Inverse Geochemical Modeling of groundwater salinization in El-Tur South Sinai, Egypt

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Abstract

This study aims to define sources and mechanism of salinization process of groundwater Quaternary aquifer in El Tur area South Sinai. Groundwater samples were collected covering three provinces (Wadi El Wadi, El Qaa, and El Gobail) in addition to Red Sea water sample (16 water samples). The hydrochemical results indicate that groundwater salinity is greatly variable; it varies from (414-4307 mg/l) at Wadi El Wadi, (1208-4973 mg/l) at Sahal El Qaa and (2176-12000 mg/l) at El Gobail area indicates that salinity increases in the direction of groundwater flow from the upstream the mountainous part in the eastern side toward the downstream in southwest direction to the Gulf of Suez. Seawater Mixing Index (SWMI) calculations divide groundwater samples into two groups; (Group I) has low groundwater salinity mainly at Wadi El Wadi and El Qaa plan. (Group II) has highly saline groundwater mainly at El Gobail area which is affected by mixing with seawater. Saturation Index calculations revealed that El Gobail samples are supersaturated in carbonate and sulphate minerals. Environmental stable isotopes ($\delta^{18}O$ and δD) showed that the precipitation is the major source of recharging Quaternary aquifer in the area. However, the sources of increasing salinity due to the dissolution process have a significant effect on the chemical composition of groundwater.

1. Introduction

Fresh groundwater stored in coastal aquifers constitutes most significant resource in several countries that have deficiency of water resources utilized in different purposes. Overexploitation of groundwater in coastal aquifers may cause severe problems (*i.e.* encroachment of seawater, physical and biological changes like destruction of the natural habitat or shore modification through erosion/sedimentation through man's activities interferences). El Tur is located in the southwestern part in Sinai Peninsula on the eastern side of the Red Sea. It is an arid area dominated by desert land as a result of limited water resources. Rainwater is the only renewable source of fresh water with variable intensity in winter season. The highest rain intensity occurs along the southern Sinai mountainous area on the eastern side. Rainfall contributes the significant recharge sources to the aquifers especially within the areas near the basement complex of South Sinai. The main source of water supply in El-Tur area is the groundwater extracted from the unconfined Quaternary aquifer. However, the complex geology of Sinai imposes difficulties in understanding the hydrogeological settings and recharge process from the catchment area in the eastern side of El-Tur area replenishing the aquifers. Many factors can affect groundwater recharge process from the catchment areas such as geologic structures, evaporation, and surface runoff. Also, topography, soil cover, and rock hydraulic properties control the surface runoff losses and the infiltration rate [1]. As groundwater flow, the hydrochemical composition of groundwater facies changes according to the mineralogical variations, dissociation process of the aquifer matrices, and type of salts deposit, which finally led to water quality degradation [2]. The groundwater quality assessment in El Tur area is a major concern of this study using an integrated geochemical modeling, hydrochemical studies, and isotopic technique are correlated to highlights and identify sources of dissolved salts to understand the processes that control the salinization processes of groundwater in El Tur area.

Study Area

El -Tur area lies within the western part of south Sinai (Fig. 1). It represents a part of the Gulf of Suez valley which extends between 28º to 28º 40' N and 33º 20' to 33º 55' E. It is affected by intensive block fault structure according to the previous studies in El-Tur area [3, 4; 5; 6; 7]. The mean

annual rainfall rate ranges from 10 mm/year on the exposed Quaternary sediments to 60 mm/year on the eastern Pre-Cambrian Mountains [4]. Rain events of magnitudes up to 76 mm/day may occur occasionally on these mountains causing severe flash floods [8] which represent the significant source replenishing the aquifers.
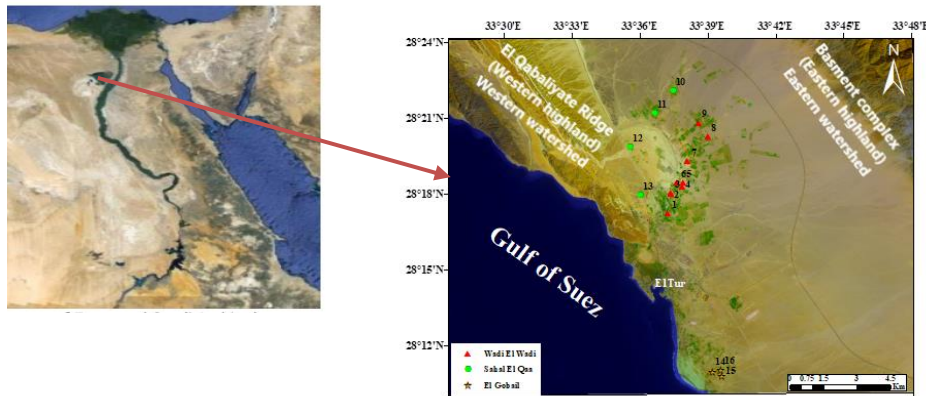

Fig (1): Location map and groundwater sampling sites at the study area

Geological and Hydrological Studies

El- Tur area covers part of El-Qaa Plain as indicated in Fig.1. El Qaa plain rises up to 200 m asl and slopes gently towards the of Gulf of Suez. It is affected by intensive block fault structure, the surface linear geologic structures were studied by different authors, among them are; [9, 10, 11].The geomorphic unit constitutes of topographic heights standing out in sharp relief, elevated up to about + 2641m (MSL) (G. Katherina). The surface is incredibly tough with prominence edges and peaks and dominated by fissures and fractures and dissected by a huge network of drainage basins that terminate in the lowland unit. They are dominated by elevated hills and recognized into series of elongated ridges arranged in NW-SE direction. The maximum elevation reaches about + 370 m (G. Abu Suwera) as indicated in Fig. (2).

The surface is dissected by dense subsequent drainages of sub parallel type following the regional slope of the land towards the east. The northwestern-relatively high mountains are built of sedimentary rocks belonging to the geologic times of Paleozoic, Mesozoic, and Cenozoic.
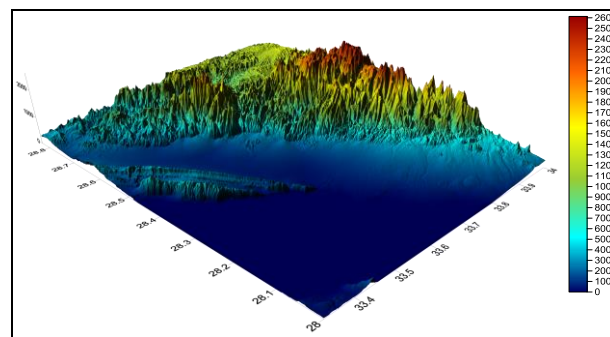

Fig (2): Digital Elevation Model (DEM)

