



*Journal*

## HYDROCHEMICAL ANALYSIS OF SALINIZATION PROCESSES IN THE QUATERNARY AQUIFER IN THE EASTERN NILE DELTA, EGYPT

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### ABSTRACT

The study of salinization of groundwater in the Quaternary aquifer of the eastern Nile Delta is highly complex due to the arid climate, the presence of evaporates and proximity to the sea. The Quaternary aquifer of the eastern Nile Delta is affected by salinization processes undoubtedly associated with intense groundwater exploitation for agriculture supply. The present research is an attempt to investigate the presence of the saltwater intrusion in this aquifer, using hydrochemical analyses and the behavior of certain minor ions that could help in the characterization process. The salinization has been characterized by jointly studying the content of a series of ionic relationships and various minor ions (B and Br). Boron content increases in more saline areas, since it is associated with the presence of evaporitic and/or marine influences. Bromine analysis enabled the identification of the principal processes that determine the salinity of the water along the coastal zone. The brackish groundwaters that are related to old raised beaches have a low Cl/Br ratio. Areas affected by marine intrusion had Cl/Br ratios similar to seawater and higher than in other areas along the coastal zone.

In the eastern Nile Delta sector, groundwater salinization does not appear to be attributable to the intrusion of seawater, but there are dissolution processes of marine deposits.

**Keywords:** Arid region; Salinization; Hydrogeochemical processes; Quaternary; Eastern Nile Delta; Egypt.

## INTRODUCTION

The groundwater reservoirs in the Nile Delta are the important source of water instead of direct irrigation from the River Nile, where greater demands for water with growing population in parallel with cultivation and industrial activities are increasingly needed. The studied area lies in the east of the Nile Delta and extends between longitudes 31° 30' 00" and 32° 6' 00" east and latitudes 30° 30' and 31° 31' 48" north. The area is bounded from the west by the River Nile (Damietta branch), Suez canal from the east, and Mediterranean Sea and Lake Manzala from the North and Ismailia canal from the south. The area has two main canals (Baher Fakous and Baher Mwas) and two drains (Baher Baker and Baher Hadous) as shown in (Fig. 1). The climate is marked by warm winters, hot summer, moderate humidity and wind of intermediate speed. A lot of studies are made on this area and among the most important of them are: "Shata and El-Fayoumy (1969), Farid, M. S. (1980), El-Dairy, M. D. (1980), Saluma, M. (1983), Nada, A. A (1984), RIGW/IWACO (1988) and Salem, W. M. (1996)".

The Quaternary aquifer in the study area is the main source of the groundwater. Excessive pumping from the aquifer causes problems such as water salinization. Most of wells became unemployed, especially in the northern part of the study area. Furthermore, farmers use drains water as standby for irrigation, hence affects badly on the groundwater quality, especially shallow groundwater. Therefore, the groundwater quality and the salinization processes of the Quaternary aquifer in the study area need to be reevaluated.

## MATERIALS AND METHODS

41 groundwater samples were collected from the study area and the measuring of chemical composition of major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Br<sup>-</sup>) were made by Ion Chromatograph, (HCO<sub>3</sub><sup>-</sup>) ion was measured immediately by titration method and (B<sup>-</sup>) by UV spectro-photometer. The sampling points were chosen on the basis of topography and geology. Sampling techniques involved Pumping the groundwater for long time enough to ensure that representative aquifer's water is being attained.

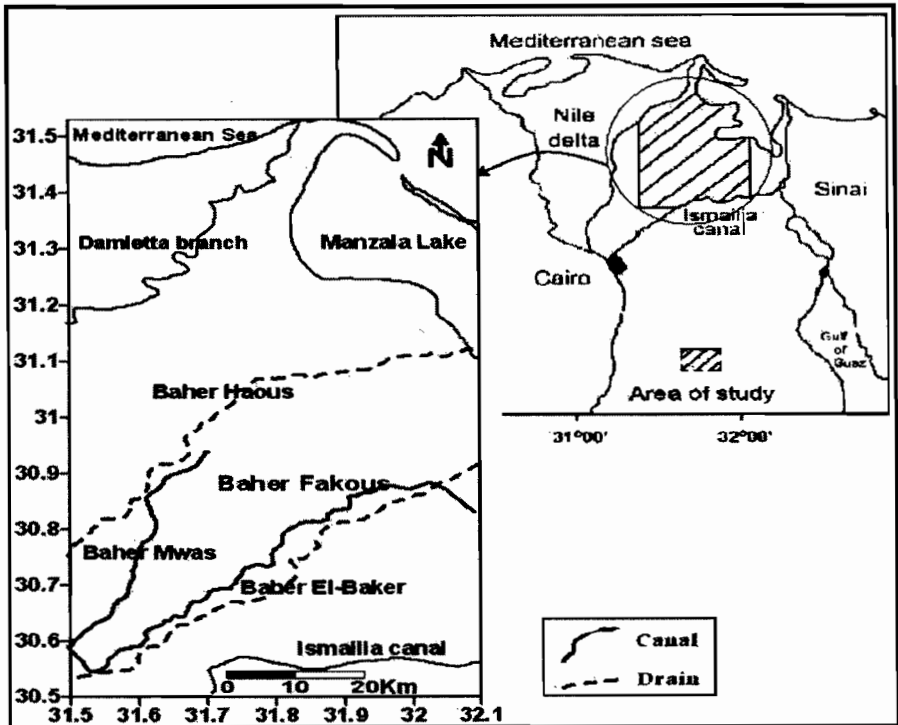
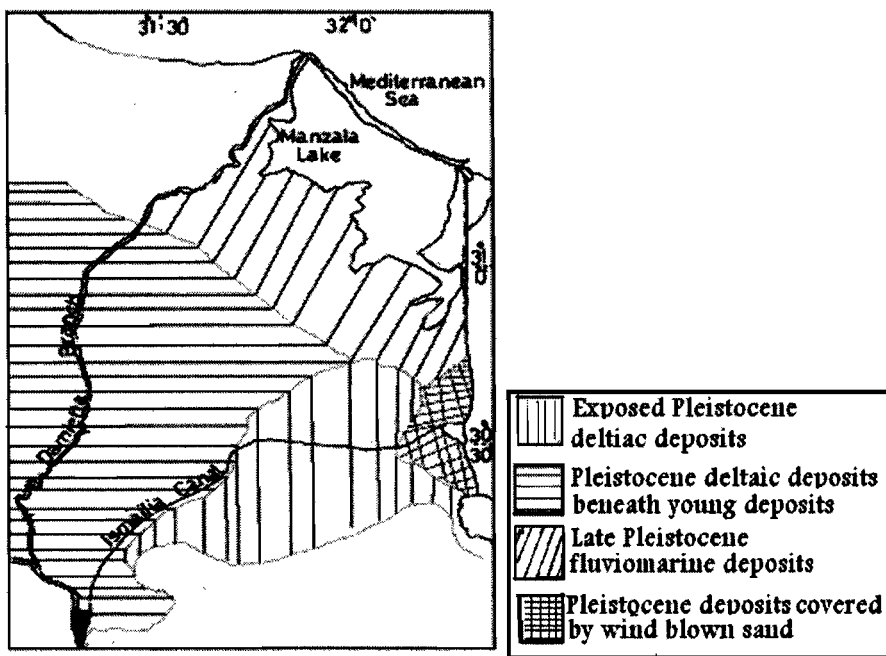


Fig. (1) Location map of the study area.

