwayrat Al Jibs</td><td>Marls, bedded gypsum, calcarenites and sandstone.</td></tr>
<tr><td>Pliocene</td><td></td><td>Al Hishah</td><td></td><td>Calcarenite and sandstone with gypsum.</td></tr>
<tr><td rowspan="3">Quaternary</td><td rowspan="3">Pleistocene</td><td rowspan="3"></td><td>QaratWeddah</td><td></td><td>Sands, with intervals of clays and marls with traces of gypsum.</td></tr>
<tr><td>Gargaresh</td><td rowspan="2"></td><td>Calcarenite and calcareous sandstone</td></tr>
<tr><td>Old Sabkha</td><td>Intercalations of greenish siltstones, claystones and evaporites</td></tr>
</table>

	Holocene		Sabkha sediments, Fluvio-Eolian Deposits, Eolian Deposits, Recent Wadi Deposits and Beach sand

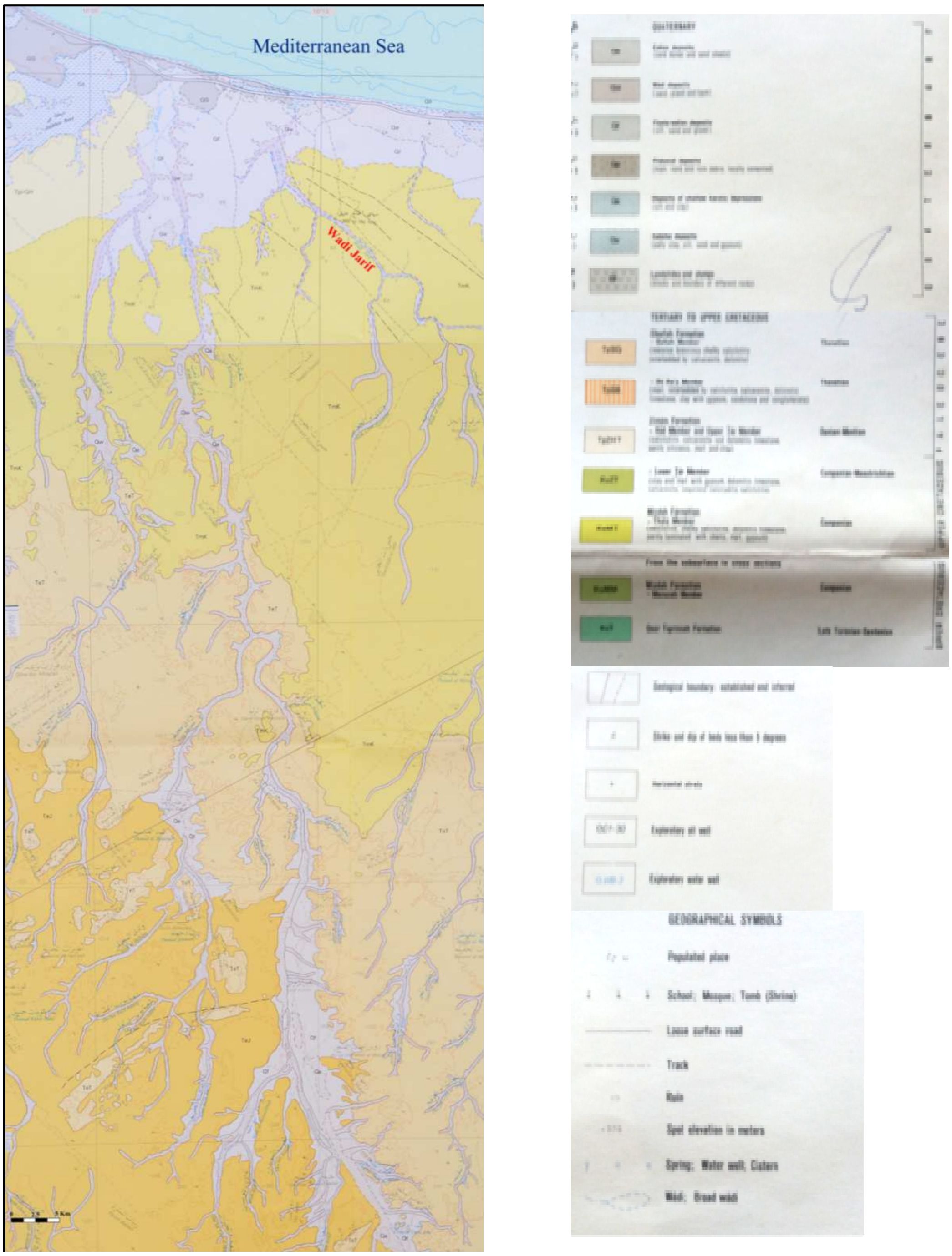
Mediterranean Sea
Wadi Jarif
GEOGRAPHICAL SYMBOLS

Figure 3.Geological map for the study area [4].

3. Methodology

The data used in this study obtained from The Libyan General Water Authority in 2012, Thirty wells, drilled along WadiJarif for domestic and irrigation needs, are chosen to assess the quality of the groundwater in the area.

Physical and chemical parameters of selected water samples; pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), Ca^{++}, Mg^{++}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{--}, SO_4^{--}, and Cl^{-}, were measured and analyzed by using Fishman and Friedman methods [6].

The classification of the groundwater is based on graphical illustration methods including Piper diagram [7] and classification of water according to Schoeller [8, 9]. While the US Salinity Laboratory's diagram [10] is used for rating the irrigation waters, where SAR is plotted against EC.

4. Hydrogeological Conditions

There are five aquifers in the study area, that being 1) Miocene aquifer, 2) Eocene aquifer, 3) Upper Cretaceous Mizda aquifer, 4) Upper Cretaceous Garian aquifer, 5) Lower Cretaceous Kikla aquifer. Not all these aquifers are confined. According to the buried conditions, the former two Tertiary aquifers are classified to be unconfined, while the later Cretaceous ones are confined.

Miocene aquifer (Tertiary) occurs widely in Al Qaddahiyah sheet of coastal area. From the lithological point of view, this aquifer consists of limestone, marly limestone and calcarenite. Its thickness ranges between 40 and 120 m.

