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Seawater Intrusion and Nitrate Pollution in the Quaternary Coastal Aquifers of Jefara Plain, Northwestern Part of Libya

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Abstract— **Jefara Plain Quaternary Coastal Aquifer is** the most important resource of water **supply in the urban coastal, in the northwest part of Libya, used for domestic, agricultural, and industrial purposes. However, groundwater overdraft and contamination are the main problems affecting the aquifer system. This study was conducted to evaluate the principal hydrogeochemical processes controlling groundwater quality in the urban coastal strip. Besides, investigation of the threats of seawater intrusion and pollution was carried out. In addition, 59 groundwater samples were collected from different wells and analyzed for various parameters. Major cations and anions analyzed in the groundwater samples reveal that groundwater is mainly affected by several factors such as dissolution of calcite and dolomite, seawater intrusion due to aquifer overexploitation, and nitrate pollution mainly caused by the intense agricultural activities and leakage of nitrate from septic pits.**

The dominant ions are Cl− for anions and Na+ for cations along the coastal strip gives a clear indication of seawater intrusion into the aquifer as also corroborative from the Na–Cl signature on the Piper diagram. The groundwater samples near to the coast area have much higher Na/Cl molar rates than the boreholes located further inland. The result of this study indicated that, the groundwater quality in the coastal aquifer system of the Jefara Plain is affected by several factors such as water-rock/soil interaction, seawater intrusion, reverse ion exchange, and intense agricultural activities. Saturation indexes (SI) of carbonate, sulfate, and halide mineral phases were calculated using Visual MINTEQ geochemical software. Carbonate minerals are present in the unsaturated zone, possibly increasing Ca2+ and Mg2+ concentrations when they are dissolved. The water suitability assessment revealed that the groundwater resources are chemically or qualitatively inadequate for drinking purposes due to the seawater intrusion regime and the NO3− contamination, whereas they are suitable for agricultural uses according to various indices (SAR, %Na, PI, and RSC). With the exception of some groundwater wells that contains a high level of salinity. Thus, proper awareness and regular monitoring have to be applied to protect the groundwater from further deterioration.

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Index Terms — Quaternary coastal aquifer, hydrogeochemical, groundwater quality, seawater intrusion, Nitrate Pollution, Jefara Plain.

I. INTRODUCTION

Coastal regions are at the complex and dynamic interface between the land and the sea. Thus, the environmental management of these regions is one of the greatest challenges of the modern world, because the majority of the global population is estimated to desire to live in coastal areas (Michael et al., 2017; Papazotos P. et al, 2019). For example, in Libya, more than 90% of population lives in the coastal areas such as Jefara plain and Benghazi Plain, (MEWINA, 2014). Therefore, higher population densities and living standards in coastal urban areas cause ever increasing demands for fresh water for industrial and domestic use. Since the surface water resources are limited and contribute less than 3% of the current water resources in use in Libya, groundwater is playing a more and more important role in water resource supply (Ghazali A. et. al., 2001 and FAO, 2015).

The groundwater quality is a function of natural influences and human activities either severally or collectively. The quality of groundwater can be affected by various geochemical factors in coastal areas, such as seawater intrusion, wastewater infiltration, the degree of chemical weathering of *various* rock types, nitrate contamination, etc (Stark et al. 2000). However, with complicated influences from many anthropogenic and natural processes in some seaside urban areas, distinguishing each affecting factor can be challenging. Moreover, in some cases, only shallow groundwater can be acquired in highly urbanized areas. Effective ways to reveal aquifer status are valuable for achieving integrated and sustainable groundwater resource management. Jefara plain is a highly urbanized coastal region located in the northwestern part of Libya. The population of 430 thousand consumes water resources of 25 million m³ per year (FAO, 2015). Seawater intrusion has been strongly attacking the local shallow aquifer since 1978 when extensive urbanization began (FAO, 2015; Gremidah S. and Alawar M., 2017)

Jefara plain was subjected to a series of seawater intrusion studies, (Cederstrom D. and Bertiola M., 1960;

GEFLI, 1972; Navarro, 1975; Krummenacher R., 1982; Gejam A., et al., 2016; Al-Farrah N., et al., 2011, 2013 and 2018). Thus, in the early 1957s, the status of seawater intrusion has been observed in the east of Tripoli region (NCB and MM, 1993).

Summarizing that, most of these studies indicate that the problem of seawater intrusion, mostly caused by human activities. Whereas, Libya has the longest coastline among the littoral states of the Mediterranean Sea with a length of approximately 1.9 km. (Sadeg S. and Karahanoglu N., 2001) suggesting that the coastal aquifers are vulnerable to the seawater intrusion due to the over-exploitation of groundwater, as has been mentioned by these studies. Also, the aquifer's over-exploitation in combination with the lack of the appropriate irrigation practices may lead to further deterioration of groundwater quality. Furthermore, many researchers have mentioned that nitrate ions (NO_3^-), which caused by the intense use of fertilizers on cultivated areas, and seawater intrusion, which resulted of changes in land use, wastewater disposal and over-pumping, are major threats to coastal areas. (Sadeg S. and Karahanoğlu N., 2001; Shakeel A. and Alkhenjary K., 2013; Abdulaziz M. and Abdulsalam M., 2020).

Due to limited surface water resources and since Libya have no perennial rivers; with surface runoff limited to short winter floods following intense rain events, it is crucial to examine closely the hydrogeochemical processes in the aquifer systems. However, the evaluation of the processes controlling the groundwater quality has a significant role in sustainable groundwater management practices. This study aims to investigate the dominant hydrogeochemical processes that affect Quaternary coastal aquifers of Jefara Plain, Northwestern part, Libya, and examine the water suitability concerning drinking and irrigational purposes. The study area is a typical Mediterranean coastal plain with distinct natural (water-rock/soil interaction) and anthropogenic (agricultural activities and aquifer's over-pumping) influences.

The approach of this study contributes to distinguishing the factors that control the groundwater chemistry using descriptive statistics, ionic ratios, hydrogeochemical scatter plots, spatial distribution maps, multivariate statistical analysis, and geochemical modeling. The research area is of great interest because it is a representative case study of intense human intervention due to the over-pumping of the aquifer to cover the water demands.

II. MATERIALS AND METHODS

A. Study area

The study area is located in the northern part of the Jefara plain and forms a rectangular area (75 km long and 18 km wide (Figure. 1). It is situated between 32°47′44″N to 32°39′01″ N latitude and 12°52′09″E to 12°24′07″ E longitudes. Therefore, the climate in this region is generally semi-arid and Mediterranean type with a dry and hot summer season and a wet and cool winter season pre-vailing high temperatures and strong wind regime (El Asswad M., 1995; Nour M. and Abufayed A., 2014).