### 3. Geological aspect

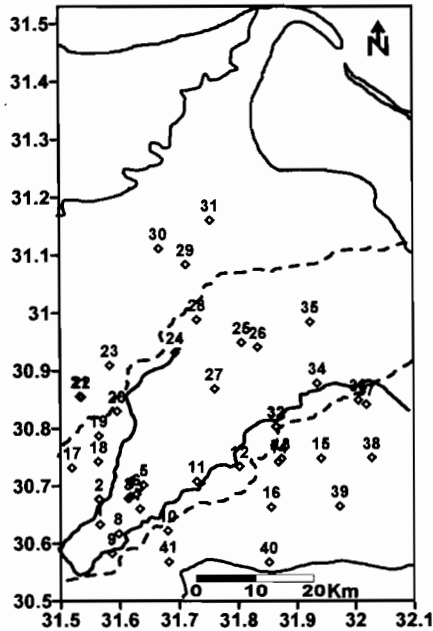
The eastern part of the Nile Delta slopes regionally in the northward direction. It is characterized by low relief and is bounded on the southern side by a moderately elevated plateau, and on the northern side by a landscape with flat plains of the Delta (Bayoumy, 1971). The Damietta branch marks the western boundary whereas the eastern side is bounded by the Bitter Lake and Suez canal which runs through the Ismailia Master plain (El-Shazly, 1975). The region east of Nile Delta is essentially, occupied by Tertiary to Quaternary rocks with Mid-Tertiary basaltic flow. This succession has a maximum thickness of 500 m. It is composed - from south to north - of complex marly Limestone and shales grading into a typical shallow marine and continental environment and Deltaic deposits (Fayoumy, 1968). Farid, et al. (1988), also investigated that the eastern Delta aquifer belongs essentially to Quaternary which is Pleistocene aquifer. Its formation is fluvio-marine deposits (Late Pleistocene) and Deltaic deposits (Early Pleistocene) (Fig. 2).



**Fig. (2) Compiled geological map of the Eastern Nile Delta**

## RESULTS AND DISCUSSION

The major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) are naturally highly variable in the groundwater due to local geological, climatic and geographical conditions. The minor ions (B and Br) can enable the identification of the principal processes that determine the salinity of the water along the coastal zone. The chemical analysis of the collected groundwater samples, including (pH, EC, TDS), major cations and major anions were carried out in the Central Laboratory for Environmental Isotope Hydrology, National Center for Nuclear Safety and Radiation Control using standard methods for the examination of water and wastewater, (1996). The results of these analyses are indicated in Table (3). The locations of the groundwater samples are shown in (Fig. 3).



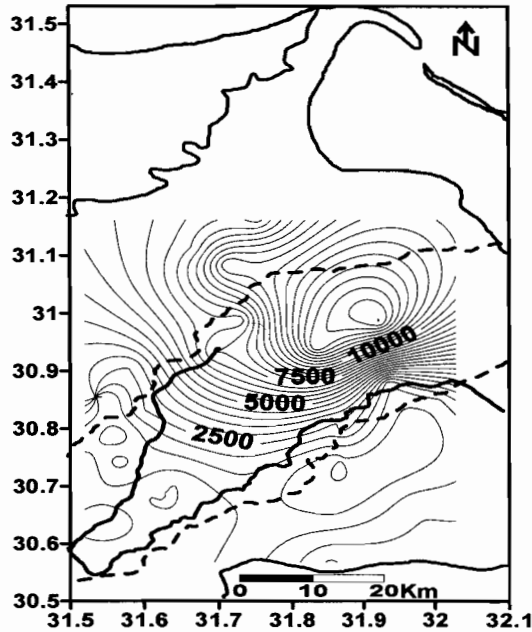
**Fig. (3):** Location map of groundwater samples.

## 1 Hydrochemical characteristics of the studied groundwater samples

### 1.1 Total Dissolved Solid (TDS)

The total dissolved solid values of the studied groundwater samples range from 391-14,552 mg/L (Fig. 4). This wide range of salinity reflects the presence of different possible sources of salinity that exist in the studied area and it may be due to:

- a. Leaching processes which accompany the intensive agriculture activities through irrigation,
- b. Dissolution processes of earth rocks and Marine deposits,
- c. Upconing of saline water from deep aquifer beneath the fresh one due to excessive pumping, and/or
- d. Salt water intrusion.



**Fig. (4) Iso-salinity (TDS) contour map in mg/L for ground water samples**

TDS values of the studied samples were classified according to Chebotarev, (1955) into three main categories:

1. 54% of the groundwater samples → Fresh water (TDS up to 1500 mg/L).
2. 24% → Brackish water (TDS (1500-4000) mg/L).
3. 22% → Saline water (TDS > 4000 mg/L).

Iso-Salinity contour map of the groundwater samples show three groups (Fig. 5):

\* The first group: This group is present in the southern part near the Dameitta branch and Ismailia canal and represents the fresh water in the study which has salinity ranges from 391 to 1,440 mg/L with good natural drainage conditions. This area is characterized by groundwater table of 1 to 2 m below land surface and the salinity of the root zone is at an acceptable level for salt sensitive crops.

\* The second group: This group is present in the middle part with salinity ranges from 1,616 to 3,559 mg/L. The increase of salinity could be attributed to dissolution and leaching of soil during irrigation processes. The average of groundwater table is from 0.5 to 1 m, and this group is acceptable for most salt sensitive crops.

\* The third group: This group is present in the northern part towards Manzala Lake of the study area and the depth of groundwater is from 0.0 to 0.5 m. It is found that samples have salinities ranges from 6,384 to 14,552 mg/L. The high salinity could be due to salt intrusion.

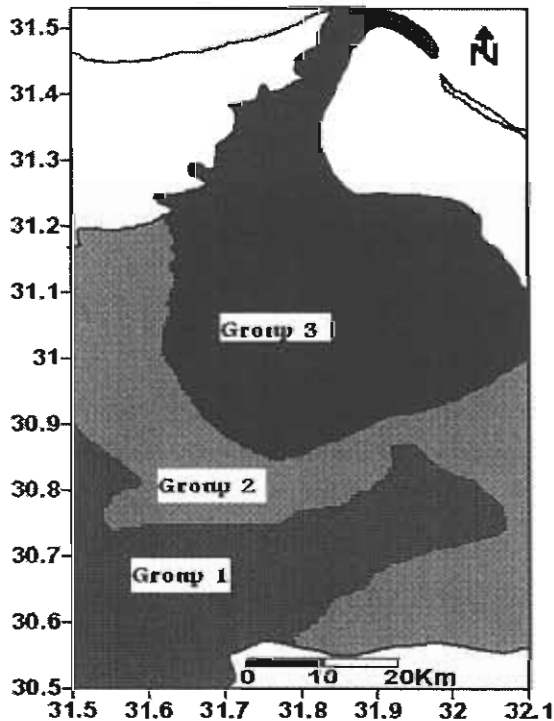


Fig. (5) Classification of the study area into three groups (1, 2 and 3)