Based on the recognized geomorphologic and geologic features, four water bearing rock units in the area is distinguished comprising the following: the fractured Pre-Cambrian basement rocks, the lower Cretaceous Malha Formation (the Nubian sandstone aquifer system), the Lower Miocene clastic deposits and the Quaternary deposits Fig. (3). The Pre-Cambrian and Nubian aquifers are not yet exploited in El Qaa plain because of relatively high costs of drilling and exploitation from great depths 2500m. While the lower Miocene aquifer was recorded by [4] and [8] to be saturated with saline water because of the dissolution of evaporates and therefore it is nearly neglected for the present time.
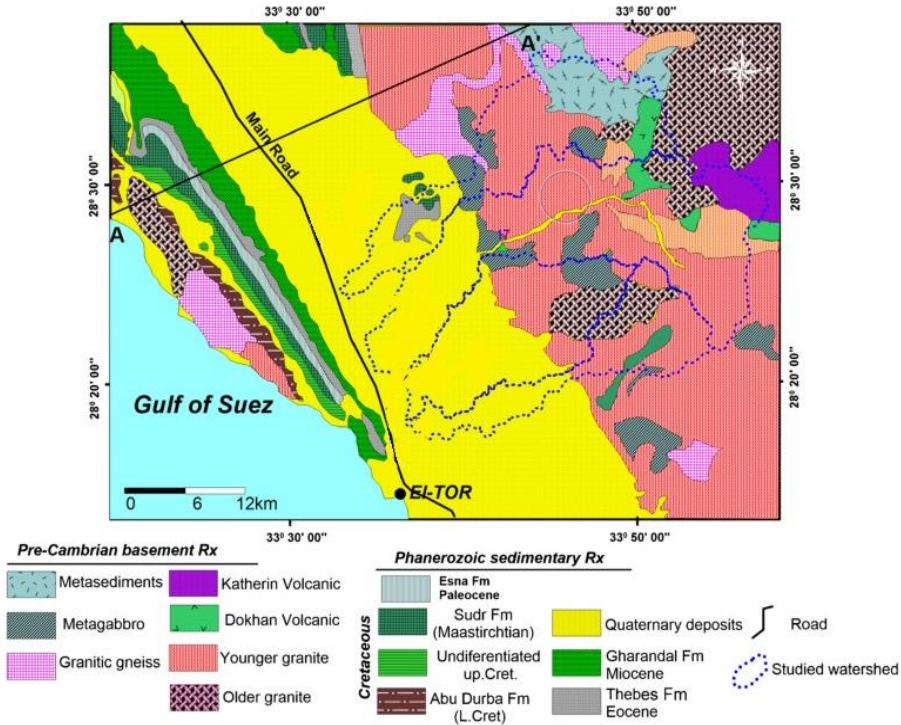
Fig (3): Geologic map of the studied area with main geomorphologic units

The Quaternary aquifer represents the available aquifer with a great potential for both quantity and quality measures, with thickness varies between 30 m close to the southwestern sedimentary hills and 1000 m within the central part of the area and 400 m in the eastern part of El Tur City. The Quaternary aquifer is composed of sedimentary facies that changing laterally and vertically in thickness and lithological characters. These deposits are mainly composed of gravels, sands, silt and coarse materials in the east and clay, limestone, coral reefs, and sabkha deposits in the western part. The contents of sands increase eastwards and mixed with cobble and boulders of weathered Pre-Cambrian rocks in some area. On the opposite, the contents of clay, limestone, coral reefs, and evaporite materials increase westwards due G. Mousa and the shoreline

2. Materials and Methods

2.1 Collection and Analysis of Hydrochemical data

A field trip was administrated in March and April 2018 to gather 16 groundwater samples covering the area of study to evaluate the groundwater quality as shown in (Fig.1). Physical measurements including (Electrical conductivity (EC), pH, temperature, TDS, and DO) were measured in situ utilizing portable meters. Laboratory measurements of hydrochemistry and environmental stable isotopes were done in the Central Laboratory of Environmental isotope hydrology, in Egyptian Nuclear and Radiological Regulatory Authority (ENRRA). The procedures and methods used for the determination of the hydrochemical species according to [12] were followed. Total Hardness (TH) as $CaCO_3$ and Ca^{2+} were analyzed using standard EDTA. Mg^{2+} was calculated by taking the difference between TH and Ca^{2+} concentrations. Na^+ and K^+ were measured using a flame photometer. Total alkalinity of CO_3^{2-}, and HCO_3^- were determined by titrating with H_2SO_4. Cl^- was determined by titration with $AgNO_3$ standard. SO_4^{2-} and NO_3^- were analyzed using a spectrophotometer. All constituents are expressed in milligrams per liter and milliequivalents per liter. Data quality was assessed using the charge balance between the difference of cations and anions (expressed in meq/l) divided by their summation which should be < ±5 %. Trace elements were measured using ICP (Inductively Coupled Plasma at Desert Research Centre DRC.

Environmental Stable isotope (^{18}O and D) were measured using Picarro Laser Spectroscopy. The (^{18}O and D) concentrations of the water samples are expressed in delta (δ) notation relative to the standard VSMOW according to the following equation:

$$\delta \text{ (‰ VSMOW)}= 1000(R_{sample}-R_{VSMOW})/ R_{VSMOW} \quad (1)$$

Where R_{sample} is the isotopic ratio ($^2H/^1H$ or $^{18}O/^{16}O$) of the sample and R_{VSMOW} is the isotopic ratio of the standard. The analytical precision based on laboratory standards is ±0.1 ‰ and ±1.0 ‰ for $\delta^{18}O$ and δD respectively. Environmental stable isotopes of δO^{18} and δD in water provide useful tracers to identify flow regimes and sources of groundwater recharge [13]. Frequently, groundwater retains its stable

isotopic signatures unless evaporation, dilution, or mixing with waters of various isotopic compositions [14; 15]. Therefore, water exposed to different processes like evaporation and /or mixing often acquires identifiable isotopic composition which can be used as natural tracers.

Ground surface elevation and the location of the sampling sites were implemented using Global Positioning System (GPS) manufactured by GARMIN in the field. This was supported by a topographic sheet made available by the Egyptian Survey Department. Graphical presentation of the ions species were used by Piper and Gibbs plot diagrams to follow the processes governing water evolution. Measured and estimated groundwater variables were analyzed within ArcGIS 10.3 package. Geochemical modeling constitutes an important method that is commonly used for determining the chemical reactions occurring along flow path [16] with supported sets of mole transfers of phases that account for water chemistry evolution or salinization between one or mixture of initial water compositions and final water compositions [17].

3. Results and Discussion

3.1 Groundwater Hydrogeochemistry

Table 1 summarizes the results of Hydrochemical parameters of the analyzed groundwater samples of the Quaternary aquifer (N=16) and seawater fraction from the study area in addition to Red Sea and Rainwater samples. Groundwater pH values range from 7 to 7.9 with an average value of 7.6 showing neutral to slightly alkaline character. EC values range from 647 to 18750 μs/cm, where 75 % of the samples are exceeding the [18] limits for drinking purpose of 1500 μs/cm. Salinity in groundwater is greatly variable; it varies from (414-4307 mg/l) at Wadi El Wadi, (1208-4973 mg/l) at Sahal El Qaa and (2176-12000 mg/l) at El Gobail area. A continual increase in salinity is observed as in (Fig. 4) from the northeast to the southwest in agreement with the direction of groundwater flow toward the Gulf of Suez which could be a dissolution of aquifer matrices or seawater effect. For cations, sodium is predominant than calcium and magnesium (Na> Ca> Mg> K) in about 69 % and Na>Mg>Ca>K for 31% of the collected groundwater samples. For anions, all samples have chloride more predominant than sulphate, bicarbonate and carbonate (Cl>SO₄>HCO₃>CO₃). Na+ and Cl- are the dominant ions with Cl-Na water type in all samples. This first indication of the dominance of Cl and Na ions associated with their concentrations can be used as the basis to classify sources of salinity in groundwater whether from terrestrial or marine sources.