Eocene aquifer (Tertiary) is mainly widespread inland. Lithologically the aquifer consists of limestone, marly limestone, dolomite and local gypsum. Its thickness ranges between 30 and 200 m. Its yield strongly depends on the degree of fracture development.

Mizda aquifer (Upper Cretaceous) is composed of limestone. The groundwater quality is poor with TDS increasing from 3000 mg/L in the inland to 30000 mg/L in the coastal region. Its thickness ranges extremely from 48 to 276 m. The depth of groundwater level varies between 548 to 933 m.

Garian aquifer (Upper Cretaceous) is widely distributed in this area, which mainly consist of dolomite, limestone, dolomitic limestone, and sandy limestone. Groundwater table ranges between 690 to 785 m with the thickness of 65-150 m. Very poor yields were determined in the Garian / Nalut from testing during drilling down to the Kikla in the 1970s, although water quality is reasonable for TDS between 3500 mg/L and 4000 mg/L.

Kikla sandstone aquifer (Lower Cretaceous) extending over some 50 % of the country, which is the main current source for domestic and agricultural water supply in Libya. It is artesian but very deep (1,210 m-1,574 m) and supplies water which is only slightly mineralized (4000 mg/L) but at high temperature more than 60°C.

These aquifers are probably recharged by occasional infiltration from sporadic heavy rains and from resulting runoff in ephemeral streams of the area.

5. Results and Discussion

5.1.Hydrochemical Characteristics

The hydrochemicalcharacteristic of groundwater of WadiJarif were discussed through the chemical analyses of thirty groundwater samples (Fig. 4). The chemical analyses were carried out according to the methods adopted from Fishman and Fridman [6]. The obtained results (Table 2) reflect the following hydrochemical characteristics:-

5.1.1. Major hydrochemical parameters;

Major anions and cations, pH, conductivity, total dissolved solids and temperature were assessed on all samples collected (Table 2).

The results show that: temperature ranges between 28 - 71 °C, pH range is 7.3 – 7.60 (average 7.19), the pH values of water fall in slightly alkaline side, conductivity between 5241 to 13150 µS/cm (25 °C) (average 8183 µS/cm(25 °C)). According to the classification of Detay [11] all the studied groundwater samples in the study area belongs to excessively mineralized water class (Ec>1000 µS/cm (25 °C). TDS range 3311 ppm to 8187 ppm (average 5806 ppm). According to the classification ofHem [12], all the studied groundwater samples can classified based on their TDS as Moderately Saline (TDS from 3000-10000 ppm).

Chloride concentration ranges from 869 to 2943 ppm (average 1880 ppm). In all studied groundwater samples, Cl^- concentration exceeded the WHO [13]value for standard drinking water (250 mg/l) and exceeded the WHO [13] highest admissible concentration (600 mg/l). This high Cl^- concentration is probably due to mixing with seawater. From the relation between major cations and major anions concentrations and distance from the coast (Fig. 5) can be observed that, the major ions increase toward the north exception for K^+ and HCO_3^-. This is attributed to the effect of sea water intrusion and as a result of sabkha deposits.

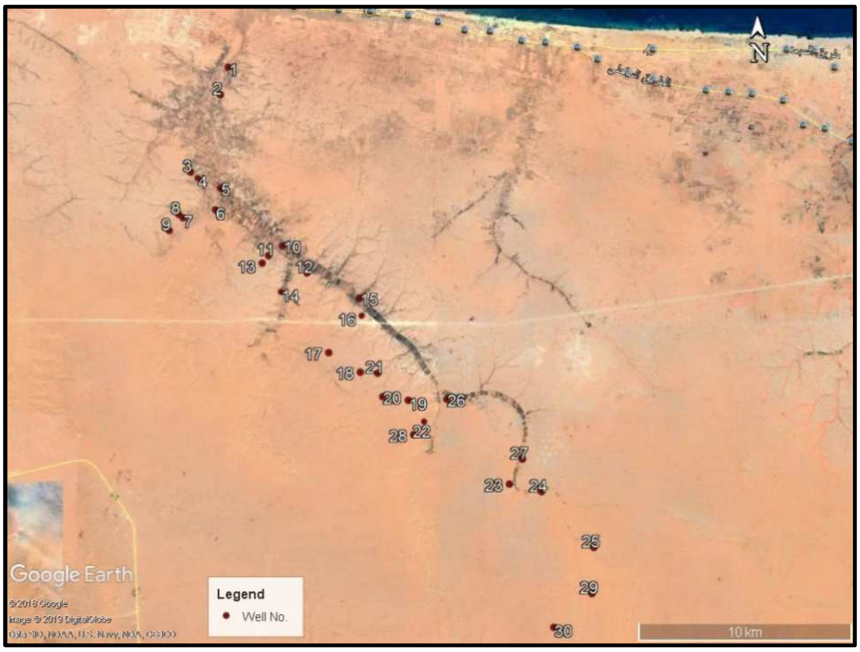

Figure 4.Location map of the investigated water wells at the WadiJarif area.

Table 2. Physical and chemical analysis of major elements of groundwater samples for WadiJarif in ppm

W.No.	T	pH	E.C	TDS	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	NO_3^{--}	SO_4^{--}	Cl^{-}	TH	SAR
1	28.3	7.14	8741	7418	471	322	1721	68	220	6.7	2295	2311	2503	15
2	28	7.12	10553	7960	662	323	1695	63	225	6.5	2311	2671	2982	14
3	28	7.11	9800	7715	645	323	1723	64	218	6.6	2215	2518	2940	14
4	29	7.14	8650	8141	601	324	1750	71	219	6.3	2335	2831	2834	14
5	28	7.13	10280	8076	648	327	1653	65	220	6.2	2324	2829	2964	13
6	29	7.15	12723	8187	646	321	1621	63	213	5.7	2383	2943	2934	13
7	29	7.16	13150	8175	645	332	1625	62	225	5.6	2335	2938	2977	13
8	28	7.38	10145	8088	614	289	1631	61	233	5.3	2314	2938	2722	14
9	30	7.3	9821	8008	618	323	1651	60	228	4.6	2245	2876	2872	13
10	30	7.15	8433	7581	624	215	1600	61	215	4.5	2146	2713	2443	14