There are no perennial rivers that cross this area. However, there is only one Wadi in the study area, which is known as Wadi Al-Majinin. It crosses the study area from the east part, sloping from the Nafusa Mountains toward the north until it ends at the Al-Majinin Dam in Al-Jawarniyah region. The mean annual rainfall ranges between 150 mm and 400 mm mostly occurs during October to January and the estimated potential evapotranspiration rates (1600-2100 mm yr^{-1}) are several times higher than rainfall. Thus, during the rainy season, the water permeates the surface of the soil and contributes to feeding the underground aquifer. The study area is a typical example of a semi-arid region where groundwater resources are intensively exploited for human needs as a result of agricultural and demographic development.

B. Geology and hydrogeology

Several authors have studied the geology of Jefara Plain, (Al-GEFLI, 1972; Kruseman P. and Floegel H, 1978;

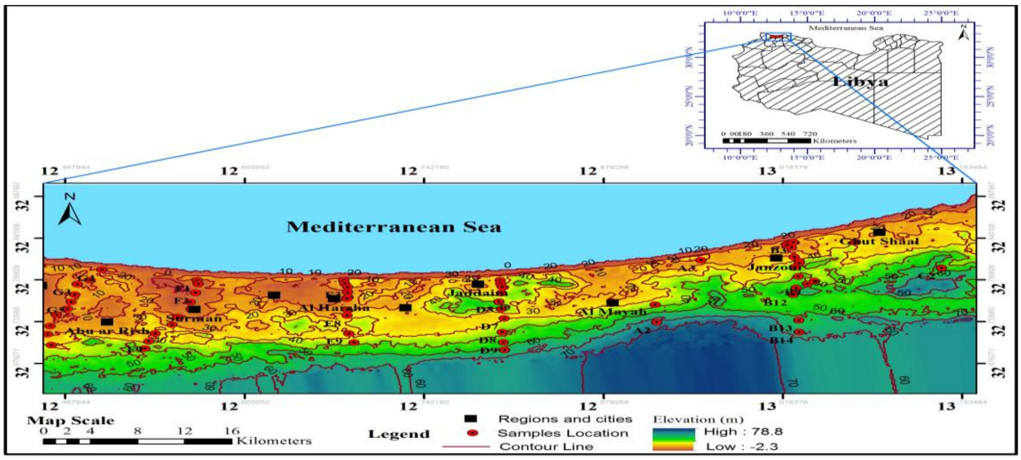

Figure 1. Location and topography map of the study area in Jefara Plain

Pallas P., 1978; Krummenacher R., 1982; IRC, 1992; Sadeg S. and Karahanoğlu N., 2001; Elgzeli M., 2010; Farrah N., et al., 2011; Giraudi C., et al., 2013; Moustafa M. et al., 2016; Gejam A. et al. 2016 and Aswed N., et al. 2018). These studies indicate that the geological formations in the study area are composed by Triassic to Quaternary formations. As shown in the lithostratigraphic column (Figure. 2). The Triassic series is constituted mainly by Carnian and Norian which is formed by limestone and dolomite that has more than 150 m of thickness and contains the Abushybah FM and Al Azixiyah FM groundwater aquifers.

Then the Cretaceous series is constituted mainly by Albian and Aptian, which is formed by sand and sandstone that has 400 m of thickness. It belongs to Kiklah aquifer system. This is followed by the Neogene series, which forms the Miocene formation, is formed by Sandy, limestone, and sandy stone that has more than 450 m of thickness. Followed by the Quaternary formation, which is formed by sand and sandstone with a crust of gypsum and sediment. Thus, the dominant geological formations in the study area are limestone.

However, The Jefara coastal aquifer consists of unconfined layers with a main geological material composed of limestone, sandy limestone, dolomitic limestone, and clay of the upper Miocene, Pliocene, and Quaternary. The coastal zone in Jefara plain is of importance in terms of economical, industrial, and agricultural activities and the groundwater is fragile in terms of their vulnerability to sea level rises and eventual salinization by seawater intrusion

Climatic factors (low rainfall recharge, high temperature) and the high reliance on groundwater resources make the problem more severe (Krummenacher R., 1982 and Gejam A. et al, 2016). The aquifer parameters in both confined and unconfined aquifer systems are shown in Table (1).

C. *Sampling and determinations*

Fifty-nine groundwater samples were collected from shallow boreholes in the Jefara plain during October 2018 (Figure. 1). in order to evaluate the suitability of water drinking, irrigation practices water quality parameters like pH, electrical conductivity, Total Dissolved Solids (TDS), Total Hardness, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO^{3-}, Cl^{-}, SO_4^{2-}, NO_3^{-} and various irrigational quality indices like Percent Sodium (%Na), Sodium adsorption ratio (SAR), Residual Sodium Carbonate (RSC), Permeability Index(PI), Magnesium Ratio(MR), and Magnesium Ratio (MR). The techniques and methods adopted for collection, parameter analytical techniques were followed according to Hem, (1970) and APHA (2005).

To measure analytical accuracy between the concentration of total cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) and the concentration of total anions (HCO_3^{-}, Cl^{-}, SO_4^{2-} and NO_3^{-}) expressed in milliequivalents per liter (meq/L) for each sample, ionic balance error (IBE) was checked to ensure the accuracy of analysis by the equation given below:

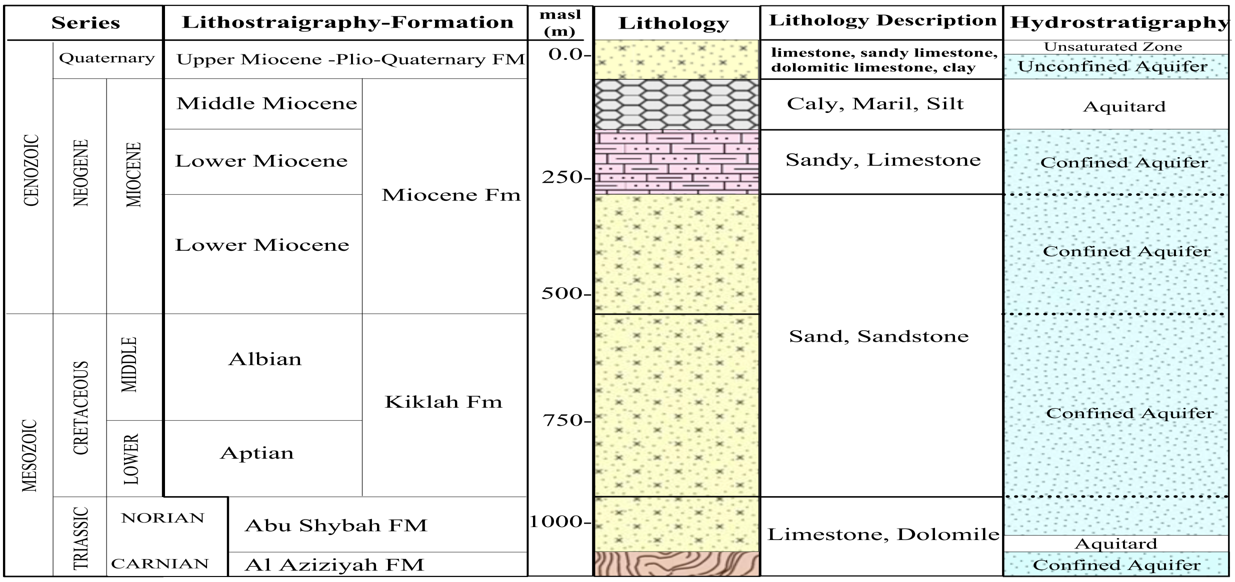

Figure 2 .Hydrostratigraphic column of the study area

Table 1. AQUIFER SYSTEM PARAMETERS (AFTER, NCB AND MM1993)

Group	Formation	Well yield m^3/h	Transmission m^2/d	Storativity	TDS (mg/l)
Quaternary- Mio	Jefara, Qasr Al Haj	15 - 30	20 - 700	Unconfiend	500 -2,000
Cretaceous	Kikla	40 - 90	Up to 520	Confined	1,000 – 1,500
Middle Jurassic Triassic	Abu Shaybah	≈ 30	Very variable	Confined	-
	Al Aziziyah	30 -110	Up to 450	Confiend	1,000 – 3,000

$$IBE = \frac{\sum Cations - \sum Anions \times 100}{\sum Cations + \sum Anions}$$

The computed ionic balance errors (IBE) were within the acceptable limit of ± 5% (Domenico and Schwartz, 1990).

The evaluation of the chemical reactions in groundwater was assessed by calculating the saturation index (SI) with respect to mineral phases using the geochemical software Visual MINTEQ v.3.1 as the main database. The sediment-water interaction controls the geochemistry of the groundwater. Thus, the geochemical model was run to provide the SI of selected minerals phases. The SI of the groundwater samples can be defined with the following equation:

$$SI = \log(\frac{IAP}{K_{sp}})$$

where IAP is the Ion Activity product and K_{sp} is the equilibrium constant. When the SI value is equal to 0, the solution is in equilibrium with the mineral phase; when the SI value is > 0, the solution is oversaturated, resulting in mineral precipitation, and when the SI value is < 0, the solution is under-saturated indicating that dissolution is required to reach equilibrium.

III. RESULTS AND DISCUSSION

A. Groundwater chemistry

Table 2, summarizes basic statistics of the major ions chemistry of the collected groundwater samples; WHO `international standards (2011), for drinking water are also presented. The pH values of the water samples ranged 7.3 to 9.2 in the study area with a median value of 7.8; these values are considered as typical for groundwater samples in a coastal area. The pH value shows the intensity of the acid or the alkaline conditions of a solution; therefore, the groundwater samples are characterized by neutral-slightly alkaline conditions. EC is an indirect measure of ionic strength and mineralization of natural water (Hem, 1970).

EC of the groundwater samples of the study area ranges from 510 µS/cm to 26,746 µS/cm with a median value of 3110.6 µS/cm. 69% of the water samples exceed the limit of 1500 µS/cm for drinking water according to WHO (2011). The seawater intrusion is indicated by the high concentrations of Cl^- (up to 10,190 mg/L) and Na^+ (up to 4288 mg/L). More specifically, the median concentration of Cl^- is 869.2 mg/L, and the median concentration of Na^+ is 363.7 mg/L, while the limits for drinking water are 250 mg/L and 200 mg/L, respectively (WHO, 2011). The highest concentrations of Cl^- are near the sea in the northwestern part of the study area, indicating that the study area is under seawater intrusion regime (Fig. 3a).

The NO_3^- pollution is a pervasive problem for groundwater resources and it is mainly attributed to the intense fertilization, septic pits effluents, urban domestic sewage, animal and human wastes (Wilson et al. 1994).

The NO_3^- is very mobile in groundwater (Hem, 1970), so the loading is transferred very quickly. The mean and the median concentrations of NO_3^- are 32.7 mg/L and 26.6 mg/L, respectively (Table 2). 19% of the collected samples exceed the maximum permitted level of NO_3^- (50 mg/L) for drinking water (WHO, 2011) and the spatial distribution map is presented in Figure. 3b.

The highest concentrations (up to 118 mg/L) are found in the eastern part of the study area, close to the septic pits and also in the extended agricultural areas, which may generate NO_3^- from nitrogen-carrying fertilizers through nitrification that occurs above the groundwater level, especially in the area, which extending from Ghout Sha'al located in the western part of the study area, includes farmland to Almamoura in the middle of the southeastern part of the study area, where there are abundant oxygen-rich organic materials (O_2) Figure. 3b.

The results suggest that several processes determine the hydrogeochemical characteristics of groundwater in the study area. Generally, the results show that the concentration of cations decreases in order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and the anions in the order of $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^-$.