Table (1): Physiochemical and Environmental Isotopes results of the collected groundwater samples.

|	Well No.	Temp °C	DO mg/l	pH	EC μs/cm	TDS mg/l	Cations concentration (meq/l)				Anions concentration (meq/l)				Water Type	$\delta^{18}O$ ‰	δD ‰	d^* ‰
							Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{--}	HCO_3^-	Cl^-	SO_4^{2-}				
Wadi El Wadi	1	30.3	3.00	7.4	1680	1075	6.38	0.59	6.09	3.34	0.4	0.70	12.32	3.22	Na-Cl	-5.14	-31.77	9.35
	2	28.3	4.68	7.6	6730	4307	51.40	0.10	5.22	6.55	0.4	0.90	53.20	9.57	Na-Cl	N/A	N/A	N/A
	3	27.3	5.62	7.8	4390	2810	37.61	0.13	3.48	3.96	0.0	0.90	42.00	4.37	Na-Cl	-3.88	-22.1	8.94
	4	25.0	4.40	7.9	647	414	3.19	0.20	2.87	0.43	0.0	1.50	4.90	0.54	Na-Cl	-4.44	-21.67	13.85
	5	28.5	4.25	7.9	1240	794	6.29	0.05	4.13	0.28	0.0	1.90	7.00	1.46	Na-Cl	-5.77	-36.55	9.61
	6	28.0	5.25	7.9	866	554	5.03	0.46	3.65	0.72	0.2	1.60	7.00	1.23	Na-Cl	-4.69	-22.81	14.71
	7	28.0	4.66	7.9	1507	965	8.88	0.08	3.26	3.31	0.0	1.90	9.24	4.68	Na-Cl	-4.08	-19.62	13.02
	8	29.9	5.30	7.0	1965	1258	9.23	0.08	3.91	4.72	0.0	2.00	9.80	6.24	Na-Cl	-4.21	-19.71	13.97
	9	30.9	5.25	7.8	2427	1553	13.22	0.46	6.09	5.70	0.0	2.00	14.00	10.40	Na-Cl	N/A	N/A	N/A
Sahal El Qaa	10	32.2	4.49	7.6	1888	1208	10.34	0.08	6.52	1.52	0.0	2.50	10.50	5.62	Na-Cl	-6.17	-43.07	6.29
	11	29.3	3.90	7.2	3850	2464	20.96	0.71	13.91	3.52	0.0	2.40	28.00	9.35	Na-Cl	-4.49	-34.31	1.61
	12	30.1	5.49	7.8	4110	2630	20.00	2.04	11.11	4.52	0.4	1.60	21.00	15.56	Na-Cl	-6.06	-43.93	4.55
	13	30.2	4.2	7.1	7770	4972	35.50	0.77	26.09	27.12	0.4	0.90	53.90	36.79	Na-Cl	N/A	N/A	N/A
El Gobail	14	27.9	7.30	7.5	13250	8480	67.39	0.54	42.54	20.73	0.4	0.80	106.40	25.47	Na-Cl	N/A	N/A	N/A
	15	27.0	6.2	7.8	18750	12000	104.35	0.41	51.40	24.58	0.0	1.10	128.80	59.49	Na-Cl	N/A	N/A	N/A
	16	27.4	6.87	7.9	3400	2176	22.26	0.23	8.70	2.64	0.0	1.30	22.40	12.01	Na-Cl	-6.02	-40.76	7.4
	Red Sea	28	4.3	8.1	61300	42203	519.50	5.897	29.88	117.91	0.0	0.90	637.07	94.27	Na-Cl	1.98	13.8	-2.04
	*Rain	18	N/A	7.7	352	214	0.434	0.23	2.77	0.255	0.0	1.70	0.785	1.18	Ca-(HCO₃)₂	-6.48	-39.6	12.24

*Saint Catherine Precipitation [19].
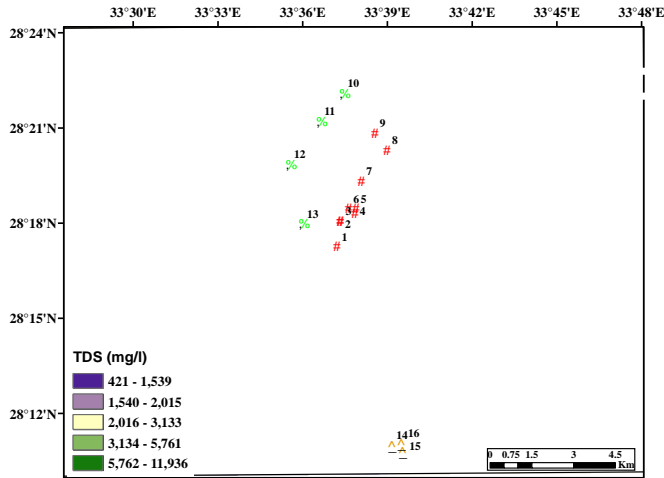
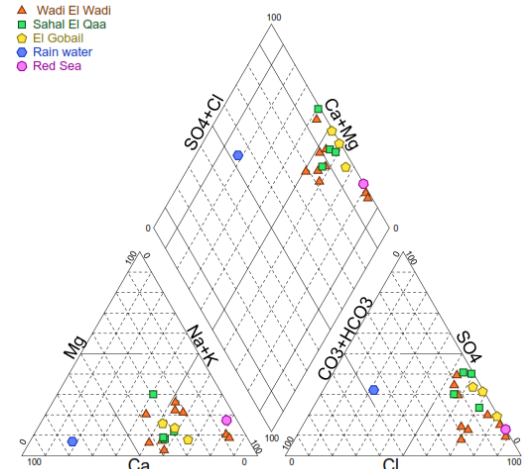Fig (4): TDS distribution map of the study area.

Fig (5): Piper diagram for collected groundwater samples.

Piper's diagram [20] clearly shows that Fig (5) all of groundwater samples have hydrochemical facies in the field of Na-Cl type. The distribution of cations tended to be clustered in the ternary diagram and was dominated by Na^+ and K^+ and Cl^- for anions.

3.2 Processes controlling groundwater salinization

The salinization processes that might contribute to salt composition of the collected groundwater samples have been examined by investigating the following mechanisms of salinization. Gibbs plot [21] introduced a presentation that helps to differentiate between the samples according to their chemical compositions which could be affected whether by seawater mixing, rock weathering or evaporation/ precipitation processes. This classification is based on the relation of TDS vs. (Na / (Na+ K) or (Cl / (Cl + HCO_3) in the cationic and anionic sides respectively. The distribution of the studied groundwater samples on Gibbs diagrams, Fig