**Table (3) Chemical composition of groundwaters of the eastern Nile Delta**

Area	S.No	E.C µs/cm	TDS mg/L	Na <sup>+</sup> mg/L	K <sup>+</sup> mg/L	Ca <sup>2+</sup> mg/L	Mg <sup>2+</sup> mg/L	Cl mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	HCO <sub>3</sub> mg/L	B <sup>-</sup> mg/L	Br mg/L	Cl/Br
Group1	1	2340	1374	323	7	72	27	230	408	308	0.31	6.5	35.43
	2	1450	868	101	15	112	31	120	140	348	1.23	1.8	66.79
	3	590	391	69	7	32	10	44	35	195	1.06	0.8	52.70
	4	950	665	147	10	24	24	103	79	277	0.73	1.7	60.88
	5	678	485	75	9	36	17	69	17	263	0.61	1.2	57.89
	6	570	482	72	5	48	12	62	17	266	0.54	0.9	69.16
	7	830	502	79	5	50	16	72	58	221	0.63	1.4	51.63
	8	1250	719	177	4	33	14	147	104	240	0.89	2.5	58.69
	9	600	525	94	4	35	12	27	8	346	0.34	0.5	51.21
	10	1040	808	99	9	70	25	62	110	432	0.80	0.9	69.32
	11	1960	1391	260	8	102	37	217	362	405	1.71	2.8	77.56
	12	1520	1118	149	11	95	40	181	123	520	0.40	2.2	82.39
	13	1480	1034	147	7	90	36	195	86	473	0.00	1.9	102.63
	14	530	402	36	5	35	19	25	33	250	0.00	0.5	53.68
	15	830	619	138	7	27	11	58	84	296	0.00	0.7	82.23
	16	930	760	196	5	20	7	35	58	440	0.15	0.6	55.90
	17	1030	681	139	6	27	21	145	32	311	0.00	2.6	55.77
19	1070	660	196	2	6	3	160	26	266	0.00	2.5	64.09	
22	1320	830	238	4	9	5	169	57	349	0.00	2.5	67.42	
36	2200	1440	245	46	121	39	253	157	579	—	3.4	74.53	
38	1910	1218	274	8	46	19	220	135	516	—	3.3	66.79	
41	1400	923	108	18	121	19	98	188	371	—	1.4	70.30	
Group2	18	2590	1734	404	5	29	57	247	396	596	0.61	3.7	66.79
	20	4090	2419	655	12	36	61	644	409	603	0.55	8.4	76.65
	21	5620	3559	973	32	14	84	1093	58	1307	0.94	18.0	60.70
	23	5050	2559	797	7	27	40	1063	149	476	0.64	14.0	75.94
	32	3100	2164	368	114	83	54	361	165	1019	—	4.6	78.37
	33	5600	2998	615	22	163	100	911	86	1101	—	14.0	65.10
	34	2400	1621	406	3	28	11	146	234	793	—	2.6	56.31
	37	2900	1616	356	44	86	28	537	175	390	—	7.1	75.60
	39	3300	1927	517	6	51	17	508	249	579	—	5.4	94.16
	40	4660	2585	543	10	214	96	900	462	359	—	8.5	105.91
Group3	24	14850	7513	1996	44	433	325	3641	833	241	0.40	54.0	67.42
	25	22700	11619	2598	50	954	551	6368	908	190	0.77	88.0	72.37
	26	24800	13544	3225	71	926	662	7494	938	228	0.00	—	—
	27	12000	6384	1758	23	237	206	2893	792	476	0.92	40.0	72.32
	28	12060	6689	1071	21	734	392	3709	505	257	0.35	52.0	71.32
	29	19330	10532	2023	32	1057	608	6059	663	90	0.00	68.0	89.10
	30	13160	7090	1567	21	508	335	4104	433	122	1.42	48.0	85.50
	31	13520	6787	1210	36	684	471	3872	428	87	0.58	56.0	69.14
35	27100	14552	3598	33	951	519	7988	1193	270	—	120.0	66.56	
Seawater		55052	35233	10672	942	1534	1026	21371	2935	134	67.70	5.30	315.67
Fresh water		522	334	44	7	15	37	37	38	198	0.55	0.54	67.43



## 1.2 Major Ions Distribution

The minimum, maximum and mean concentration of ( $\text{Na}^+ + \text{K}^+$ ),  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  ions values of the groundwater samples are shown in Table (4). Iso-contour maps show the major ion distributions in the study area (Fig. 6). Consistence exists between distributed pattern of different ions and that of TDS. The increase of solute content in the samples of the second group relative to the first one is mainly due to the dissolution and leaching mineralization of rocks occurring in this area and extensive use of fertilizers. But the third group has concentrations that could be due to the effect of dissolution of marine deposits and evaporate salts or the seawater intrusion from Mediterranean Sea.

**Table (4) the minimum, maximum and mean concentration values of the major ions of the groundwater samples.**

GW group		( $\text{Na}^+ + \text{K}^+$ ) ppm	$\text{Mg}^{++}$ ppm	$\text{Ca}^{++}$ ppm	$\text{Cl}^-$ ppm	$\text{SO}_4^{--}$ ppm	$\text{HCO}_3^-$ ppm
Group 1	Min	40.9	2.92	5.98	25.23	8.4	195.05
	Max	329.8	40.19	120.84	253.41	361.9	578.72
	Mean	185.4	21.55	63.41	139.32	185.15	386.89
Group 2	Min	400.9	11.05	13.61	146.4	57.74	358.55
	Max	1004.3	96.44	214.45	1092.52	462.35	1306.86
	Mean	702.6	53.75	114.03	619.46	260.05	832.71
Group 3	Min	1070.6	206.08	236.92	2892.98	433.24	86.68
	Max	3598	661.7	1056.8	7987.57	1192.74	475.8
	Mean	2334.3	433.89	646.86	5440.28	812.99	281.24

## 1.3 Minor Ions Distribution

### a. Boron

Boron compounds are used in manufacture of glass, soaps and detergents and as flame retardants. The general population obtains the greatest amount of boron through food intake, as it is naturally found in many edible plants. Boron is found naturally in groundwater; but its presence in surface water is frequently consequence of a discharge of treated sewage effluent, in which it arises from use some detergents into surface water. Boron is found in very different geological environments, associated with the presence of volcanic rocks, geothermal processes and material deposited in very saline environmental (Leeman and Sisson, 1996). Because boron it is highly