W.No.	T	pH	E.C	TDS	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	NO_3^{--}	SO_4^{--}	Cl^{-}	TH	SAR
11	28	7.2	8513	7421	573	245	1579	60	230	3.6	2071	2657	2439	14
12	29	7.23	8641	7273	572	332	1524	58	218	3.2	1922	2641	2794	13
13	28	7.14	7620	7022	570	218	1487	57	234	3.13	1887	2563	2320	13
14	28	7.14	7418	6978	560	214	1631	52	219	2.7	1875	2421	2279	15
15	28	7.22	8120	4440	437	190	955	61	216	2.3	1605	971	1873	10
16	29	7.23	7925	3830	331	139	945	63	221	3.5	1234	891	1398	11
17	30	7.6	7611	3766	469	245	869	55	218	3.3	1050	854	2179	8
18	28	7.21	5732	3668	486	165	724	58	222	2.4	1122	869	1893	7
19	28	7.18	5771	3311	422	167	665	52	231	2.6	935	834	1741	7
20	28	7.08	5541	3382	460	152	712	68	231	1.8	913	842	1774	7
21	70	7.1	8441	4432	447	190	825	56	271	0.35	1660	981	1898	8
22	63	7.2	6771	3630	486	155	640	73	283	0.41	1122	869	1851	6
23	62	7.2	8410	5282	452	232	1200	130	419	0.92	1723	1123	2083	11
24	71	7.1	8430	5259	522	229	955	122	464	0.18	1705	1260	2246	9
25	75	7.2	6395	4041	388	139	995	78	310	4.6	1234	891	1541	11
26	70	7.15	6420	3504	375	122	665	81	228	5.82	1153	872	1438	8
27	58	7.03	6541	4383	435	195	919	45	213	0.14	1612	961	1889	9
28	66	7.27	7330	4573	442	183	941	62	252	0.17	1630	1060	1857	9
29	67	7.05	5241	4174	423	172	820	63	212	0.6	1520	962	1764	8
30	68	7.25	6320	4455	433	193	960	55	290	0.82	1572	950	1875	10

W.No.= Well Number, T =Temperature (^{o}C) pH = Hydrogen ion concentration E.C.= Electric Conductivity (micro mhos/cm), TDS = Total Dissolved Salts (ppm), TH = Total Hardness(ppm), SAR = Sodium Adsorption Ratio

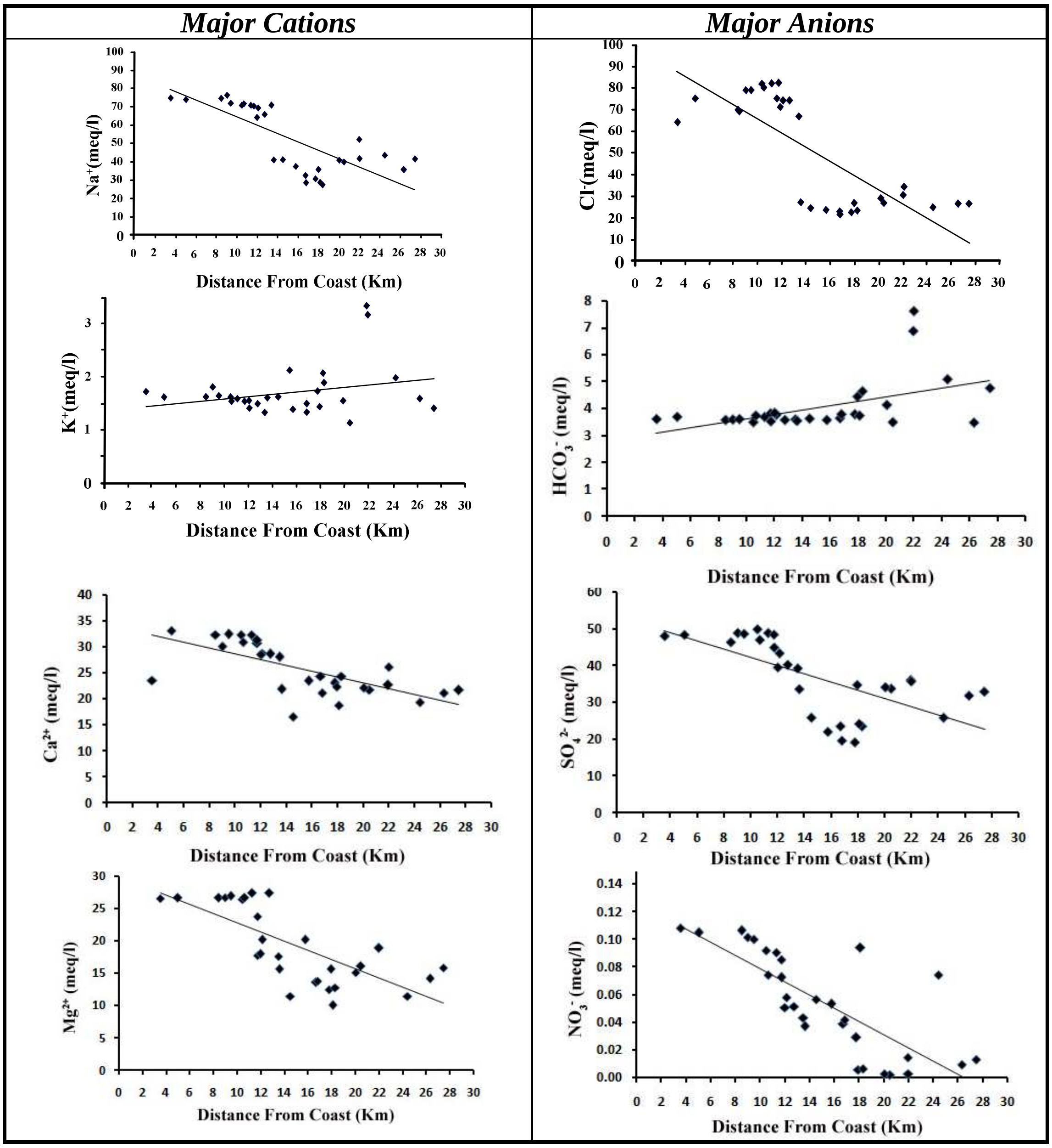

Figure 5. Relation between major cations and major anions concentrations and distance from the coast

5.1.2. Ion dominance

The ion dominance concerned in groundwater of this aquifer, two main sequences are recognized (Table 3).