(6) reflects three groups. The first group in area influenced by rock-dominance slightly elevated dissolved solids to less than 1000mg/l representing Wadi El Wadi groundwater samples in the eastern part near the catchment area. Most samples from the Wadi el Wadi, Sahal El Qaa and in El-Gobail area were distributed in the second group in the middle of the diagram point to seawater-rock dominance could be attributed to leaching of rock matrices and sea salt deposits. Finally, the third group was affected by saline water as mixing or sea salt dissolution processes with the groundwater at El-Gobail south El-Tur area.
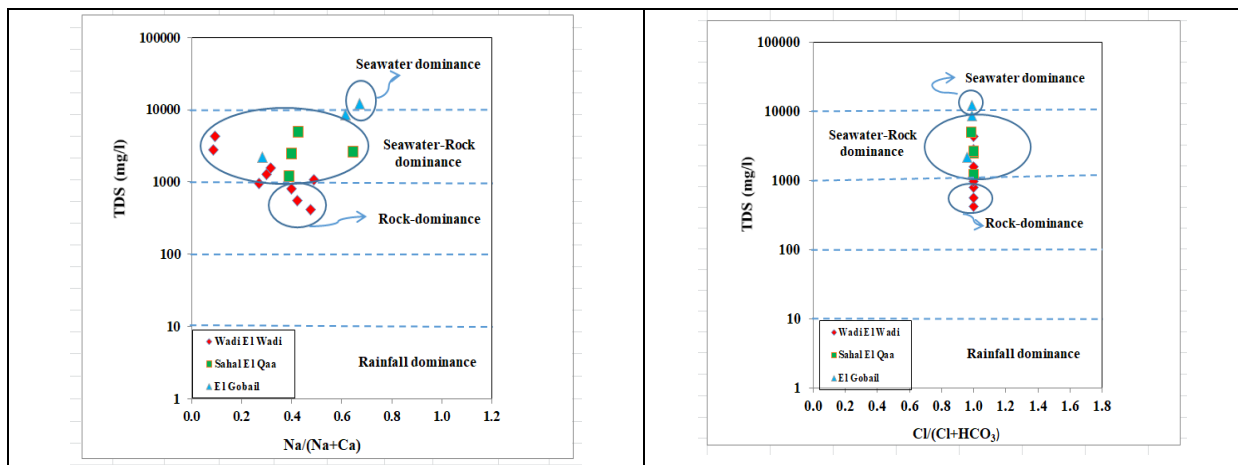

Fig (6): Gibbs plot for collected groundwater samples.

The ionic ratios are commonly accustomed to evaluating the salinization sources and origin of groundwater in coastal aquifers [22]. Na/Cl ratio of the major ions is highly affected

by the interaction of freshwater and saltwater by oxidation reduction, ion exchange reactions. Though it can distinguish between fresh and saline water, where the values of this ratio

is close to unity indicate fresh and meteoric water while less than unity (0.84) indicates mixing with seawater [23]. According to the calculating values of the ion ratio of the groundwater samples in Table.2, about 56% of the groundwater samples have Na/Cl ratio close to unity (>0.90) indicate fresh to brackish water, while the rest of the samples have Na/Cl ratio less than 0.84 indicating mixed saline water character. Study of Ca/Mg ratio in groundwater supports the dissolution of calcite/dolomite minerals present in the aquifer. If Ca/Mg =1, dissolution of dolomite may occur, whereas a higher ratio is indicative of calcite dissolution [24]. Higher Ca/Mg ratio>1 in about 68 % of the samples may indicate calcite dissolution and weathering of silicate minerals which contribute calcium and magnesium ions to the groundwater. The ionic relationship between Ca and SO_4 indicates gypsum or anhydrite dissolution. About 56% of the samples have Ca/SO_4<1 indicating the dominance of SO_4 over Ca due to the dissolution of gypsum, while the rest of

samples (44%) have Ca/SO_4>1 indicating the deficiency of SO_4 ions with respect to Ca could be as a result of sulfate reduction and increase of calcium source. The impact of seawater encroachment in groundwater of coastal aquifers can be traced through Mg/Cl where the 50% of the samples show the dominance of Cl over Mg (low ratio < 0.2) enhancing terrestrial source, while the other samples have marine source.

Simpson′s ratio (Cl/ (HCO$_3$+CO$_3$) is important as evident for seawater intrusion into freshwater aquifer [25] the hydrochemical data in Table.2 showed that the collected groundwater samples in El Tur area have Cl/ (HCO$_3$+CO$_3$) ratio ranged between (3.27- 46.68) in Wadi El Wadi, (4.2- 41.48) in Sahal El Qaa and (17.23- 117.1) in El Gobail area. According to Simpson classification [26], the effect of seawater encroachment could be classified into six classes using Cl/HCO$_3$+CO$_3$ ratio.

Table (2): Hydrochemical coefficients and seawater fraction results of groundwater samples.

	Well No	Na/ Cl	Ca/Mg	Ca/SO4	Mg/Cl	Cl/ (HCO3+CO3)	Cl-Na/Mg	f_{sea} %
Wadi El Wadi	1	0.52	1.82	1.89	0.27	11.21	1.78	0.018
	2	0.97	0.80	0.55	0.12	40.94	0.28	0.083
	3	0.90	0.88	0.80	0.09	46.68	1.11	0.065
	4	0.65	6.71	5.35	0.09	3.27	3.99	0.007
	5	0.90	14.60	2.83	0.04	3.68	2.52	0.010
	6	0.72	5.06	2.97	0.10	3.89	2.72	0.010
	7	0.96	0.99	0.70	0.36	4.86	0.11	0.013
	8	0.94	0.83	0.63	0.48	4.9	0.12	0.014
	9	0.94	1.07	0.59	0.41	7.00	0.14	0.021
Sahal El Qaa	10	0.98	4.30	1.16	0.14	4.2	0.11	0.015
	11	0.75	3.95	1.49	0.13	11.67	2.00	0.043
	12	0.95	2.46	0.71	0.22	10.5	0.22	0.032
	13	0.66	0.96	0.71	0.50	41.48	0.68	0.084
El Gobail	14	0.63	2.05	1.67	0.19	88.71	1.88	0.166
	15	0.81	2.09	0.86	0.19	117.10	0.99	0.201
	16	0.99	3.29	0.72	0.12	17.23	0.05	0.034
Red Sea		0.84	0.21		0.19:0.30			

Two samples in El Gobail are severely contaminated by seawater, in Wadi El Wadi two samples are moderately contaminated (samples no. 1, 9) and two samples are severely contaminated (samples no.2, 3). Sahal El Qaa samples are classed as highly contaminated in one sample (samples no. 13) was severely contaminated. In Areas with seawater intrudes a fresh coastal aquifer, reverse ion exchange between Na$^+$ in groundwater with Ca^{2+} or Mg^{2+} in the aquifer matrix and is marked by (Ca+Mg) > (HCO$_3$+SO$_4$) ratio as in Fig.7a. where all the samples are

clustered around 1:1 line support the dissolution process of calcite/dolomite/gypsum and have (Ca+Mg) in the same weight (HCO$_3$+SO$_4$) except 4 samples affected by reverse ion exchange reaction. Also, the hydrogeochemical characteristics of groundwater are supported by Chadha's plot (Fig.7b) it gives little evidence for groundwater salinization conditions from seawater where Na-Cl are slightly exceeding Ca and Mg ions in the groundwater of the quaternary aquifer in El Tur area.
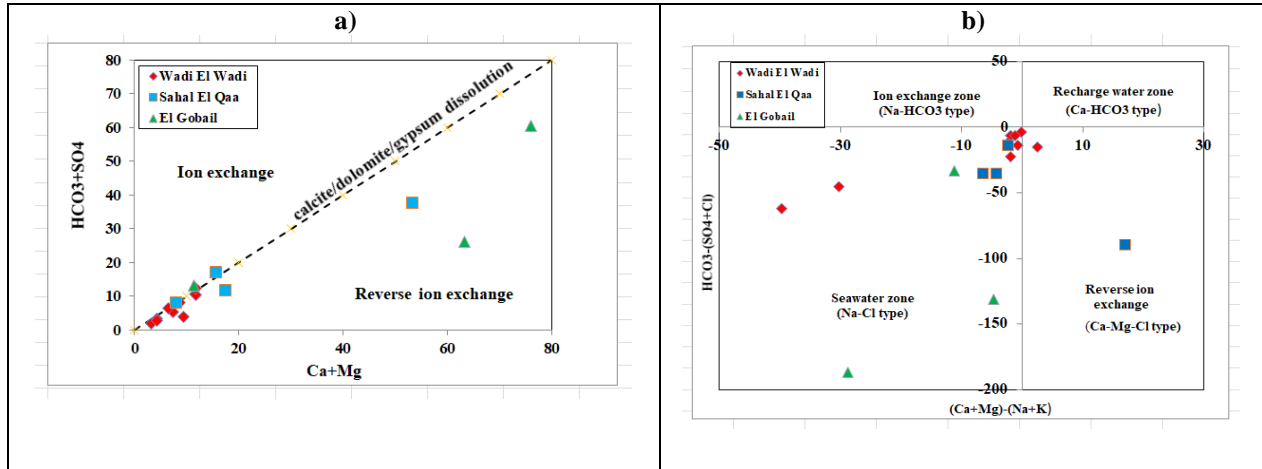
Fig (7): Relationships of a) (Ca+Mg) vs. (HCO$_3$+SO$_4$) b) Chadha's plot (Ca+Mg)-(Na+K) vs. HCO$_3$- (SO$_4$+Cl)