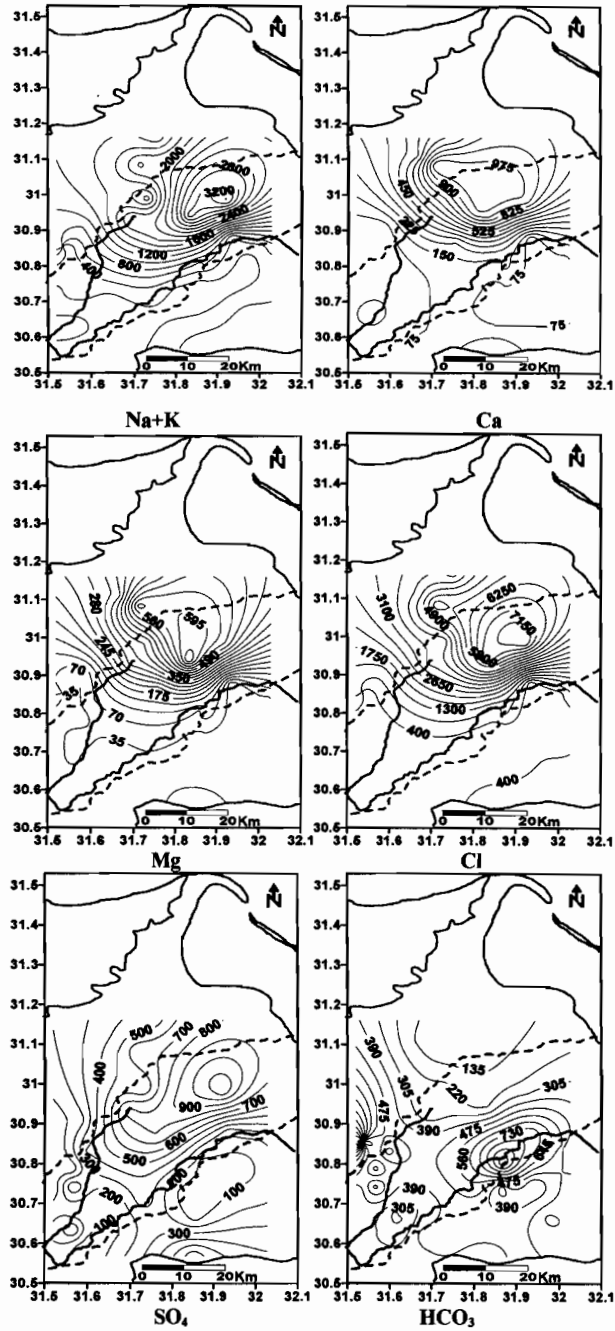
soluble, it tends to concentrate in environments that have a limited circulation, in evaporates or brines of marine or continental origin (Uhlman, 1991). For this reason, the dissolution of evaporate rocks has been considered to be a possible source of boron (Harder, 1974; Rose et al., 2000). The relatively high concentration of boron in seawater leads it to be considered as an indicator of marine intrusion, though in some cases the elevated boron – with respect to the theoretical mixing between fresh and seawater – has been related to other sources. Such sources include anthropogenic pollution of groundwater (Uhlman, 1991; Mirecki and Parks, 1994; Leenhouts, et al. 1998; Vengosh, et al. 1994) and of surface waters (Neal, et al. 1998) and/or deep flows (Gimenez and Morell 1991).

The concentrations of boron in the groundwater samples range between 0.0 to 1.7 mg/L (Fig. 7) and these values are quite distinct compared to the boron content of the seawater, where seawater has boron concentration of 5.3 mg/L (Martos, F. 2001). The relatively high concentration of boron in seawater leads it to be considered as an indicator of marine intrusion. Consequently, no marine intrusion in the studied area.

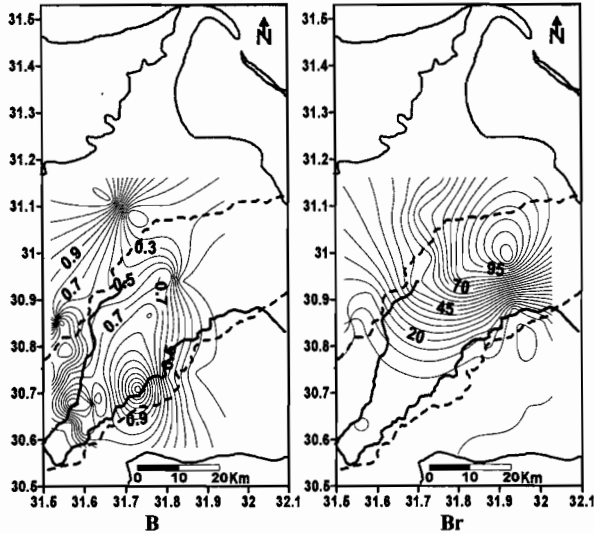
#### **b. Bromide**

Bromide is basically important for the study of saline waters and brines, since its concentration allows the degree of evaporation of seawater to be known, as bromine accumulates in the residual brine (Sanders, 1991; Richter and Kritler, 1993). Its distribution in groundwater is related to the presence of evaporates and an analysis of the Cl/Br ratio can be used to indicate the degree of development of brines, (Edmunds, 1996 and Whittemore, 1995). This ratio has also been used to identify different saline flows and their relative contribution (Dror, et al. 1999). Also to distinguish between natural and anthropogenic causes of salinization (Andreasen and Fleck, 1997) and to identify the genesis of deep saline waters (Stober and Bucher, 1999). In respect, Davis, et al. (1998) extensively revised the use of the Cl/Br ratio in groundwater studies.

The concentrations of bromine ranges in the first group of the groundwater samples between 0.47 to 6.5 mg/L, while with the second group from 2.5 to 18 mg/L. Third group shows a jump with Boron that ranges between 49 to 120 mg/L (Fig. 7), reflecting dissolution of evaporitic seawater, as bromine accumulates in the residual brine.



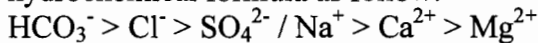
**Fig. (6) Distribution of the major ions of the groundwater samples**



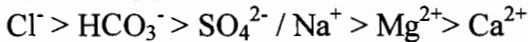
**Fig. (7) Distribution of the minor ions of the groundwater samples**

#### 1.4 Hydrochemical Formula and Water Type

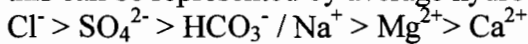
The hydrochemical formula are arranged in order from the highest ion percent to the lowest one, while the highest concentration of the anions and cations gives the water type of the sample. According to the classification of groundwater samples into three groups: The sum of the first group samples gives bicarbonate-sodium water type and this group can be represented by average hydrochemical formula as follow:



The sum of the second group samples gives chloride-sodium water type and this can be represented by average hydrochemical formula as follow:



The third group includes wells of chloride-sodium water type; this can be represented by average hydrochemical formula as follow:



The variation in chloride percentage value in both hydrochemical formulas of the second and third groups relative to that of Na, Mg and Ca ions reflect the leaching process and beginning of salt water interface in the second group and major contribution of salt water intrusion in the third group.

## 1.5 Graphical Presentation of Hydrochemical Data

### 1. Bar Graph

The Hydrochemical Data and Hypothetical Salt Combinations can be presented graphically by Bar Graph. The salt combinations can be detected hypothetically by using Bar graph (Collins, 1923). It is presented as a vertical bar having the total concentration of anions and cations expressed as the percentage of equivalent part per million (epm %), the left side shows the cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and the right side shows the anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ). The hypothetical combination between cations and anions for each sample to form salts depend mainly on the dominance ions and the chemical affinity of these ions to combine with each other according to Palmer method (Palmer, 1911).