Table 2. Statistical summary of hydrochimical parameters of groundwaters samplesP

Parameter	Std (WHO,2011)	aquifer water samples						
		Min	Max	Mean	SD	Medium	std.deviation	>
Ca^{2+} mg/l	200	24.05	841.3	185.4	167.1	123	167.1	15
Mg^{2+} mg/l	50	4.9	948	109	140.8	77	140.8	13
Na^+ mg/l	200	41	4288	363.7	674.3	184	674.3	24
K^+ mg/l	-	2	91	12.1	13.6	8	13.6	-
$SO4^{2-}$	250	46	1157	274.3	250.2	162	250.2	21
$HCO3^-$ mg/l	240	67.2	323	139.6	78.1	98.4	78.1	8
Cl^- mg/l	250	39	10,190	869.2	1556.1	441	1556.1	45
NO_3^- mg/l	50	5	118	32.7	22.3	26.6	22.3	11
EC µS/cm	1500	510	26,746	3110.6	4073.3	1954.8	4073.3	41
pH	6.5 – 9.5	7.3	9.2	7.8	-	7.8	-	-
TDS mg/l	1000	341	17,109	1986	2584	1275.4	2584.5	40
TH mg/l	500	160	6004	911	944	628.3	944.1	39

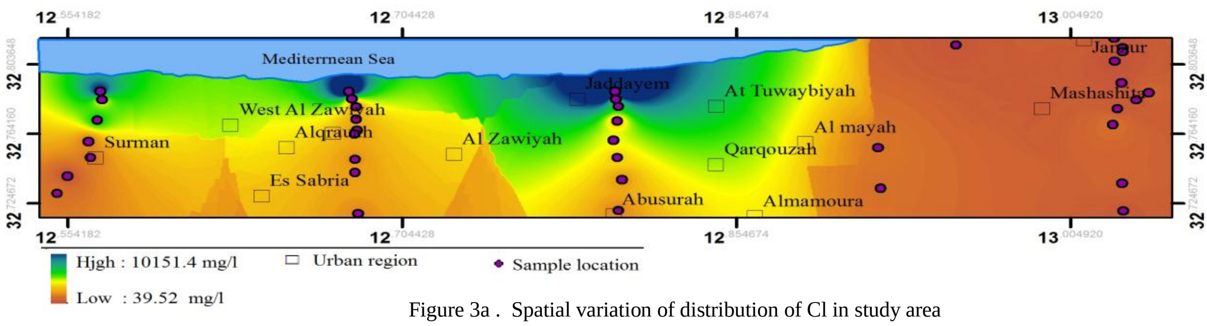

Figure 3a . Spatial variation of distribution of Cl in study area

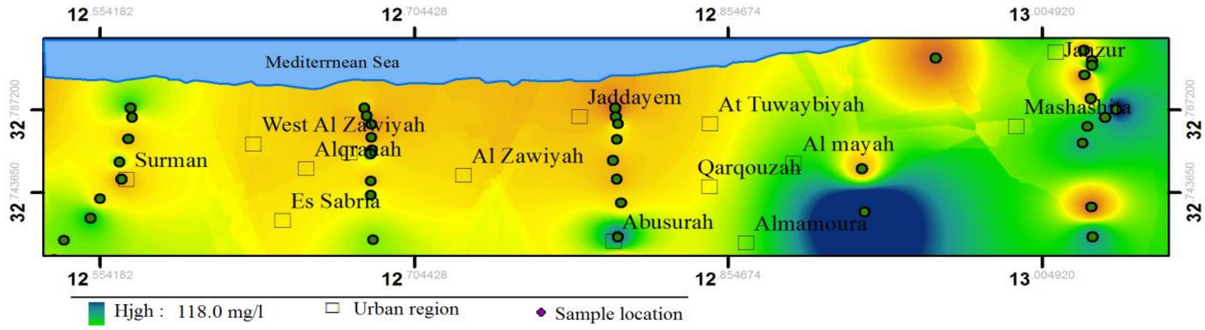

Figure 3b. Spatial variation of distribution of NO_3 in study area

Statically, the Pearson's correlation coefficients of the examined parameters are shown in Table 3. Strong positive correlation coefficients are observed between TDS and Cl^- (0.99) and between Na^+ and Cl^- (0.98), perhaps, because of the seawater intrusion regime. As well as, a strong positive correlation coefficient between Ca^{2+} and Mg^{2+} (0.79) is attributed to the common origin of these elements and points out the impact of natural processes such as the dissolution of Ca- and Mg- bearing minerals like calcite, dolomite, clays. Also, the positive relationship presented in table 3 between SO_4^{2-} and NO_3^- may be an indication of the use of nitrogen fertilizers in the various agricultural processes in the study area.

Table 3. Pearson correlation matrix of the groundwater samples in the Jefara plain

	TDS	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	TH
TDS	1									
Ca	0.86	1.00								
Mg	0.94	0.79	1.00							
Na	0.98	0.78	0.88	1.00						
K	0.91	0.70	0.91	0.89	1.00					
HCO_3	-0.14	-0.23	-0.12	-0.14	-0.06	1.00				
SO_4	0.42	0.47	0.54	0.31	0.49	0.01	1.00			
Cl	0.99	0.84	0.91	0.98	0.89	-0.19	0.31	1.00		
NO_3	-0.08	-0.09	-0.05	-0.10	-0.15	0.43	0.03	-0.12	1.00	
TH	0.96	0.93	0.96	0.88	0.87	-0.17	0.54	0.93	-0.07	1.0

(Ca/Mg) and (Ca+Mg)/Cl are used to delineate the region affected by seawater intrusion, Table 4. Thus, the Cl/(HCO_3) ratio is significant as evidence for seawater intrusion into the freshwater aquifer, (Todd, 1959) and one of the most widely used, (El-Moujabber M. et al., 2006). The Geochemical ionic ratios and evidence of seawater influence ionic ratios are commonly used to evaluate the seawater intrusion and the source and nature of the salinity present in the coastal aquifers (El-Moujabber et al., 2006). The hydrochemical values in the study area showed that the collected groundwater samples have Cl/(HCO_3) ratio ranging between 0.62 and 2.50, Table 4. According to Simpson (reported by Todd 1959), the effect of seawater encroachment could be classified using the Cl/(HCO_3) ratio into two classes, slightly affected and moderately affected classes, Fig 4.

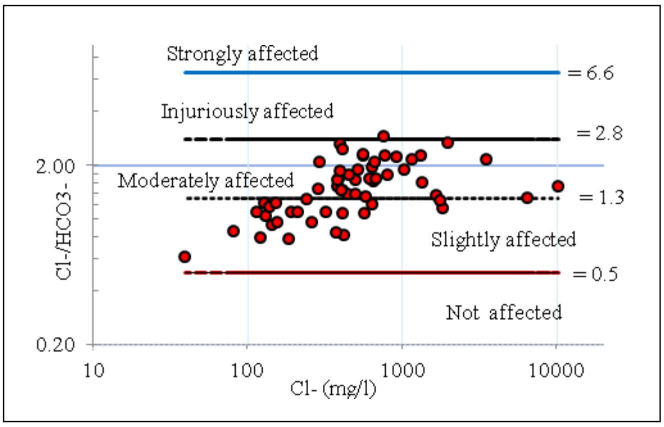

Figure 4. Scatter plots of a Cl/HCO_3 versus Cl of the 59-groundwater samples from Jefara plain

The impact of seawater intrusion in the study area, further, confirmed by the scatter Na/Cl vs. Cl^- (Figure 5). The ratio Na/Cl ranged from 0.35 to 1.62 with an average value of 0.71 as showing in table (4). On the other hand, according to (Sánchez-Martos F. et al, 2002), the salinization of the groundwater is divided into two grouped using the ionic ratio of Na/Cl. Values lie above 0.86 indicate that groundwater samples are unaffected by seawater, while values lie below 0.86 indicted that the groundwater samples are affected by seawater intrusion. In this case, more than 73% of the samples of the study area lay below the seawater dilution line (0.86). As shown in Figure 5, suggesting evidence of a seawater intrusion in this system as a consequence of anthropogenic and agricultural actives and geochemical processes.