2.2 Seawater Mixing Index (SWMI)

Statistical methods for chemical data were employed in the coastal area to understand how geochemical processes affect groundwater quality. For quantitative estimation of the relative degree of seawater mixing with groundwater, a parameter called Seawater Mixing Index (SWMI) is proposed based on the concentrations of four major ions (Na$^+$, Cl$^-$, Mg^{2+} and SO$_4^{2-}$) as follows:

$$SWMI = a\frac{C_{Na}}{T_{Na}} + b\frac{C_{Mg}}{T_{Mg}} + c\frac{C_{SO4}}{T_{SO4}} + d\frac{C_{Cl}}{T_{Cl}} \qquad (2)$$

The constant factors a, b, c and d denote the relative proportions of Na$^+$, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ in seawater, respectively[27]. T represents the calculated regional threshold values of the selected ions, which may be estimated from the cumulative probability curves for every ion in a specific site. C is the measured ion concentration in mg/l. SWMI calculations of the groundwater samples divide the samples into two groups as shown in (Fig.8); Group I include most of Wadi El Wadi samples and two samples from Sahal El Qaa. While Group 2 has SWMI >1 indicate mixing with seawater represented by El Gobail samples, while the four other samples from Sahal El Qaa and Wadi El Wadi have relatively high EC and high SWMI index values reflecting the salinization problem at these locations could be related to other process.
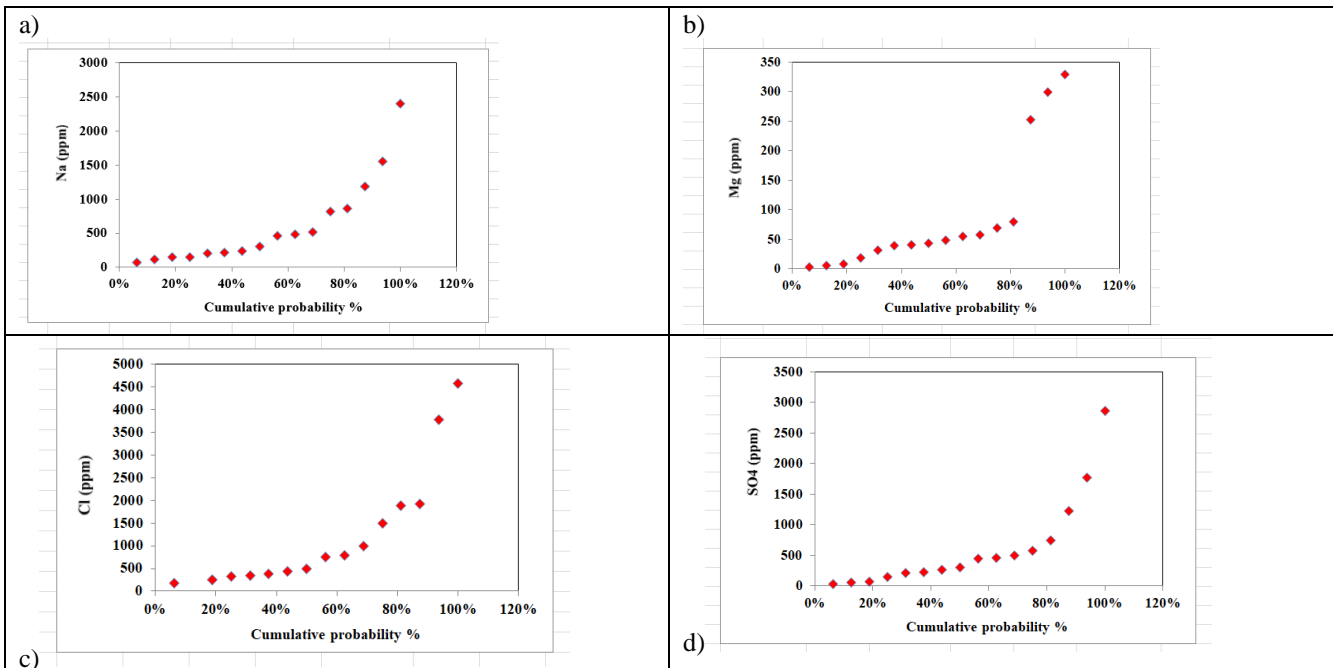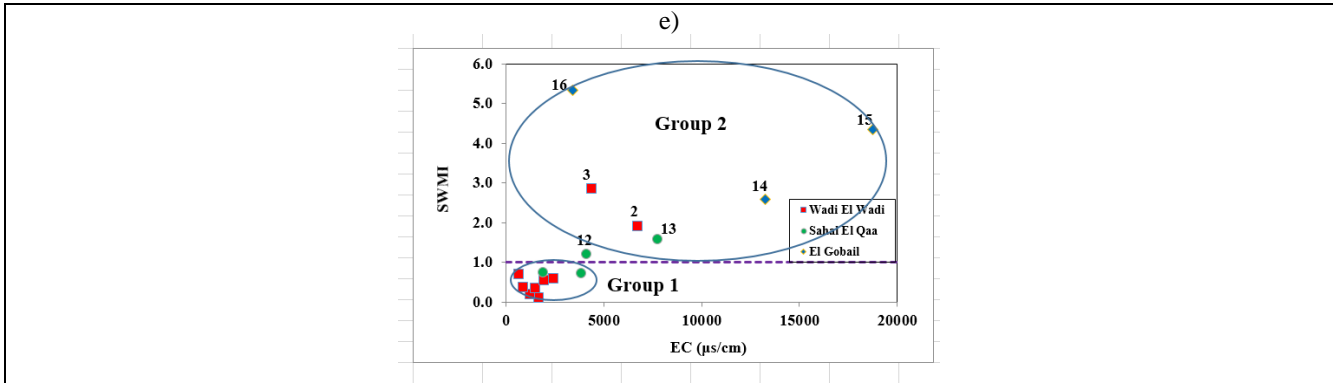
Fig (8): Cumulative probability curves for the distribution of a) Na^+, b) Mg^{2+}, c) Cl^- and d) SO_4^{2-} in groundwater of Quaternary aquifer. e) Cross-plot of SWMI vs. EC (μScm^{-1}) of the studied groundwater samples.
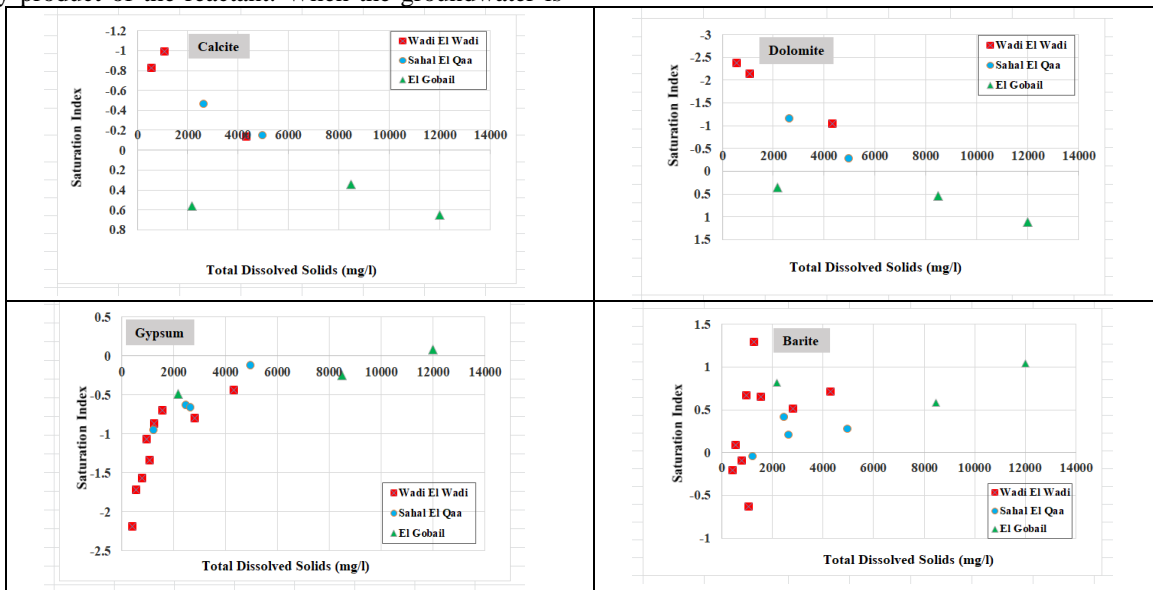
2.4 Saturation indices:

The saturation index is an important geochemical parameter within many fields of hydrogeology and geochemistry, often useful for identifying the behavior of some common minerals in the groundwater system as continual dissolution, saturation, or precipitation (oversaturation) states [28]. During the present study saturation indices (SIs) was calculated by the geochemical model PHREEQC [29] regarding the subsequent equation [30]:

$$SI = \log (IAP/ k_{sp}) \dots\dots\dots\dots\dots\dots (4)$$

Where IAP is the relevant ion activity product, which can be calculated by multiplying the ion activity coefficient γ_i and the composition concentration m_i, and k_{sp} is the solubility product of the reactant. When the groundwater is saturated with certain mineral, SI will be equal zero; while positive values of SI represent oversaturation, and negative values show undersaturation of the relevant mineral [31; 32]. The output calculation of the saturation indices by PHREEQC program are graphically illustrated in Fig. 9. El Gobail groundwater samples are supersaturated in carbonate minerals such as Calcite ($CaCO_3$), Dolomite Ca $Mg(CO_3)_2$, Aragonite $CaCO_3$ and sulphate minerals like Barite $BaSO_4$ and Gypsum $CaSO_4.2H_2O$. These results suggested that carbonate and sulphate minerals may have an impact on the chemical composition of groundwater in El Gobail area. On the other hand, Wadi El Wadi and Sahal El Qaa samples are undersaturation with respect to Anhydrite ($CaSO_4$), Calcite ($CaCO_3$), Dolomite $CaMg(CO_3)_2$ and Gypsum ($CaSO_4.2H_2O$).
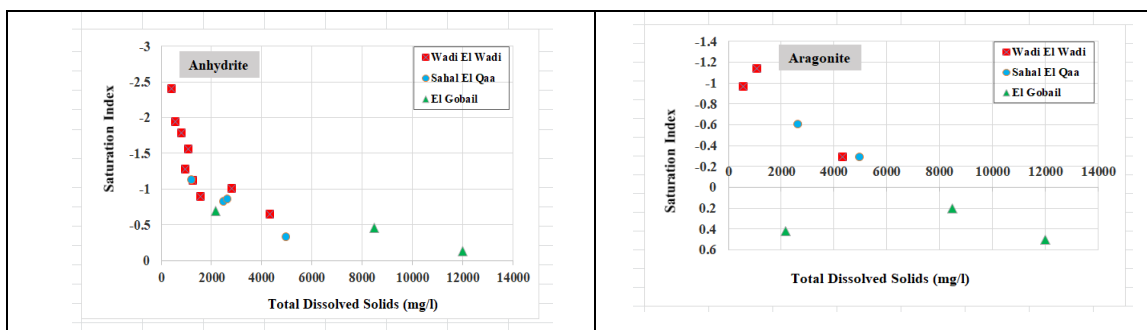
Fig (9): Plots of saturation Indices computed with PHREEQC against Total Dissolved Solids in (mg/l).

4. Inverse Geochemical Modeling

To further evaluate possible salinization problem along flow paths, inverse mole-balance models were developed using PHREEQC program. This program can be used to calculate the mass transfer amount of dissolved or precipitated minerals and gases between two phases as initial and final points along groundwater flow path. Each mole transfer of minerals and gases responsible for chemical properties changes of the two water samples was calculated, according to the mass balance method and chemical reactions occurring along the groundwater flow path. Three general processes contribute to the generations of solutes in groundwater: evaporation, carbonate dissolution/ precipitation and silicate weathering [33]. Two modeling stages were assumed; the first model was the first evolution stage of rainwater (recharge water) having TDS value of 214 mg/l to the lowest salinity water (Final water) (sample 4)

having TDS value of 342 mg/l. The second model used for tracking higher stage of evolution from rainwater to the highest salinity water (Final water) (sample15) which has TDS value of 12000 mg/l at El Gobail area. These models include some minerals as calcite, dolomite, aragonite, barite and gypsum. Ten and Twenty solutions were returned from model1 and model 2 respectively. To limits the solutions output, selection was based on the solutions that have the smallest sum of residuals were chosen as illustrated in Table.3. The selected results of the first model forced rainwater to interact with sulphate minerals (Anhydrite $CaSO_4$ or gypsum $CaSO_4.2H_2O$) or with dolomite $CaMg(CO_3)_2$ to provide sample (4) with the lowest salinity at the El Qabaliyat ridge. The second model results include the dissolution of Anhydrite $CaSO_4$ and precipitation of gypsum $CaSO_4.2H_2O$ that interact with rainwater to produce sample (15) of the highest salinity.

Table (3): Results of inverse hydrogeochemical modeling using PHREEQC.

Model 1		Model 2	
Initial water	**Final water**	**Initial water**	**Final water**
Rainwater	Sample (4)	Rainwater	Sample (15)
Phase	**Amount (mole/l)**	**Phase**	**Amount (mole/l)**
Anhydrite	**2.403E-08**	**Anhydrite**	**-8.172E-03**
H2(g)	**5.551E+01**	**Gypsum**	**8.172E-03**
O2(g)	**2.775E+01**	**H2(g)**	**-2.570E+02**
H2S(g)	**-2.403E-08**	**O2(g)**	**-1.285E+02**
		Witherite	**3.988E-02**
Dolomite	**1.202E-08**	**Barite**	**-3.988E-02**
CO2(g)	**-2.403E-08**	**CO2(g)**	**-3.988E-02**
H2(g)	**5.551E+01**	**H2(g)**	**-2.570E+02**
O2(g)	**2.775E+01**	**O2(g)**	**-1.284E+02**
		H2S(g)	**3.988E-02**
Gypsum	**2.403E-08**		
H2(g)	**5.551E+01**	**Anhydrite**	**1.285E+02**
O2(g)	**2.775E+01**	**Gypsum**	**-1.285E+02**
H2S(g)	**-2.403E-08**		

Note: Positive values of phase mole transfers indicate dissolution of minerals and negative values represent precipitation of minerals.