The hypothetical salt combinations of the three groups of the groundwater samples in the studied area as shown in (Fig. 8) are:

**\*Group 1:** KCl, NaCl,  $\text{Na}_2\text{SO}_4$ , NaHCO<sub>3</sub>,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{Ca}(\text{HCO}_3)_2$   
(Meteoric water)

**\*Group2:** KCl, NaCl,  $\text{Na}_2\text{SO}_4$ , NaHCO<sub>3</sub>,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{Ca}(\text{HCO}_3)_2$   
(Low-salinity meteoric water)

**\*Group3:** KCl, NaCl,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{HCO}_3)_2$   
(Marine water)

- In the first group, 54 % of the groundwater samples represent fresh water with sodium-bicarbonate water type (meteoric water type).
- In the second group, 24 % of the groundwater samples represent low salinity meteoric water with  $\text{Mg}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2$  salts which can be attributed to dissolution of calcite and dolomite deposits.
- In the third group, 22 % of the groundwater samples contain  $\text{MgCl}_2$  and  $\text{CaCl}_2$  salts that refer marine origin.

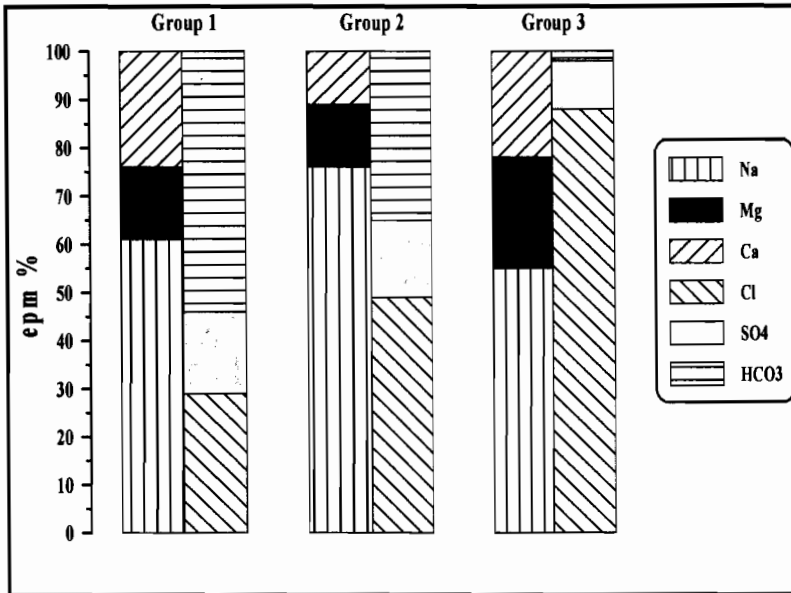
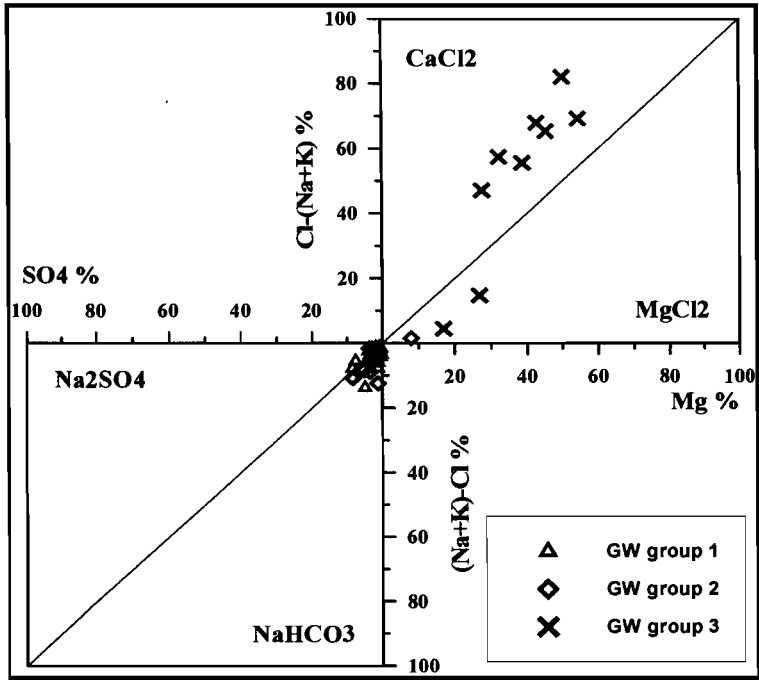


Fig. (8) The hypothetical salt of groundwater samples

## 2. Sulin Diagram:

Sulin diagram (Sulin, 1948) represents the genesis of water (Fig. 9). The points which lie in the lower quadrant in both the two triangles represent the meteoric water genesis. The lower triangle represents  $\text{NaHCO}_3$  water type where the ratio  $(r\text{Na}^+ + r\text{K}^+) - r\text{Cl}^- / \text{SO}_4^{2-} > 1$ , as with most of samples of first and second groups. While the upper triangle represents  $\text{Na}_2\text{SO}_4$  water type where the ratio  $(r\text{Na}^+ + r\text{K}^+) - r\text{Cl}^- / \text{SO}_4^{2-} < 1$ , that with the rest of the first groundwater group samples (1, 2, 11, 12, 13 and 41) and samples (33 and 37) from the second group.

The points lie in the upper quadrant, which represent marine water genesis. The lower triangle represents  $\text{MgCl}_2$  water type where the ratio  $r\text{Cl}^- - (r\text{Na}^+ + r\text{K}^+) / \text{Mg}^{2+} < 1$ , this appears with sample (40) from the second group and samples (24 and 27) from the third group. While the upper triangle represents  $\text{CaCl}_2$  water type where the ratio  $r\text{Cl}^- - (r\text{Na}^+ + r\text{K}^+) / \text{Mg}^{2+} > 1$ , as appears with the rest of the third group samples.



**Fig. (9) Sulin diagram of groundwater samples**

**2 Analysis of salinization processes in the Quaternary aquifer of the study area**

According to the hypothetical salt classification of the groundwater samples in the study area, there are three types. The triangular diagram of the three ions ( $\text{SO}_4\text{-Cl-HCO}_3$ ) (Fig. 10) shows that the first group is surrounding the fresh water (Nile) and the second group shows more salinization while the third group coincides with the Mediterranean Sea point (seawater) (Salem, W. 1996).

The distribution of the samples points over the plot is heightened with the proportion of  $\text{Cl}^-$  that considered to be a conservative tracer of the seawater intrusion process. So salinization can be determined by ion ratios especially that bring out an increase in the percentage of  $\text{Cl}^-$ .