A. $Cl^{-} > SO_4^{--} > HCO_3^{-} / Na^{+} > Ca^{++} (Mg^{++}) > Mg^{++} (Ca^{++})$, is detected in water samples No. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 17, 18, 19, 20, 22, 24 and 26.

B. $SO4^{--} > Cl^{-} > HCO3^{-} / Na^{+} > Ca^{++} > Mg^{++}$, is represented by water samples No. 15, 16, 21, 23, 25, 27, 28, 29 and 30**.**

The chemical water types are Na_2SO_4 and NaCl. These chemical water types reflect the impact of the basin bearing facies, leaching processes and sea water intrusions.

Table 3.Hydrochemical parameters for collected groundwater samples.(Ion dominance and water type).

W.No.	Ion Dominance	Water type	W.No.	Ion Dominance	Water type
1	Na > Mg >Ca $Cl > SO_4 > HCO_3$	NaCl	**16**	Na >Ca> Mg $SO_4 > Cl > HCO_3$	Na_2SO_4
2	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**17**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
3	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**18**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
4	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**19**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
5	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**20**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
6	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**21**	Na >Ca> Mg $SO_4 > Cl > HCO_3$	Na_2SO_4
7	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**22**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
8	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**23**	Na >Ca> Mg $SO_4 > Cl > HCO_3$	Na_2SO_4
9	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**24**	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl
10	Na >Ca> Mg $Cl > SO_4 > HCO_3$	NaCl	**25**	Na >Ca> Mg $SO_4 > Cl > HCO_3$	Na_2SO_4

W.No.	Ion Dominance	Water type	W.No.	Ion Dominance	Water type
11	Na >Ca> Mg Cl> SO_4> HCO_3	NaCl	**26**	Na >Ca> Mg Cl> SO_4 >HCO_3	NaCl
12	Na >Ca> Mg Cl> SO_4 > HCO_3	NaCl	**27**	Na >Ca> Mg SO_4>Cl> HCO_3	Na_2SO_4
13	Na >Ca> Mg Cl> SO_4 >HCO_3	NaCl	**28**	Na >Ca> Mg SO_4>Cl> HCO_3	Na_2SO_4
14	Na >Ca> Mg Cl> SO_4 >HCO_3	NaCl	**29**	Na >Ca> Mg SO_4>Cl> HCO_3	Na_2SO_4
15	Na >Ca> Mg SO_4>Cl> HCO_3	Na_2SO_4	**30**	Na>Ca> Mg SO_4>Cl> HCO_3	Na_2SO_4

5.1.3. Hypothetical salt assemblages:

Palmer[14] proposed a bar graph representation of chemical data for groundwater. The bar graph is divided into three vertical columns. The left represents cations in epm %, while the right represents anions in epm %. The middle is the intersection between cations and anions at a hypothetical salt combination. In his study, Palmer[14] used the graphs to determine the hypothetical salt combinations and to calculate them theoretically. According to Palmer[14]**,** the hypothetical salt combinations of the studied groundwater samples are classified into four assemblages as follows (Table 4):

- **Assemblage I :**NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, $Ca(HCO_3)_2$ is encountered in wells No. 2, 3, 4, 5, 6, 7, 8, 9,10, 11,12, 13, 14, 17,18,19, 20 and 22. It represents about 60% of the studied samples, regardless of their total salinities. This assemblage includes two chloride salts and two sulphate salts and one bicarbonate salt, reflecting the effect of marine salt contamination (marine facies groundwater) with some contribution of cation exchange process.

- **Assemblage II:** NaCl, Na_2SO_4, $MgSO_4$, $CaSO_4$, $Ca(HCO_3)_2$ is detected in wells No. 1, 15, 16, 21, 23, 24, 25, 26, 27, 28, 29 and 30. About 40% of groundwater samples are characterized by combination ***II*** (Three sulphate salts). This reflects the effect of leaching and dissolution of terrestrial salts (continental facies groundwater).

5.1.4. Hydrochemical coefficients (ion ratios)

The hydrochemical coefficients are important for possible determination of the geochemical origin of groundwater and the various chemical processes contributing in water quality development. The values of r Na^+/ r Cl^-, r Ca^{++} / r Mg^{++}, r SO_4^- / r Cl^- and r Cl^- / r HCO_3^{--} of the investigated aquifer were calculated (Table 5). The following results are recorded:

- **(r Na^+ / r Cl^-) ratio:** this parameter is of special importance, as it gives an indication about the water origin (marine or meteoric fresh water). Water is meteoric when the ratio is greater than unity, marine when it is less than unity [15] .For WadiJarif, the mean value of rNa^+/rCl^- is 1.23 (0.87 -1.87). About 33.33% of samples have values of rNa^+/rCl^- ratio less than unity, which is quite close to rNa^+/rCl^- ratio of sea water (0.85)., while the rest are of more than unity.
- **(r Ca^{++} / r Mg^{++}) ratio:** the ratio of Ca^{++}/Mg^{++} helps in tracing groundwater affected by marine intrusions or by mixing of the surface water through recharge processes. Higher values may indicate a source of Ca as evaporates and active Base Exchange processes. In groundwater of WadiJarif, the mean values of rCa^{++} / rMg^{++} reach 1.41 (ranges of 0.89 to 42.21) (Table 5). Calcium exceeds the magnesium content in all samples except sample

number (1). It is attributed to the dissolution of calcium carbonate of limestone.

- **($r\ SO_4^{--}$ / $r\ Cl^-$) ratio:** the value of $r\ SO_4^{--}/Cl^-$ is less than unity in 66.67% of measured samples. Excess of chloride over sulphate may attribute to the contamination with the sea water intrusion and /or to the abundance of the halite (NaCl) in the aquifer deposits. While the ratio is higher than unity in 33.33% of these samples, indicating that sulphate content increased relative to chloride content. This may be confirmed by the increase of the concentration of sulphate ion in the aquifer, which is mainly due to the leaching process of meteoric water percolation.