Table 4. Descriptive statistics of ionic ratios (in meq/L) in Jefara plain

Ionic ratio	Cl/HCO_3	Na/Cl	Ca/Mg	(Ca+Mg)/Cl
Mean	1.57	0.71	2.03	1.13
Stdev	0.53	0.26	2.34	0.57
Min	0.62	0.35	0.28	0.33
Max	2.50	1.62	10.99	3.24
Medium	1.47	0.68	10.9	1.00
Seawater	<1	<0.86	> 0.9	>0.5
freshwater	**> 6.6**	0.86 - 1	-	<0.5

The cations Ca^{+2} and Mg^{+2}, belonging to the most abundant of the alkaline-earth metals, are major constituents of most freshwater systems. Although the Ca^{+2} concentrations in 75% of the groundwater samples in the study area were below the permissible 200 mg/l , the most of groundwater samples had high Mg^{2+} concentrations (Table 2). Here, more than 66% of the groundwater samples' ratio value were exceeded the Hen's ratio (Figure 6), (Hem D., 1970). This gives a clear indication of seawater intrusion in the study area and poses an important threat to groundwater in the Jefara Plain.

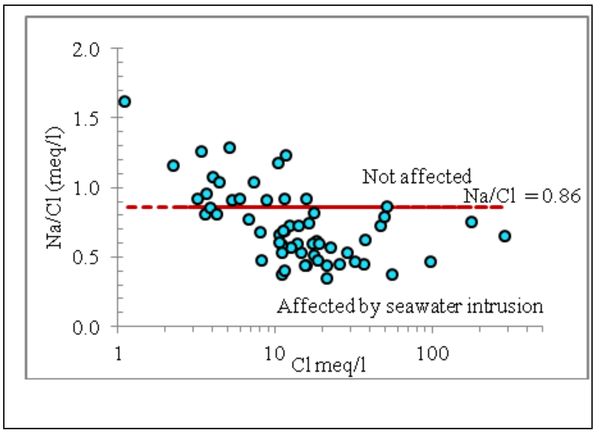

Figure 5. Ionic ratio of Cl versus Na/Cl concentration in meq/L in Jefara plain where dashed lines indicates seawater ratio value

Examination of the Mg^{2+}/Ca^{2+} ionic ratio content shows that there is a clear relationship between these parameters and the Cl− content, i.e., that they are indicative of the degree of mixing between fresh and saltwater in the groundwater of the Jefara plain (Figure 7).

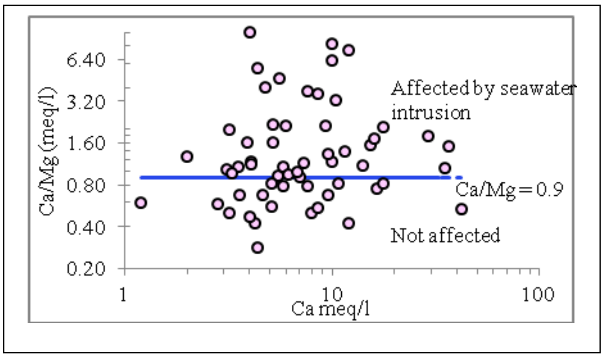

Figure 6. Ionic ratio of Ca versus Ca/Mg concentration in meq/L in Jefara plain where dashed lines indicates seawater ratio value

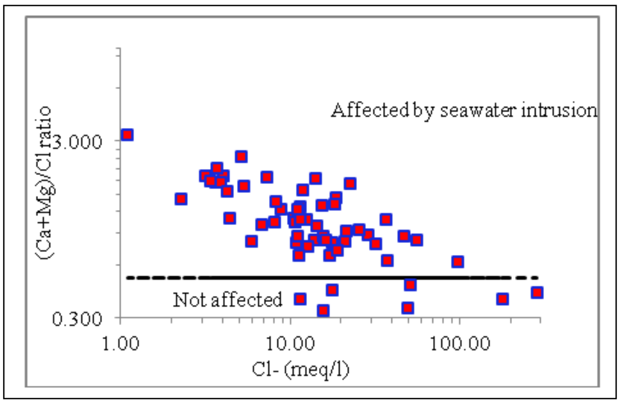

Figure 7. (Mg + Ca)/Cl ratio as a function of the Cl content (meq/l) in Jefara plain where dashed lines indicates seawater ratio value

C. Water type

For recognize the chemical character of groundwater in the study area, samples have been plotted in Piper trilinear diagram (Piper, 1944) using Rockware software v17 (Figure. 8). The samples are classified as various chemical facies on the Piper diagram for the study period. Major types of groundwater in the study area are in the order of Ca–Na-Cl > Na–Ca-Cl; Na–Ca > Ca-Cl > Na-HCO_3-Cl. However, the majority of the samples are gathering in NaCl and CaMgCl field. Water types such as (mixed $CaHCO_3$, mixed CaMgCl and NaCl) broadly avail in the study region during the study period and imply the mixing of high-salinity water caused from surface infectivity sources such as domestic wastewater, irrigation return flow and septic pits effluents with water followed by ion exchange reactions.

The $NaHCO_3$ and $CaHCO_3$ water types represent the process involve mineral dissolution which is representing the sediment-water interaction facies in the Piper plot (Gopinath et al. 2019). The samples representing Na–Cl and mixed CaMgCl types are identified as seawater intrusion facies present along the coastal part of the study area. The maximum Cl concentration of high saline water (Na–Cl type) is 10,190.4 mg/l present in the coastal part. From the Piper diagram, the general trend of groundwater chemical composition shows from mixed Ca–Mg–Cl waters to Na–Cl waters from inland toward the coast, Especially in the western part and adjacent to the coastal strip of the study area.