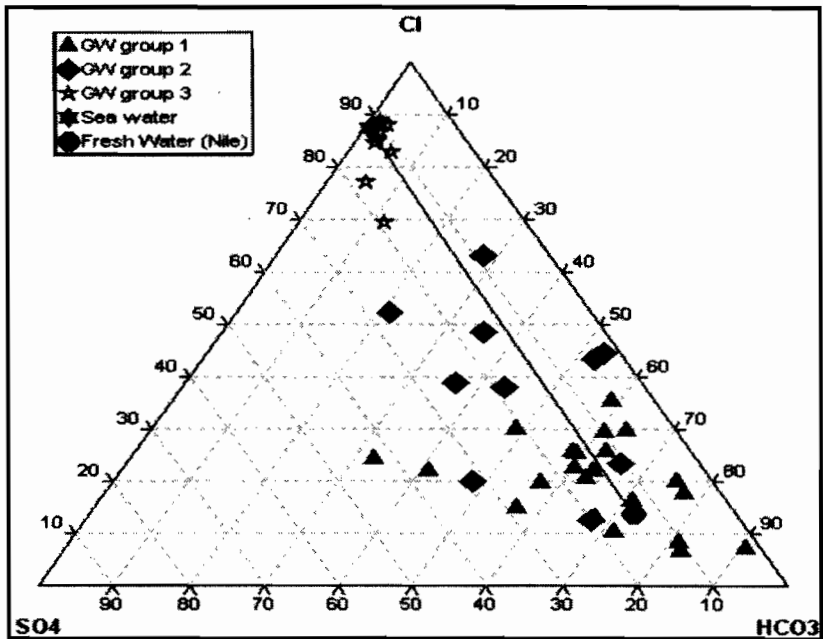


Fig. (10) Triangular diagram of  $\text{SO}_4\text{-Cl-HCO}_3$  for the groundwater samples

### 2.1 Ion Ratios of major ions

Table (5), include ion ratios expressed as epm, such as  $r\text{Na}^+/\text{rCl}^-$ ,  $r\text{Mg}^{2+}/\text{rCl}^-$ ,  $r\text{Ca}^{2+}/\text{rSO}_4^{2-}$ ,  $r\text{Ca}^{2+}/r\text{Mg}^{2+}$ , and  $r\text{Cl}^-/\text{rHCO}_3^-$  for groundwater samples, fresh water and seawater, which are useful criteria used to detect the salinization sources in the analyzed water samples.

#### a- $r\text{Na}^+/\text{rCl}^-$ Ratio:

The variation in  $r\text{Na}^+/\text{rCl}^-$  ratio is used for differentiating between fresh and saline water. The values of this ratio are always higher than unity in fresh and meteoric water, while that is less than unity is marine water. The first and the second group samples - except sample (40) - have  $r\text{Na}^+/\text{rCl}^-$  ratio exceeding unity indicating fresh water origin. Shift toward sodium refers to natural ion exchange, where Na-clay reacts with calcium and/or magnesium and releases sodium (Natural softening). The third group has  $r\text{Na}^+/\text{rCl}^-$  ratio less than unity and may be referred to the salt water intrusion. Figure (11) represents the relationship between  $\text{Na}^+$  and  $\text{Cl}^-$  Concentrations. The



samples in general have concentrations of  $\text{Na}^+$  related to the influence of seawater, but there are some deficits can be appreciated with respect to the mixing of fresh and seawater in the more saline waters.

**b-  $\text{rSO}_4^- / \text{rCl}^-$  Ratio:**

The relation between  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  is represented by (Fig. 11) indicates that the saline water adapts roughly to the mixing process identified by dilution line. The third group shows a  $\text{rSO}_4^{2-} / \text{rCl}^-$  ratio quite similar to that of seawater, although slightly enriched in  $\text{SO}_4^{2-}$ . Most of the rest samples show significant enrichment in  $\text{SO}_4^{2-}$  with respect to the  $\text{Cl}^-$  concentration.

**c-  $\text{rMg}^{2+} / \text{rCl}^-$  Ratio:**

This ratio represents a relative relationship between the less abundance ion ( $\text{Mg}^{2+}$ ) and the conservative ion ( $\text{Cl}^-$ ) and is helpful in studying the modification of groundwater composition due to seawater intrusion and/or leaching action of different salts such as carbonate rocks and dolomite. Fresh water mostly has values of  $\text{rMg}^{2+} / \text{rCl}^- > 0.5$  (Custodio and Bruggeman 1987). About 34 % of groundwater samples have  $\text{rMg}^{2+} / \text{rCl}^-$  higher than 0.5, while the rest of the second group (except sample 18) and the third group samples have  $\text{rMg}^{2+} / \text{rCl}^-$  less than 0.5. This reflects the leaching action of earth salts and higher

**d-  $\text{rCa}^{2+} / \text{rCl}^-$  Ratio:**

The relationship between the concentrations of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  (Fig. 11) shows a significant increase in  $\text{Ca}^{2+}$  with respect to  $\text{Cl}^-$  concentration. Slight lack of  $\text{Ca}^{2+}$  reflects the fresh water charging while excess of  $\text{Ca}^{2+}$  with the saline samples away the mixing line between seawater and fresh water reflects ionic exchange processes.

**e-  $\text{rCa}^{2+} / \text{rMg}^{2+}$  Ratio:**

This ratio is useful in studying water from limestone and dolomite and help in tracing seawater contamination (Meisler, et al. 1967). Calcium is the predominant cation in the Nile water, which is produced from dissolution of calcite carbonate rocks and dolomite containing mainly both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Base Exchange process of  $\text{Mg}^{2+}$  ion against  $\text{Na}^+$  or  $\text{Ca}^{2+}$  is another source of magnesium ion. Hem, (1985) suggests that a low  $\text{Ca}^{2+} / \text{Mg}^{2+}$  ratio may indicate salt water intrusion.

It is noticed that the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio is more than unity for 68 % of the groundwater samples have values exceed unity ( $\text{Ca}^{2+} > \text{Mg}^{2+}$ ) which occur when the dissolution of calcite, gypsum and anhydrite is greater than dolomite. About 32 % of the analyzed groundwater samples indicating that the dissolution of  $\text{Mg}^{2+}$  exceeds  $\text{Ca}^{2+}$ . Figure (11) shows the relation between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for the studied groundwater samples. The saline samples show that no mixing with seawater and confirming dissolution processes earth rocks.

**f-  $\text{rCa}^{2+}/\text{rSO}_4^{2-}$  Ratio:**

Sulphate, in general, is the result of direct dissolution of gypsum (or anhydrite) or the neutralization of acid waters by limestone or dolomite. In the latter case, magnesium may be prominent. If sulphate > Calcium, calcium has been removed from solution, most likely by the precipitation of calcite or by ion exchange reactions. Figure (11) shows the relation between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  for groundwater samples and no seawater intrusion in the northern part of the studied area. About 39 % of the groundwater samples have the  $\text{rCa}^{2+}/\text{rSO}_4^{2-}$  values less than unity that refers dissolution of gypsum deposits or intensive use of fertilizer source. The rest of the samples have  $\text{rCa}^{2+}/\text{rSO}_4^{2-} > 1$  indicating that the dissolution of  $\text{Ca}^{2+}$  source as calcite is greater than solubility of sulphate compound as gypsum.

**g-  $\text{r}(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{rHCO}_3^-$  Ratio:**

The relation between  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  and  $\text{HCO}_3^-$  is shown in (Fig. 11). It is clearly noted that the third group of the groundwater samples has  $\text{Ca}^{2+} + \text{Mg}^{2+}$  more abundant than  $\text{HCO}_3^-$  and may be attributed to the high salinity of these samples with dissolution of evaporate rocks and brine.