Table 4**.**The Hypothetical Salt Combination of the Studied Water Samples.

W.No.	NaCl	Na_2SO_4	$MgCl_2$	$MgSO_4$	$CaSO_4$	$Ca(HCO_3)_2$
1	56	4		21	16	3
2	56		3	17	21	3
3	56		3	17	21	3
4	58		2	18	19	3
5	56		4	16	21	3
6	55		6	14	22	3
7	55		6	15	21	3
8	57		4	15	21	3
9	56		6	14	21	3
10	59		2	13	23	3
11	59		3	14	21	3
12	55		8	14	20	3
13	59		4	12	22	3
14	61		1	14	21	3
15	43	11		19	22	5
16	46	15		16	16	7

W.No.	NaCl	Na_2SO_4	$MgCl_2$	$MgSO_4$	$CaSO_4$	$Ca(HCO_3)_2$
17	48		1	23	21	7
18	47		1	18	27	7
19	47		3	18	24	8
20	48		3	15	26	8
21	41	8		21	23	7
22	45		2	17	27	9
23	43	14		20	14	9
24	45	5		21	19	10
25	45	15		15	16	9
26	47	5		17	24	7
27	43	9		20	23	5
28	44	9		19	22	6
29	43	8		20	23	6
30	42	11		20	20	7

- **(Cl^-/HCO_3^{--}) ratio:** the rCl^-/HCO_3^- ratio increases as the total water salinity increases. The groundwater samples, of WadiJarif has mean a value of $rCl^-/rHCO_3^-$ of 13.14 (ranges of 4.61 to 23.78) as stated in table (5). All the groundwater samples show value lower than that in sea water (253.02) and higher than that of rain water (0.64). The original meteoric water which recharging the aquifer is modified through processes increasing the chloride or decreasing the bicarbonate. This could be resulted from seawater intrusion. The effect of salinization can be classified using the $Cl\text{-}/HCO_3^-$ ratio, as follows: <0.5 for unaffected, 0.5–6.6 for slightly and moderately affected and >6.6 for strongly affected [16,17] .The studied groundwater samples of WadiJarif can be classified as 70% strongly affected by the saline water and 30% are moderately contaminated. We can note that the highly contaminated samples are the nearest samples from the coast.

Table 5.Calculated Values of Some Hydrochemical Coefficients for the Study Samples.

W.No.	Unit	r(Na+K)/Cl	rCa/rMg	rSO4/rCl	rCl/HCO3
1	epm	1.17	0.89	0.73	18.07
2	epm	1.00	1.24	0.64	20.43
3	epm	1.08	1.21	0.65	19.88
4	epm	0.98	1.13	0.61	22.24
5	epm	0.92	1.20	0.61	22.13
6	epm	0.87	1.22	0.60	23.78
7	epm	0.87	1.18	0.59	22.47
8	epm	0.87	1.29	0.58	21.70
9	epm	0.90	1.16	0.58	21.71
10	epm	0.93	1.76	0.58	21.71
11	epm	0.94	1.42	0.58	19.88
12	epm	0.91	1.05	0.54	20.85
13	epm	0.91	1.59	0.54	18.85
14	epm	1.06	1.59	0.57	19.02
15	epm	1.57	1.40	1.22	7.74
16	epm	1.70	1.44	1.02	6.94
17	epm	1.63	1.16	0.91	6.74
18	epm	1.35	1.79	0.95	6.74
19	epm	1.29	1.53	0.83	6.21
20	epm	1.38	1.84	0.80	6.27
21	epm	1.35	1.43	1.25	6.23
22	epm	1.21	1.90	0.95	5.28
23	epm	1.75	1.18	1.13	4.61
24	epm	1.26	1.38	1.00	4.67
25	epm	1.80	1.69	1.02	4.95
26	epm	1.26	1.87	0.98	6.58
27	epm	1.52	1.35	1.24	7.76
28	epm	1.42	1.47	1.14	7.24
29	epm	1.37	1.49	1.17	7.81

W.No.	Unit	r(Na+K)/Cl	rCa/rMg	rSO4/rCl	rCl/HCO3
30	epm	1.61	1.36	1.22	5.64
Average	epm	**1.23**	**1.41**	**0.84**	**13.14**
Rain water	epm	0.64	7.18	0.86	0.64
Sea water	epm	0.85	0.185	0.10	253.02

5.2. Hydrochemical classification:

Different methods were proposed for the chemical classification of groundwater some are based mainly on anions. While others make use of both anions and cations. The latter methods lead to a more coherent picture of type of water. Two methods of graphical representations and one calculated method for water classifications in the area of study are used;

5.2.1. The Piper diagram [7] is considered to be one of the natural water classifications. Major cations and anions were plotted in piper diagram to evaluate the hydrochemistry of groundwater of WadiJarif fig. (6). The water were classified into hydrochemicalfacies representing water types based on the subdivisions of the piper diagram suggested byBack [18] .

The plot shows that most of the groundwater samples fall in the field of alkalies (Na^+, K^+) with some contribution of no dominant cations type and in Cl^- type, SO_4^{2-} type and no dominate anions type. The plot shows that the chemical composition obtained of groundwater fall in the field of Na-Cl type and mixed Ca^{2+}-Mg^{2+}-Cl^- type.

5.2.2. Schoeller classification [7]:The plotting of the chemical analysis data of the groundwater on Schoeller graph (Fig. 7) indicates that, the sodium and calcium represent the major cations while chloride and sulphate represent the major anions. The main chemical water types are NaCl and Na_2SO_4. The sulphate concentrations might be originated mainly from the presence of gypsum and anhydrite deposits of Al Hishah and Al Khums formations while the sodium chloride could be product of dissolved halite of the old and recent sabkhas intercalations.