Calculation of Seawater fraction

The increase in total dissolved solids or electrical conductivity (EC) could be a common simple indicator of salinity increase [34; 35] without defining the source of such increase whither mixing or dissolution. The chloride concentration is a good indicator to calculate sea water fraction in groundwater. The fraction of seawater (f_{sea}) in a water sample can be approximated from the concentrations of Cl-(m_{Cl}) in meq/l as expressed in Equation (4) [36]:

$$f_{sea} = m_{Cl\ (sample)} - m_{Cl\ (freshwater)} / m_{Cl\ (seawater)} - m_{Cl\ (freshwater)} \quad (3)$$

Calculation of seawater fraction in groundwater samples in Table.2 reveals that f_{sea} of all the samples range from 1 to 20 %. Sea water fractions f_{sea} in Wadi El Wadi have the lowest values of sea water fractions ranging from (1 to 8.3%) with the average value of 3%, in Sahal El Qaa, f_{sea} values have relatively the same as the previous area ranging from (1.5 to 8.4%) with the average value of 4.6%. For El Gobail area, f_{sea} have higher values range from (3.4 - 20 %) with an average value of 12.7% confirming that El-Gobail are more affected by seawater than the other areas. This means that mixing with sea water is not significant in groundwater Wadi El Wadi and Sahal El Qaa areas, while it is slightly appearing in El Gobail area.

5. Trace Elements Distribution

Trace elements in subsurface environments may come from natural from rock weathering or anthropogenic sources as fertilizers, industrial effluents and leakage from service pipes. Twelve trace elements concentrations were detected include: Al, Cd, Co, Cr, Cu, B, Mo, Ni, Pb, Sr, V, and Zn as shown in Table (4).

Table (4): Trace elements concentrations (mg/l) in the study area.

	Well	Al	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sr	V	Zn
	No	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Wadi El Wadi	1	<0.01	<0.0004	0.0102	<0.0006	<0.001	<0.01	<0.006	<0.02	<0.002	0.0194	<0.002	<0.008	2.516	<0.01	<0.0006
	2	<0.01	<0.0004	0.2273	<0.0006	<0.001	<0.01	<0.006	<0.02	<0.002	0.0085	<0.002	<0.008	24.67	<0.01	.0052
	3	<0.01	<0.0004	0.2305	<0.0006	<0.001	.0362	0.026	.1568	<0.002	0.0183	0.0044	<0.008	13.17	.2461	<0.0006
	4	<0.01	<0.0004	0.0885	<0.0006	<0.001	<0.01	<0.006	<0.02	<0.002	0.0359	<0.002	0.0105	1.05	<0.01	.0307
	5	<0.01	<0.0004	0.0568	<0.0006	<0.001	.0511	0.0405	<0.02	<0.002	0.0139	<0.002	0.0098	2.451	<0.01	.0149
	6	<0.01	<0.0004	0.0972	<0.0006	<0.001	<0.01	<0.006	0.043	<0.002	0.0329	<0.002	<0.008	1.655	<0.01	<0.0006
	7	<0.01	<0.0004	0.174	<0.0006	<0.001	0.062	0.0147	<0.02	<0.002	0.0199	<0.002	<0.008	3.235	.4381	<0.0006
	8	<0.01	<0.0004	0.1592	<0.0006	<0.001	0.115	<0.006	<0.02	<0.002	0.0202	<0.002	<0.008	4.441	<0.01	<0.0006
	9	<0.01	<0.0004	0.1261	<0.0006	<0.001	0.0421	<0.006	<0.02	<0.002	0.0166	<0.002	0.0133	5.665	<0.01	.0862
Sahal El Qaa	10	.2122	<0.0004	0.0353	<0.0006	<0.001	<0.01	<0.006	<0.02	<0.002	0.0192	0.0036	<0.008	2.264	<0.01	<0.0006
	11	0.1997	<0.0004	0.0898	.0008	.0020	<0.01	0.0458	12.65	.1968	0.0028	0.0033	<0.008	6.313	.1302	.0072
	12	<0.01	0.1915	0.036	<0.0006	<0.001	0.051	0.1067	<0.02	.0043	0.0208	0.0064	<0.008	4.23	.0346	<0.0006
	13	.2667	2.610	0.0341	.0013	<0.001	0.072	0.0288	0.156	.0162	0.0195	0.0031	<0.008	13.31	.4705	<0.0006
El Gobail	14	<0.01	1.795	0.1127	<0.0006	<0.001	<0.01	0.0384	0.038	<0.002	0.0147	0.0052	<0.008	17.79	<0.01	.0033
	15	<0.01	2.281	0.1827	.0015	<0.001	<0.01	<0.006	<0.02	<0.002	0.0135	<0.002	<0.008	19.77	<0.01	<0.0006
	16	<0.01	<0.0004	0.1719	<0.0006	<0.001	0.093	0.0205	<0.02	<0.002	0.0038	<0.002	<0.008	7.14	<0.01	<0.0006
WHO (2011)		0.2	1	2	0.003	<0.05	0.05	1	0.3	<0.1		0.01	0.01	0.11		3

According to the international drinking water guidelines WHO (2011), most values of trace elements are within the permissible limits for drinking water purpose (except some samples. Aluminium concentration exceeding the limits in samples (No.s 10,11,13). Boron concentration exceeding the limits in samples (No.s 13,14,15) and seawater value (0.004 mg/l) [37]. could reflect seawater contamination, and Chromium concentration is slightly increase in samples (No.7,13,16). One samples only exceeding the limit of iron concentraion (No.s 11) while mostly all samples have the same values of the Pb pemissible limits. High concentrations of Sr in all samples exceeding the permissible limits and sea water value may be attributed to disolution of calcium rocks enriched with Sr and mixning with sea water (0.008 mg/l) [37].Whereas the other trace elements are below the WHO theatening limits. The obovious increse in B and Sr ions in samples (No.s 13,14,15) could point to sea water intrusion.

6. Environmental Isotope studies

6.1 Isotopic composition of groundwater samples

Stable isotopes composition (δ^{18}O and δD) of groundwater samples were measured to provide basic information on the origin and sources of recharge for the Quaternary aquifer in the studied area. The stable isotope composition of groundwater samples with the d-excess values is compiled in (Table.1). Wadi El Wadi groundwater isotopic composition values of δ^{18}O range between (-5.77 and -3.88 ‰) with an average value of -4.65‰ and δD values fall between (-