**Table (5) Major Ion ratios of groundwater samples**

S.Type	S.No.	r Na <sup>+</sup> /Cl <sup>-</sup>	r SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup>	r Mg <sup>2+</sup> /Cl <sup>-</sup>	r Ca <sup>2+</sup> /Cl <sup>-</sup>	r Ca <sup>2+</sup> /Mg <sup>2+</sup>	r Ca <sup>2+</sup> /SO <sub>4</sub> <sup>2-</sup>	r (Ca <sup>2+</sup> + Mg <sup>2+</sup> )/HCO <sub>3</sub> <sup>-</sup>
GW Group 1	1	2.16	1.31	0.34	0.55	1.62	0.42	1.15
	2	1.30	0.86	0.75	1.65	2.21	1.91	1.43
	3	2.39	0.59	0.64	1.27	1.99	2.20	0.75
	4	2.18	0.56	0.69	0.41	0.60	0.73	0.70
	5	1.67	0.18	0.71	0.92	1.29	5.15	0.74
	6	1.80	0.20	0.58	1.38	2.40	6.78	0.78
	7	1.69	0.60	0.65	1.21	1.87	2.03	1.05
	8	1.86	0.52	0.27	0.40	1.47	0.77	0.71
	9	5.33	0.23	1.29	2.26	1.75	9.87	0.48
	10	2.48	1.32	1.20	2.01	1.67	1.53	0.79
	11	1.85	1.23	0.50	0.83	1.66	0.68	1.23
	12	1.26	0.50	0.65	0.93	1.43	1.86	0.95
	13	1.16	0.33	0.54	0.81	1.51	2.50	0.96
	14	2.18	0.95	2.16	2.45	1.14	2.57	0.80
	15	3.69	1.07	0.54	0.83	1.53	0.77	0.46
	16	8.58	1.22	0.54	0.99	1.82	0.81	0.21
	17	1.48	0.16	0.43	0.33	0.77	1.99	0.60
	19	1.89	0.12	0.05	0.07	1.24	0.56	0.12
	22	2.18	0.25	0.08	0.10	1.23	0.40	0.15
36	1.49	0.46	0.45	0.84	1.85	1.85	0.98	
38	1.92	0.45	0.25	0.37	1.47	0.81	0.45	
41	1.69	1.41	0.55	2.17	3.92	1.54	1.24	
GW Group 2	18	2.52	1.18	0.67	0.21	0.31	0.17	0.62
	20	1.57	0.47	0.28	0.10	0.36	0.21	0.69
	21	1.37	0.04	0.22	0.02	0.10	0.56	0.35
	23	1.16	0.10	0.11	0.05	0.41	0.44	0.60
	32	1.58	0.34	0.44	0.40	0.92	1.20	0.51
	33	1.04	0.07	0.32	0.32	0.99	4.53	0.90
	34	4.28	1.18	0.22	0.34	1.53	0.29	0.18
	37	1.02	0.24	0.15	0.28	1.86	1.17	1.03
	39	1.57	0.36	0.10	0.18	1.81	0.49	0.42
40	0.93	0.38	0.31	0.42	1.35	1.11	3.17	
GW Group 3	24	0.85	0.17	0.26	0.21	0.81	1.25	12.24
	25	0.63	0.11	0.25	0.27	1.05	2.52	29.80
	26	0.66	0.09	0.26	0.22	0.85	2.37	26.90
	27	0.94	0.20	0.21	0.14	0.70	0.72	3.69
	28	0.45	0.10	0.31	0.35	1.14	3.49	16.37
	29	0.51	0.08	0.29	0.31	1.05	3.82	69.74
	30	0.59	0.08	0.24	0.22	0.92	2.81	26.46
	31	0.48	0.08	0.35	0.31	0.88	3.83	51.28
35	0.69	0.11	0.19	0.21	1.11	1.91	20.34	
Sea water		0.77	0.10	0.21	0.08	0.41	0.84	80.30
Fresh water		1.84	0.75	1.15	1.74	1.51	2.33	0.94

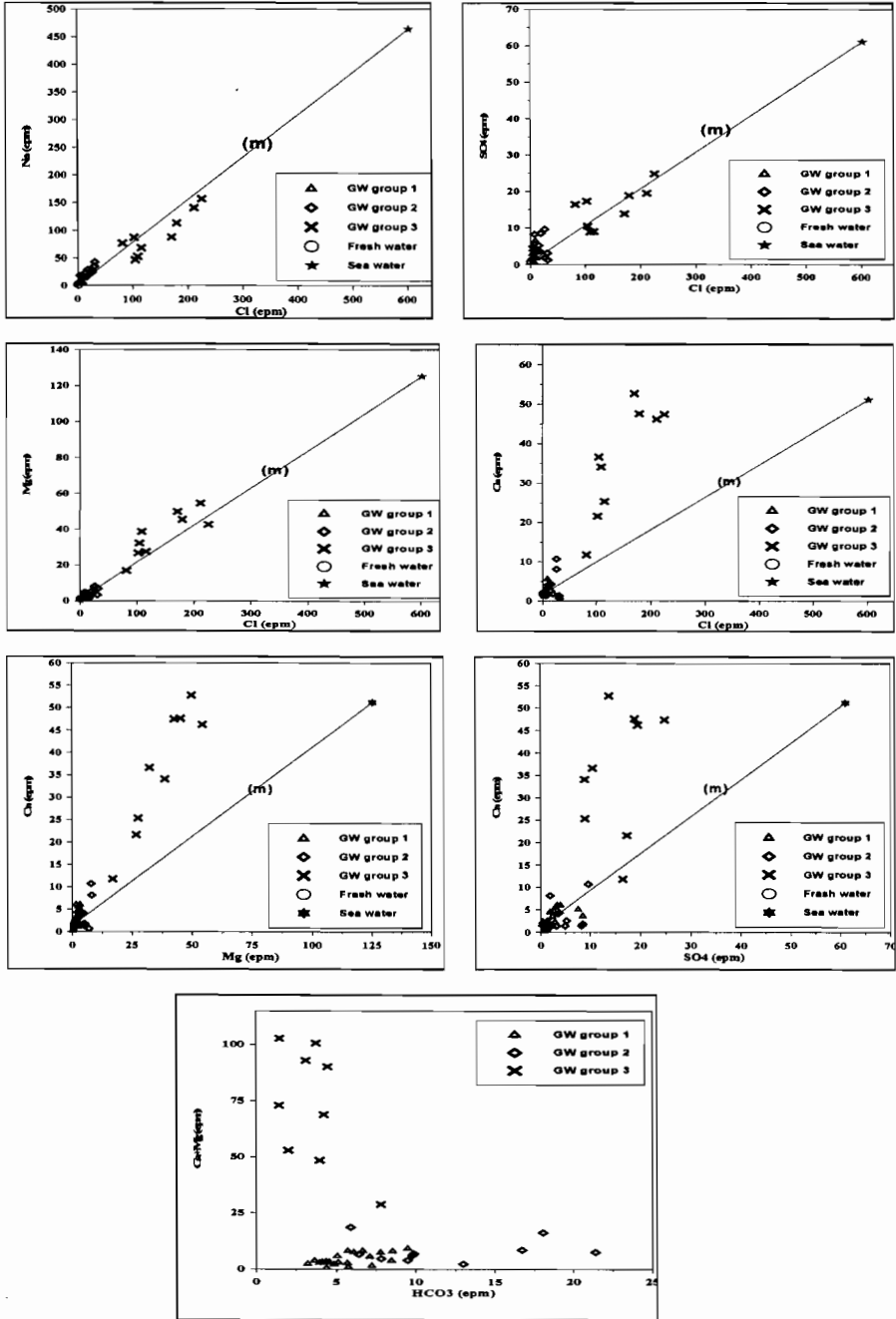


Fig. (11) Relation between the major ions for the groundwater samples, (m): mixing line between fresh and seawater