The groundwater samples in this area were plotted on the graphs as cations versus anions expressed in milli-equivalent percentage on the modified form of tri-linear diagram of Piper proposed by Chadha, (1999). Four water fields that can be identified from the diagram depend on the relationship between alkaline earths (calcium and magnesium), alkali metals (sodium and potassium), weak acidic anions (carbonate and bicarbonate) and strong acidic anions (chlori

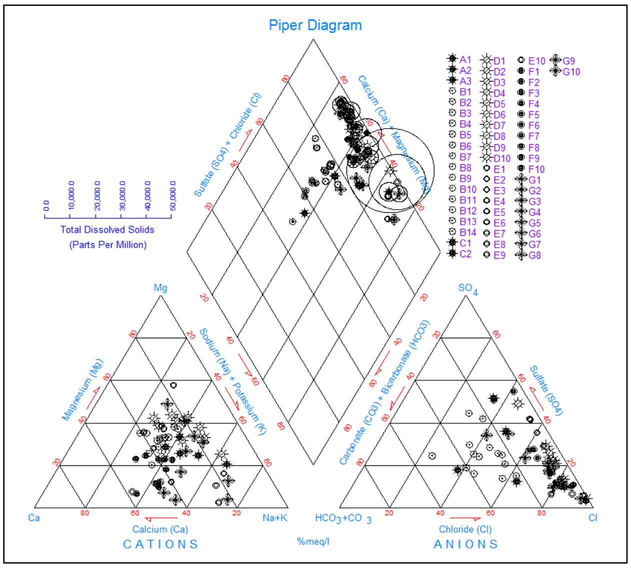

Figure 8. Piper trilinier plot showing the groundwater types in the study area

Figure. 9, the majority of the samples (77%) are plotted in the 2nd field, representing Ca-Mg-Cl-SO_4 type, where (Ca + Mg) > (Na + K) and (Cl + SO_4) > (CO_3 + HCO_3), this water type is generally characterized by permanent hardness. While the rest of samples (13%) are plotted in the 3rd field, representing the Cl-SO_4-Na-Mg type, where the sodium and chloride are the dominant on groundwater thus showing a probable marine intrusion in this area, where (Na + K) > (Ca + Mg) and (Cl + SO_4) > (CO_3 + HCO_3), such a water type generally creates salinity problems. This indicates that the aquifer is essentially recharged by the excess of irrigation water and reuse water of wastewater treatment, and also due to the pumping reduction.

D. Geochemical modeling

The Miocene age (the shallow aquifer) mainly consist of limestone, dolomite and calcarenite (Miocene age).These soluble minerals at a certain extent change the composition of groundwater in this area. In order to examine the occurrence of these minerals dissolution, a geochemical software Visual MINTEQ v.3.1 was used to determine the degree of over- or under-saturation with such carbonates (calcite, aragonite, and dolomite), sulfates (gypsum and anhydrite) and halide (halite) in groundwater. For each mineral, the proximity to equilibrium was expressed as the saturation index (SI): A SI of zero indicates that the solution is in equilibrium with a particular mineral. A SI < 0 indicates that the solution is under-saturated with respect to a particular mineral and a SI > 0 indicates over-saturation.

The mean, maximum, medium and standard deviation (stdev) SI values of carbonates (calcite, aragonite, and dolomite), sulfates (gypsum and anhydrite) and halide (halite) Mineral phases are presented in Table 5.
All the SI values for calcite, dolomite and Anhydrite are greater than zero in groundwater samples. The groundwater is therefore over-saturated with respect to these minerals, and precipitation results. The reactions are described as:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$
$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \leftrightarrow CaMg(CO_3)_2$$
$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_4$$

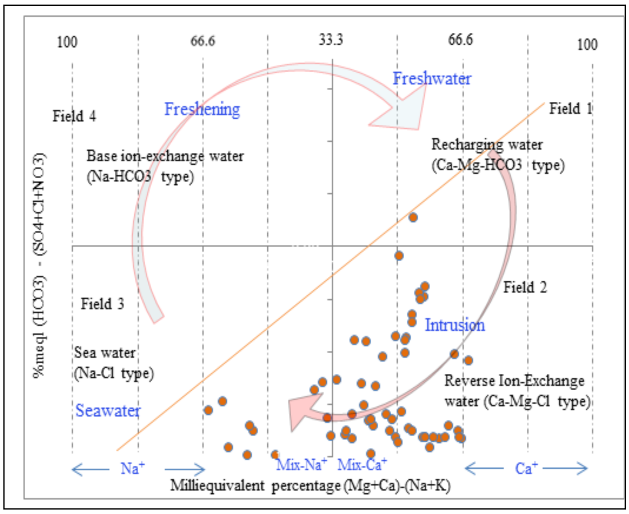

Figure 9. Hydrochemical faces Evaluation diagram (HEF-D) explaining the seawater–groundwater mixing process

The seawater intrusion might be responsible for the precipitation of carbonate mineral phases in the Quaternary Coastal Aquifer. Considering Table 2, the concentrations of C^{l-} are much higher compared to Ca^{2+} which can be an indication of Ca^{2+} removal as a result of calcite precipitation. The saturation index values for halite, gypsum, and anhydrite are negative, Table 5. This indicates that the aforementioned halide and sulfate mineral phases are undersaturated in the water samples, suggesting that they are minor or absent in the host rock. As shown in Fig. 10, the elevated values of TDS increase, in turn, the SI values of halite, gypsum, and anhydrite due to the process of seawater intrusion shifting the chemical equilibrium and affecting the precipitation reactions.

E. Suitability of groundwater quality for different uses

In general, the groundwater in Jefara Plain (shallow aquifer) is used for several purposes such as domestic,

Table 5. SI of calcite, aragonite, dolomite, gypsum, anhydrite and halite

Mineral		Ch. symbol	Mean	Min	Max	stdev	Mediam
Carbonate	Calcite	$CaCO_3$	0.39	0.01	1.84	0.32	0.34
	Aragonite	$CaCO_3$	0.29	0.01	1.69	0.29	0.23
	Dolomite	$CaMg(CO_3)_2$	0.80	0.06	3.85	0.66	0.63
Sulfate	Gypsum	$CaSO_4{\cdot}2H_2O$	-1.30	-2.06	-0.43	0.41	-1.37
	Anhydrite	$CaSO_4$	-1.55	-2.32	-0.69	0.40	-1.61
Halide	Halite	NaCl	-5.62	-7.33	-3.16	0.76	-5.65