5.2.3. Water type classification; According to Schoeller[8] groundwater can be classified into chloride, sulphate and carbonate water depending on major anions Cl^{-}, SO_4^{2-} and HCO_3^{-} (Table 6). The studied groundwater samples of WadiJarif are classified as 46.7 % medium chloride water (samples 1-14), 53.3 % oligo chloride water (samples 15-30). The majority of these samples are classified as 83.4 % sulphate water, meanwhile few samples 16.6 % are classified as oligosulphate water (samples 17, 18, 19, 20 and 22). All the studied samples are classified as normal carbonate water, except (sample 24) is classified as super carbonate water.

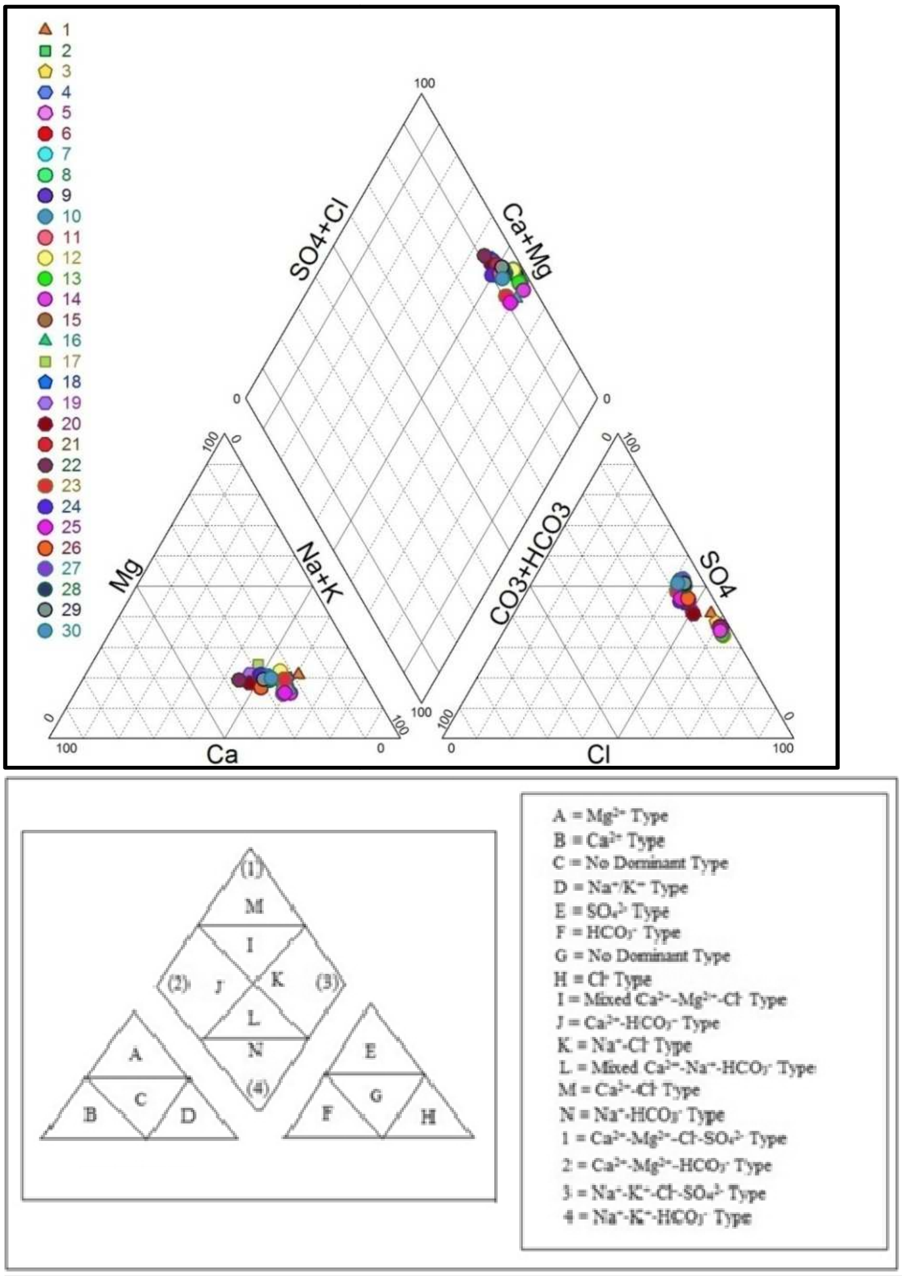

Figure 6.Piper diagram of the studied groundwater samples of WadiJarif.

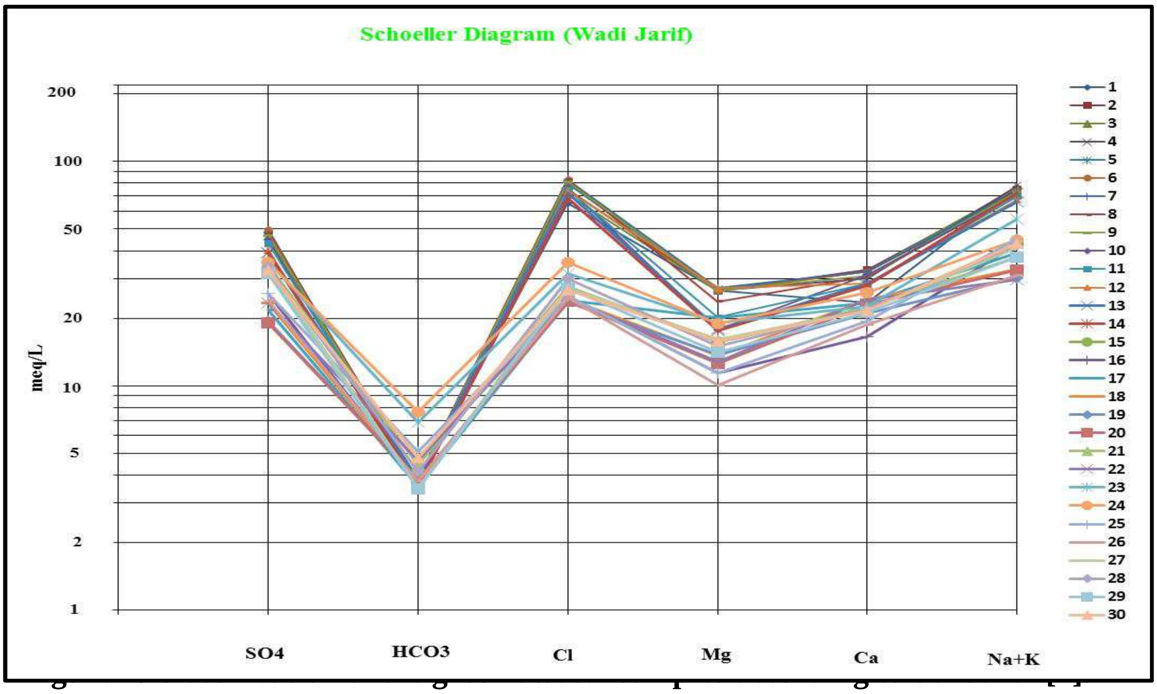

Table 6.Classification of groundwater according to Schoeller [8].