## 2.2 Ion Ratios of minor ions

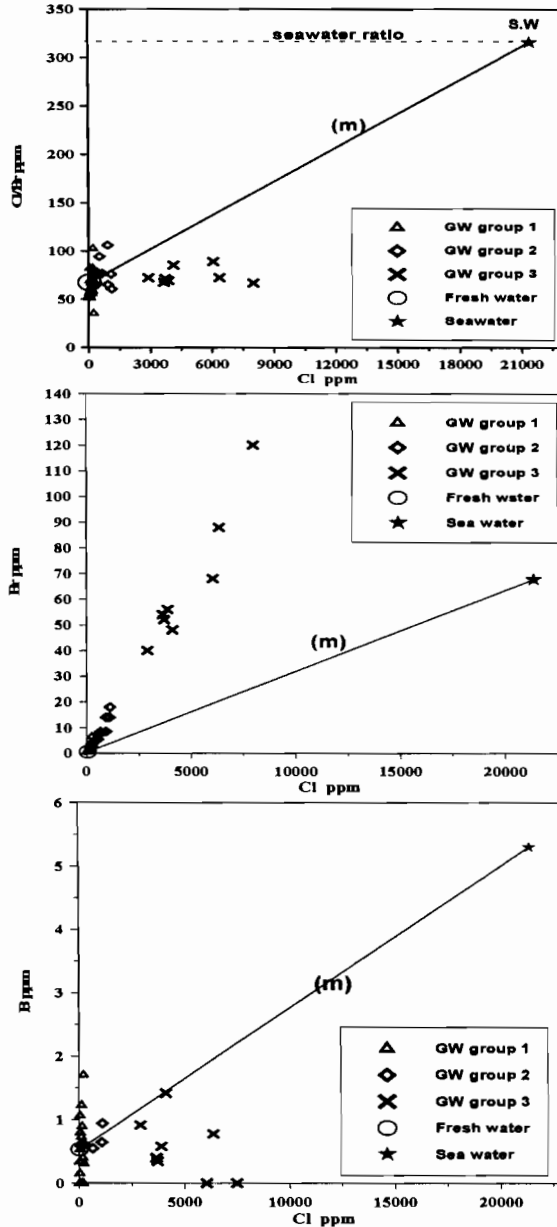
The studying of salinization of groundwater in the Quaternary aquifer of the study area is complicated due to the arid climate, the presence of evaporites and proximity to the Sea. The salinization has been characterized by jointly studying the content of various minor ions (B and Br) and a series of ionic relationships. Table (3) includes the concentrations of minor ions B and Br for the groundwater samples of the study area and the fresh water and seawater (Martos, F. 2001).

Boron content increases in more saline areas, since it is associated with the presence of evaporitic and/or marine influences. Bromide analysis enables the identification of the principal processes that determine the salinity of the water along the coastal zone as the presence of the Quaternary marine sediments and present day marine intrusion. The brackish groundwater that is related to old raised beaches shows low Cl/B ratio and areas affected by marine intrusion had Cl/B ratios similar to seawater than in the other areas along the coastal zone.

The processes that contribute in the salinization of the studied groundwater samples can be more classified by considering Br and Cl together, since they have different affinities in the evaporation of seawater, Cl being prone to form salts. The Cl/Br ratio can vary over several orders of magnitude and so it is widely used to study of the processes of evaporation and salinization of water because it has a conservative behavior and is not affected by water-rock interactions (Edmunds, 1996; Davis et al., 1998; Whittemore, 1995). A plot of Cl against the Cl/Br ratio indicates no mixing with seawater, where the Cl/Br ratios of the groundwater samples of the studied area are ranged between 35.4 and 105.9. These values are lower than that of seawater (315) and refers to old raised beaches as shown in (Fig. 12) that also shows increasing of Cl more than the Cl/Br for the third groundwater group.

Figure (12) shows the relation between the concentrations of Br and Cl, which appears that no mixing between seawater and freshwater. This means that no seawater intrusion. Also the relatively high concentration of boron in seawater leads it to be considered as an indicator of marine intrusion. The concentrations of B in the study area show lower values than that of seawater and the relationship

between B and Cl concentrations shows no mixing with seawater (Fig. 12).



**Fig. (12) Relationship between the (major – minor) and (minor-minor) ions concentrations of the groundwater samples, (m) mixing line between freshwater and seawater, (SW) seawater**

## Conclusion

The origin of salinization in the waters of the Quaternary aquifer of the eastern Nile delta is highly complex, given the arid climate of the area, the presence of evaporates, and its proximity to the Sea. The salt water may have intruded into the aquifer during past and remained trapped. So, the groundwater pumping would not cause the direct intrusion of the seawater but rather a rise in the saline level. The study of the TDS and the major ions indicated that there are three groups of the groundwaters. Increase of TDS in the second group than the first group reflects leaching of ground layers with the recycling pumping of the groundwater. The third group in the north part of the study area - with high salinity - reflects salt water intrusion. The salinization of the waters is studied by the major ions relationships alongside (B and Br). Boron increases in concentration in areas

where the waters are more saline. The coastal zone is the most complex as a consequence of the water flow across the Quaternary aquifer, in which the salinity is closely related to the presence of evaporite salts that arise from the Quaternary raised beaches. These marine materials, which may include residual brines, extend at depth throughout the delta.

This multiparametric study, involving major and minor ions, and comparing the hydrochemical data with those corresponding to the seawater-fresh-water mixing, provides a useful tool to determine the hydrochemical features affecting to the aquifer.

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## التحليل الهيدروكيميائي لعمليات التملح في الخزان الجوفي الرباعي في منطقة شرق الدلتا- مصر

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تمت دراسة تملح مياه الخزان الجوفي الرباعي في منطقة شرق الدلتا وقد أجريت التحاليل الكيميائية للأيونات الشائعة ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ) والغير شائعة (B, Br) لمعرفة مصادر وعمليات التملح. وللوصول إلي هذه المصادر تم تجميع 41 عينة مياه جوفية ممثلة لمنطقة الدراسة وتم تقسيمها تبعاً لدرجة ملوحتها إلي ثلاث مجموعات.

ملوحة المجموعة الأولى التي تقع في الجنوب والجنوب الغربي والمجموعة الثانية التي تقع في شرق ووسط منطقة الدراسة كانت نتيجة إذابة المياه لأملاح التربة مع السحب المتكرر للمياه الجوفية. أما المجموعة الثالثة التي تقع شمال منطقة الدراسة فهي عالية الملوحة مما يدل علي وجود تداخل مصدر آخر عالي التملح. وتم دراسة العلاقات بين الأيونات الشائعة والغير شائعة مع المقارنة بمياه البحر ومعرفة نسبة الخلط معها. أوضحت هذه الدراسة السبب في ملوحة المياه الجوفية في المنطقة الشمالية إلي وجود أملاح بحر قديمة متبخرة ونتيجة السحب الجائر للمياه الجوفية أدي إلي ذوبان هذه الأملاح ولا يوجد تداخل لمياه البحر الحديثة.