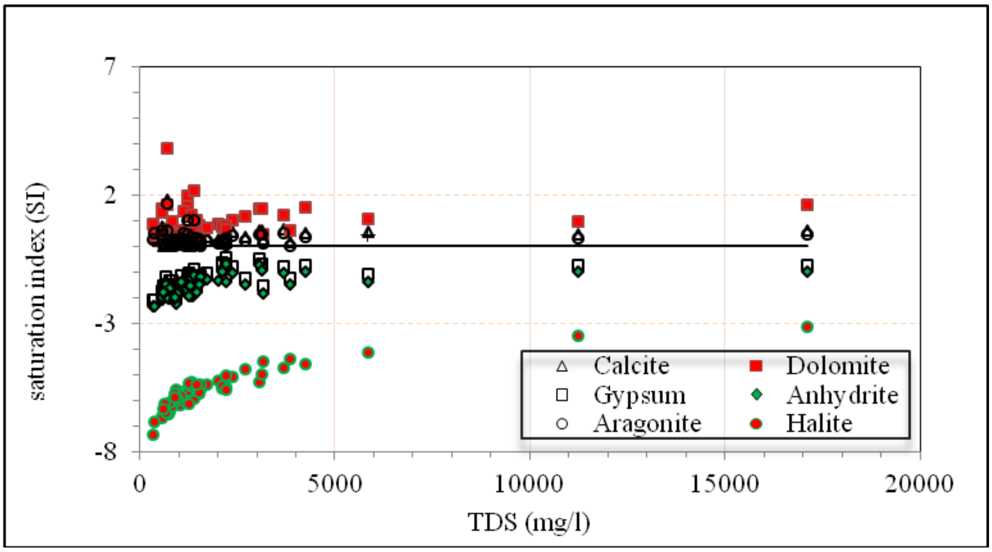

Figure 10. SI of selected mineral phases (calcite, aragonite, dolomite, gypsum, anhydrite, and halite) vs. TDS of the 59 groundwater samples in Quaternary coastal aquifers of Jefara Plain

irrigation, and industrial purposes. The groundwater used for drinking has to meet with (WHO) standards. On the other hand, irrigation water tests should be based on the sodium absorption ratio (SAR), EC, soluble sodium percent (SSP), Cl^- and SO_4^{2-}. These evaluations will be made in the following section.

As for, required groundwater quality for industrial purposes depends on the different industrial uses, and cannot be generalized. However, high salinity is undesirable.

1) *Groundwater quality for domestic purposes*

Evaluation of groundwater for domestic purposes (drinking and household) generally depends on its salinity, pH, chemical, and physical characters comprising odor, color, taste and turbidity. The studied groundwater is evaluated for drinking (Table 2.) based on the guidelines established by the World is evident that most of the studied groundwater wells generally did not meet all of the water quality standards for the major inorganic constituents, except the K and pH values, which were suitable in all samples. The TDS values are high in 40 groundwater samples, and considered unacceptable for drinking uses as drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 ppm (WHO, 2011) In addition, some major elements of cations and anions exceeded the guideline values excessively in some groundwater samples, as indicated in Table 2. Thus, they are considered unsuitable for drinking use.

2) *Groundwater quality for irrigation purposes*

The quality of irrigation water plays an important role in agricultural development. Irrigation with poor quality water may cause an excessive accumulation of salts in the root zone of soil, which affects crop yield and quality of the products. The Food and Agriculture Organization (FAO, Ayers and Westcot, 1985) and the US Salinity Laboratory Staff (USSL, 1954) classifications are used for the evaluation of the irrigation water quality throughout the world. In general, the classification of the irrigation water quality criteria depends on TDS and sodium content. Presence of sodium reduces the aeration in soil and thus reduces the permeability. The factors controlling irrigation water quality are sodium percentage (Na%), sodium adsorption ratio (SAR), permeability index (PI) and residual sodium carbonate (RSC). High sodium percentage influence the permeability of soil and makes it unfit for plant growth. It is controlled by cations (meq/l) and this is obtained by:

$$Na\% = \frac{(Na^+ + K^+) \times 100}{(Ca^{2+} + Ma^{2+} + Na^+ + K^+)}$$

Wilcox, (1955), used percentage sodium and electrical conductance (µS/cm) in evaluating the suitability of groundwater for irrigation. According to the sodium percentage, the water samples are varying from excellent to doubtful classes for irrigation and the result is shown in Table 6. Fig. 11 shows Wilcox diagram in which 28 samples are not fit for irrigation, 3 samples falling in excellent to good and the rest are falling in and good to permissible categories.

Table 6. Classification of water based on sodium percentage

Water Calss	Na %	No. of samples
Excellent	< 20	Nil
Good	20 - 40	32
Permissible	40 - 60	19
Doubtful	60 – 80	8
Unsuitable	➢ 80	Nil

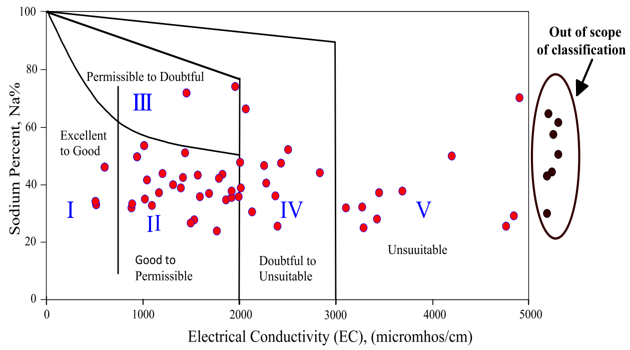

Figure 11. Position of water samples on the Wilcox plots (Wilcox, 1955)

Sodium adsorption ratio (SAR) is calculated by the relationship of the three major ions, (Na, Ca and Mg), (meq/l). The formula by Richards (1954), is used to calculate SAR and according to sodium adsorption ratio.

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

85 % of the groundwater samples fall in high and very high electrical conductivity categories with low SAR. Fig. 12 shows the relationship between salinity and sodium hazard.