Water type	Cl^- (meq/l)	Water type	SO_4^{2-} (meq/l)	Water type	HCO_3^- (meq/l)
Super chloride water	more than 700	Super sulfate water	more than 58	Super carbonate water	more than 7.0
Marine chloride water	700 – 420	Sulfate water	58 – 24	Normal carbonate water	7.0 – 2.0
Strong chloride water	420 – 140	Oligo sulfate water	24 – 6.0	Under carbonate water	less than 2.0
Medium chloride water	140 – 40	Normal sulfate water	less than 6.0		
Oligo chloride water	40 – 15				
Normal chloride water	less than 15				

5.3.Groundwater Evaluation:

The groundwater of study area is evaluated for drinking, domestic and irrigation purposes.

5.3.1. Groundwater quality for drinking use: according to the international standard of drinking water suggested by the World Health Organization [13, 19] (Tables 7 & 8). The groundwater of WadiJarif were discussed as following:-

a. pH value: most of the groundwater samples are suitable for drinking use, where pH values of the investigated samples are ranging between 7.03 and 7.6 (Table 2).

b. Total dissolved solids (TDS): the groundwater samples of the investigated aquifer can be classified as unsuitable water where (TDS > 1500 ppm); where TDS values of the investigated samples are ranging between 3311 and 8187 (Table 2).

Table 7.Standards for drinking water [19]

Substance or characteristic	***Undesirable effect may Be produced***	***Highest desirable level***	***Maximum Permissible level***
T.D.S	Gastrointestinal	500 mg/l	1500 mg/l
PH range	Corrosion	7.0 to 8.5	6.5 to 9.2
Total hardness	Excess scale formation	100 mg/l	500 mg/l $CaCo_3$
Calcium (Ca^{++})	Excess scale formation	75 mg/l	200 mg/l
Magnesium (Mg^{++})	Hardness taste Gastrointestinal irritation in the presence of sulphate.	Not more than 30 mg/l if there are 250mg/l sulphate. If there is less sulphate Mg^{++} up to 150 mg/l may be allowed.	150 mg/l
Sulphate ($SO4^{--}$)	Gastrointestinal irritation where magnesium or sodium are present.	200 g/lm	400 mg/l
Iron total as (Fe)	Discolouration, deposits and growth of iron, bacteria turbidity	0.1 mg/l	1.0 mg/l

Table 8. Guide lines of water suitability for drinking uses [13]

Parameter	*Unit*	*M.a.c.**	*Allowable water samples*
pH		6.5-8.5	All samples
EC	µs/cm	1500	---
TDS	Mg/l	1000	---
TH($CaCO_3$)	Mg/l	500	---
Na	Mg/l	200	---
Ca	Mg/l	150	---
Mg	Mg/l	150	Samples No. 16, 25 and 26
K	Mg/l	10	---
Cl	Mg/l	250	---
SO_4	Mg/l	400	---
HCO_3	Mg/l	200	---

(*) Maximum acceptable concentration

5.3.2. Groundwater quality for domestic purpose: the classifications of WadiJarif groundwater for domestic purposes were obtained using the characteristic properties such as Total Dissolved Solids (TDS) and Total Hardness (TH)**.**

a. Total dissolved solids (TDS); high TDS values may be associated with excessive corrosion and scaling in pipes, fittings and household appliances [20]. Comparing the TDS values of WadiJarif groundwater with the classification proposed byBruvold andDaniels [21], revealed that all the studied groundwater samples can be classified unacceptable for domestic use (Table 9).

Table 9.Suitability of WadiJarif groundwater for domestic purpose based on TDS according to Bruvold and Daniels [21].

TDS (mg/l)	Water class	Samples	Percentage %
<80	Excellent	---	---
80-500	Good	---	---
500-800	Fair	---	---
800-1000	Poor	---	---

TDS (mg/l)	Water class	Samples	Percentage %
>1000	Unacceptable	All samples	100 %

b. ***Total Hardness (TH):*** the groundwater was classified into six categories based on the total hardness (TH); Very soft (<30 mg/l); Soft water (30 to 60 mg/l); Slight hard (61 to 90 mg/l); Moderately hard (91 to 120 mg/l); Hard (121 to 180 mg/l); and Very hard (> 180) [22]**.** All of the groundwater samples are of very hard class where the values of total hardness are > 180 (1398 and 2982 ppm see table 2). This water is poor classes for domestic purposes.

5.3.3. Evaluation of groundwater for irrigation use:the groundwater quality is subjected to evaluation measures in the area of study is carried out to determine their suitability for agricultural purposes. The groundwater class for irrigation is defined by the U.S. Salinity Laboratory staff classification [9] andthe following results are obtained Fig (8).

Accordingly, the majority of groundwater samples of WadiJarif lie in class C4-S4 of very high salinity (class C3-S4). The water is not suitable for irrigation under ordinary conditions due to its high salinity, but it could be used for the irrigation of salt tolerant crops in permeable soils under good management practices.