36.55and -19.62 ‰) with an average value of -25.6 ‰ and d-excess values range from (1.61 to 14.71‰). While Sahal El Qaa isotopic composition range from (-6.17 to -4.49 ‰) with an average value of -5.47 ‰ for $\delta^{18}O$ and (-43.93 to -34.31 ‰) with an average value of -39.91‰ for δD as illustrated in (Fig.10a). The relationship of $\delta^{18}O$ vs. δD of the groundwater samples with respect to the Global Meteoric Water Line (GMWL) ($\delta D= 8\delta^{18}O+10$) [38] and the Mediterranean Meteoric Water Line (MMWL) ($\delta D= 8\delta^{18}O+22$) was depicted as shown in (Fig.10). The

distribution of isotopic data fit a linear relationship expressed by the equation ($\delta D= 9.28\ \delta^{18}O+17.8$) with a slope 9.28 and intercept of 17.8 that is close to global meteoric water line and the weighted mean value of Saint Catherine precipitation ($\delta^{18}O = -6.48$ ‰, $\delta D = -39.6$ ‰ [19]. This depletion in the isotopic values of the groundwater samples reflects a direct replenishment of rainwater from the fractures of the mountainous area in the east without significant evaporation.
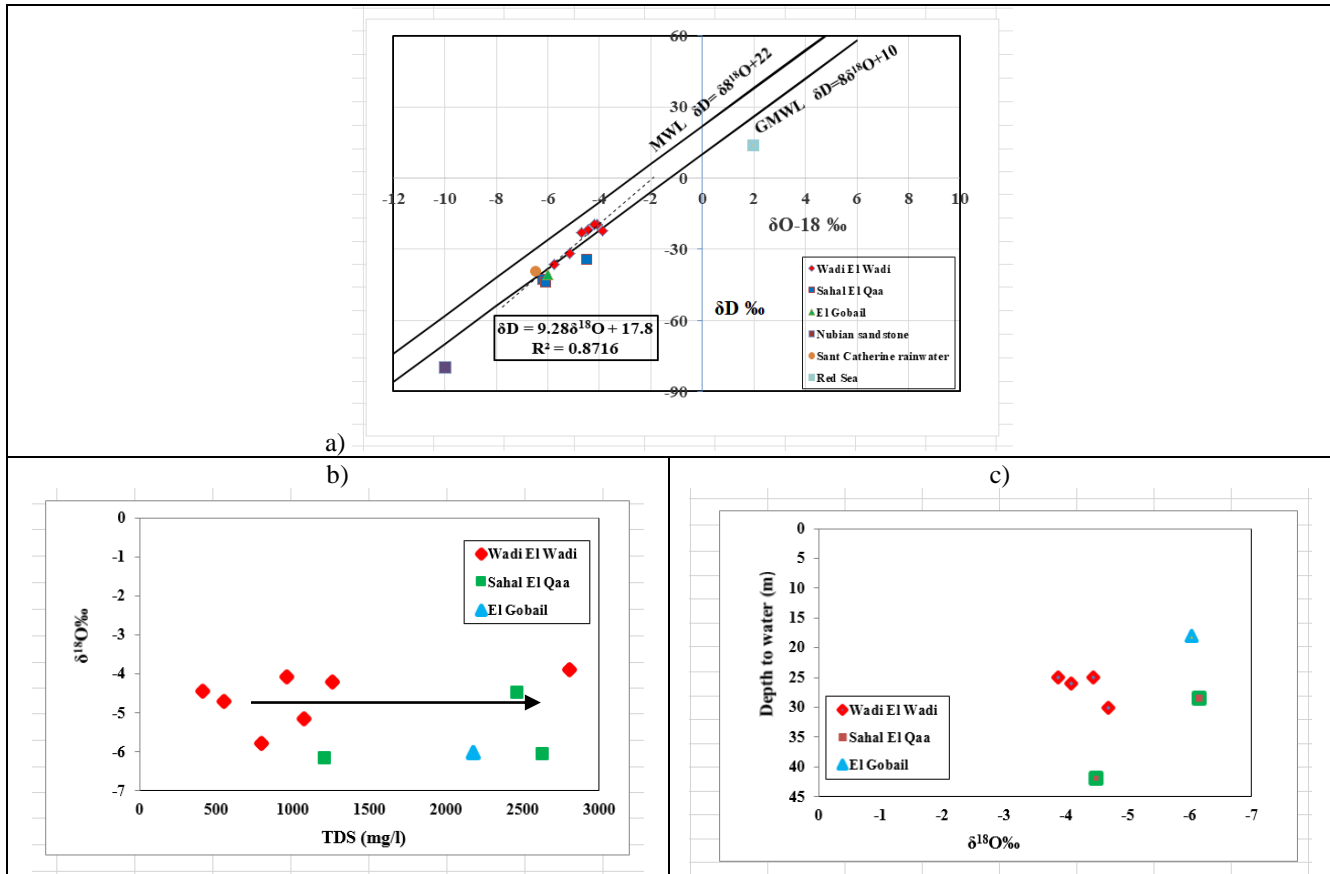

Fig (10): a) $\delta^{18}O$ vs. δD relationship in permil (‰).   b) TDS in (mg/l) vs. $\delta^{18}O$ in permil (‰) indicates dissolution effect.   c) $\delta^{18}O$ in permil (‰) vs. Depth to water in (m).

The slight variation of the $\delta^{18}O$ isotopic composition with respect to TDS in (mg/l) (Fig.10b) reveal that dissolution process is the main factor for increasing salinity in most samples. However, a minor contribution from sea water could be mixed with groundwater samples which close to the Gulf of Suez at El Gobail. The groundwater depth does not correlate to the isotopic variations of $\delta18O$ as shown in (Fig.10c). Calculating of mixing ratio of the two end members (Sant Catherine rainwater , upward of more depleted water from Nubian sandstone aquifer through faulting) supported $\delta^{18}O$ values revealed that contribution of precipitation was in Wadi El Wadi >Sahal El Qaa > El

Gobail area by values reaches of 1.073> 0.9666>0.698% respectively.

7. Conclusion

The Quaternary aquifer represents the most water resource in El Tur area, southwest Sinai. An effort was done to study the groundwater quality of the aquifer in addition to the salinization problem in this area using an integrated technique including hydrochemical, isotopic investigations in addition to applying inverse geochemical modeling using PHREEQC software. Hydrochemical data of 16 groundwater samples reveal that, Salinity in groundwater is greatly variable; it varies from (414-4307 mg/l) at Wadi El Wadi, (1208-4973 mg/l) at Sahal El Qaa and (2176-12000 mg/l) at

El Gobail area with slightly alkaline character and main water type (Na-Cl) indicating high stage of groundwater evolution in the Quaternary aquifer in El Tur area. Saturation Index (SI) indicates the dissolution or precipitation level of some minerals dissolved in the collected groundwater. The groundwater is saturated with respect to Gypsum, Anhydrite as a result of the dissolution of evaporites, Barite, and Goethite minerals present in the host rocks. Halite mineral is undersaturation with a continual dissolution in the groundwater. Inverse geochemical modeling for salinization tracking implies that, the reactions responsible for salinization problem in El Tur area fall into two categories: (1) dissolution of carbonate minerals and (2) precipitation of sulphate minerals (Gypsum, Barite). The stable isotopes of $\delta^{18}O$ and δD suggest that the recharge source is mainly from the direct replenishment of rain to the quaternary aquifer in the studied area.

Author contributions:
[1]**Rasha Abd Allah Hussien:** Developing the idea of the research paper, analyze Environmental stable Isotopes. Analyzed and interpreted different satellite images and digital elevation model, prepared the maps through the application of ArcGIS and run geochemical model PHREEQC.
[2] **Raafat Ahmed Rayan:** Collecting the geology, geomorphology and hydrology of the study area and try to interpret the hydrochemical and isotopic data.
[3] **Abdel Hameed Mostafa El Aassar:** Collecting samples from the study area, carrying out the chemical analyses in addition to the interpretation of hydrochemical data.
Availability of data and materials: All data generated or analyzed during this study are included in this manuscript.

Compliance with ethical standards
Conflict of interest: The author declares there are no competing interests.

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