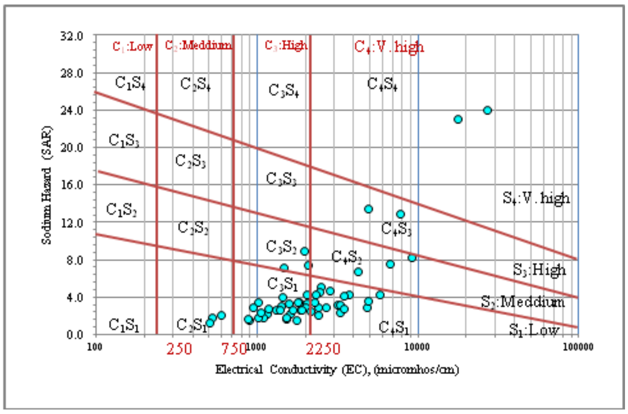

Figure 12. Salinity diagram of groundwater samples from the study area (USSL, 1954)

Doneen, (1962) proposed a classification of water based on the permeability (PI). The PI is affected by long term use of irrigation water. It is influenced by sodium, calcium, magnesium and bicarbonate ions and expressed as follows, (Ragunath, 1987):

$$PI = \frac{(Na^+ + \sqrt{HCO_3^-}) \times 100}{(Ca^{2+} + Mg^{2+} + Na^+)}$$

The water of the study area have been classified for irrigation purposes (based on PI) and presented in Table 7. This Table reveals that the calculation values of the PI are ranging from 27.8% to 81.1% with average of 49.8%. According to Doneen's diagram (Figure. 11), the suitability of groundwater for irrigation based on PI was determined. This criterion categorizes the water into three classes. Based on the classification, water with PI > 75% (Class I) is good, 25–75% (Class II) is suitable, and PI < 25% (Class III) is unsuitable for irrigation. As can be seen in Figure 13, most of samples fall in class (I). However, only two samples (E3 and E4) fall in class (II). This indicates that 97% of the groundwater wells are suitable for irrigation based on PI in the study area.

Residual Sodium Carbonate (RSC) has been calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purposes by the following equation (Eaton, 1950):

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}),$$

all concentrations are expressed in meq/L.

According to the RCS index, water can be classified into three different classes. The classes are 0–1.25 meq/L, 1.25–2.5 meq/L, and > 2.5meq/L which correspond to bad, medium and good water for irrigation purposes, respectively (Table 8). All the samples belong to the good category.

Table 7. Classification of irrigation water based on PI index

Parm.	Min	Max	Mean	Category	No.	Class
PI	28	81.1	49	< 20	Nil	Good
				20-40	15	Medium
				40-80	41	Bad
				>80	1	unsatisfactory

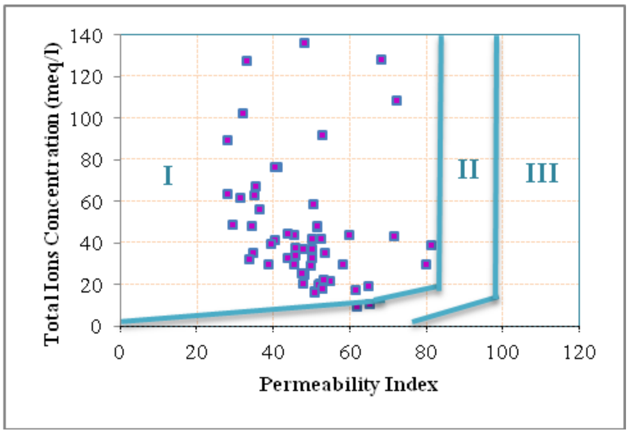

Figure. 13 USSL Classification of irrigation water in study area, based on permeability index.

Table 8.Classification of irrigation water based on RCS index

Parm.	Min	Max	Mean	Category	No. S	Class
RSC	-118.3	-1.3	-16.6	<1.25	59	Good
				1.25 – 2.50	Nil	Medium
				>2.50	Nil	Bad

IV. CONCLUSION

The hydrochemistry of groundwater in the Quaternary Coastal Aquifer of Jefara Plain seems to be influenced by various processes including seawater intrusion, anthropogenic contamination, and water-rock interaction, as indicated by very wide ranges and high standard deviations of most Hydrochemical parameters. However, Seawater intrusion is limited to the area near the coast, whereas pollution by sewage is more widely spread. The concentrations of total dissolved solids (TDS), chloride, and nitrate exceeded the (WHO) drinking water standards in about 67.8, 76.3, and 18.6% of the collected samples (n=59), respectively. This indicates that groundwater in the study area is significantly degraded in water quality and suffers from extensive salinization due to anthropogenic pollution as well as seawater intrusion.

The study highlights that the groundwater samples in the study area are mostly of MixedCaNaHCO_3 is the most common type, followed by CaCl, then NaCl, and only one sample of $CaHCO_3$ groundwater type.

Dissolution of carbonate minerals in the aquifer sediments in the recharge regions; weathering of silicate minerals, as well as cation exchange also modify the concentration of ions in groundwater. The study area can be divided into two areas based on the lithology: (I) coastal strip, the area adjacent to the sea with limestone; (II) inland area adjacent to the coastal strip which consists of sands and clay. Saturation indices indicate the geology in the study area has a potential influence on the saturation status towards carbonate minerals. Most of the groundwater samples from the coastal strip range from equilibrium to oversaturation with respect to carbonate minerals (calcite and dolomite). However, all groundwater samples are undersaturated with respect to sulphate minerals (gypsum and anhydrite) and halite.

The results of the hydrogeochemical investigations illustrate that various processes determine the major ionic composition of groundwater in the study region. The distribution pattern of major ions shows a compositional variation in the groundwater samples. In general, the concentration of cations decreases in the order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and of anions in the order $Cl^- >$ SO42− $>HCO_3^- > NO_3^-$ dominates over Cl^- in the most of the samples. Correlation analysis indicates that most of the ions are positively correlated. The reasonably positive and strong correlation among the ions especially Na^+, Cl^-, and Mg^{2+}, indicates that such ions are mainly derived from the same source of saline waters. Thus, it could be indicated that the salinization of the study region is associated with seawater intrusion.

Groundwater suitability for agricultural purposes was accessed from SAR, Na%, PI, and RSC. According to SAR, the majority of the samples in the area have low sodium hazard except for few samples with moderate to high sodium, and in terms of salinity hazard, the samples in the area have moderate to very high salinity. Soluble sodium percentage values (Na %) indicate that 42% of the samples are not suitable for agricultural purposes, as, for the remaining samples, they range from good to permissible. RSC values of few samples show that long-term usage of the water may affect the crop yield.

Finally, the hydrogeochemical investigations reveal that groundwater quality in the study area is affected by both natural and anthropogenic sources. Human activities such as sewage disposal, intense use of fertilizers, over-drafting of groundwater along the coastal area lead to inland migration of saline water into the coastal aquifers. Proper awareness and routine monitoring have to be implemented to preserve the groundwater from further deterioration.

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