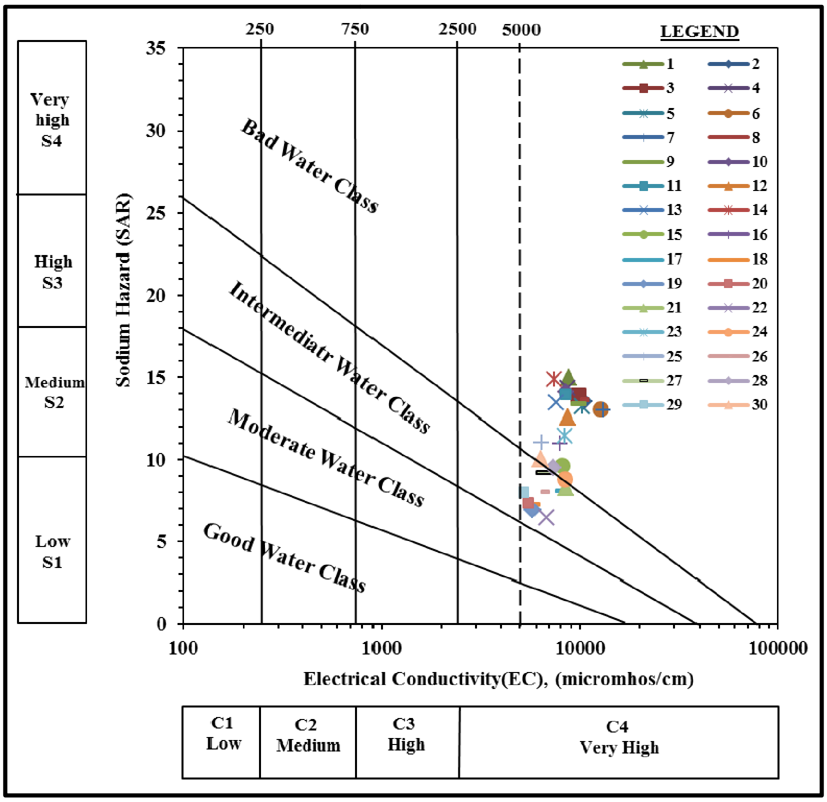

Figure 8. Salinity Diagram for Classification of Irrigation Water in the study area based on Richards [9] .

6. Conclusion

WadiJarif area is located between longitude 16º 12` 00" E to 16º 30' 00" E and latitude 30º 12` 00" N to 31º 15` 00" N. The length of this valley is approximately (31 km) which stream tube tightens at the heights of the valley and increases in width at the bottom of the valley. It is characterized by the dominance of typical continental arid and semi-arid features with little rainfall, hot and dry weather in summer and cold and rainy in winter.

Five aquifers are detected in the study area including; Eocene, Miocene, Upper Cretaceous Mizda, Upper Cretaceous Garian, Lower Cretaceous Kikla (Sandstones) aquifers. Not all these aquifers are confined.

Thirty groundwater samples were collected from WadiJarif. The collected samples were subjected to different analyses in order to conduct hydrochemical study of the study area, assess the available water resources and to examine water quality and suitability for different uses.

From the foregoing discussion, the physicochemical parameters of the studied groundwater samples revealed that groundwater of WadiJarif are mainly slightly alkaline (pH ranges from 7.03 to 7.60), excessively mineralized water (EC values ranges from 5241 to 13150 µS/cm) and moderately saline water (The total dissolved salts (TDS) ranges from 3311 to 8187ppml).

The major ions show an observed decrease away from the sea coast with exception for K^+ and HCO^{3-}. This distribution may be related to the origin of these ions.

From the major ions relationships in the groundwater of WadiJarif two main sequences are recognized: $Cl^- > SO_4^{--} > HCO_3^- / Na^+ > Ca^{++} (Mg^{++}) > Mg^{++} (Ca^{++})$ and $SO4^{--} > Cl^- > HCO3^- / Na^+ > Ca^{++} > Mg^{++}$.

The chemical water types are Na_2SO_4 and NaCl. These chemical water types reflect the impact of the basin bearing facies, leaching processes and sea water intrusions.

The hypothetical salt combinations of groundwater are classified into two groups as follows:

NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, $Ca(HCO_3)_2$ and NaCl, Na_2SO_4, $MgSO_4$, $CaSO_4$, $Ca(HCO_3)_2$.

The sea water intrusion is detected by ion ratios and the hypothetical salt combinations. In conclusion, the groundwater in the coastal aquifer is laterally affected by seawater due to excessive pumping.

With respect to the hydrochemicalfacies and groundwater types, the groundwater of WadiJarif samples classified on the basis of dominant major cations as 46.7% medium chloride water, 53.3% oligo chloride water. The majority of these samples are classified as 83.4% sulphate water, while few samples 16.6% are classified as oligosulphate water. Most of the studied samples are classified as normal carbonate water. On the other hand, on the basis of dominant major ions it classified as sodium-calcium type (76.7%) and calcium-sodium type (23.3%), and all the studied samples are classified as chloride-sulphate type. On the basis of Piper diagram [7] , most of the groundwater samples fall in the field of alkalies (Na^+, K^+) with some contribution of non-dominant cations type and in Cl^- Type, SO_4^{2-} type and non-dominate anion type. Schoeller classification indicates that, the sodium and calcium represent the major cations while chloride and sulphate represent the major anions. The main chemical water types are NaCl type close to the sea and Na_2SO_4 in the south. The NaCl water indicates a strong relationship with seawater. The sulphate concentrations might be originated mainly from the presence of gypsum and anhydrite deposits, while the sodium chloride should be product from the halite dissolution of the sabkha intercalations

Assessment of groundwater of WadiJarif for different uses indicates that the groundwater are classed as unsuitable for drinking (all studied samples TDS more than 1500), also, this groundwater can't be used for domestic purposes for its high TDS and TH. Most of the groundwater of the study area is not recommended for irrigation under normal conditions. However, they are possible for the salt tolerant crops in high permeable soils under good irrigation management.

7. Recommendation

According to the results of this study we recommend the following:

- The groundwater of the area needs a substantial degree of purification treatment before using for drinking and domestic purposes.
- Putting a permanent monitoring program to observe groundwater quality and determine the annual and seasonal changes in order to put a proper strategy to protect and remediate the aquifer especially that the groundwater is the lonely water resource in WadiJarif area.
- The producing wells must not operate at the same time and the total yield of these wells must be decreased.
- To minimize water level decline, the efficiency of the irrigation system should be increased by using the sprinkler irrigation methods, in order to minimize the consume of groundwater resources in the study area.

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