

Possibilities of Groundwater Pollution in Some Areas, East of Nile Delta, Egypt

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ABSTRACT

The chemical analyses, we performed a case study of the surface water and groundwater quality in east of Nile delta –Egypt, in order to understand the hydrogeochemical aspects and the possibilities of groundwater pollution. Concentrations of major chemical elements in the polluted surface water were related to reaches of good groundwater quality, where the Bahr El-Baker reservoir was seriously polluted, with different pollutions. Hydrogeochemical study has been carried out for 72 water samples from the study area, 16 surface water samples and 56 groundwater samples. Total dissolved solid (TDS) contents of groundwater are highly variable rising along flowpath from the south (271 mg/L) to the north (20274 mg/L), implying significant deterioration and salinization of groundwater. Based on TDS and ionic ratios, groundwater samples were classified into three groups. In fresh water (group A) brackish water (group B), water chemistry is greatly influenced by cation exchange, mineral dissolution/precipitation, anthropogenic pollutants and mixing with surface water, whilst, in saline water (group C), water chemistry is affected by salt-water intrusion, reverse cation exchange and evaporation. The south and central groundwater of study areas is influenced by TOC, COD, NO₃⁻ and NH₄⁺ pollutions confirming the seepage of surface water to groundwater.

Key words: Groundwater salinization -water-rock interaction- ionic ratios- ionic deltas - groundwater pollution, eastern Nile Delta

Introduction

Water is the artery of our life and one of the most important gifts from our God to mankind. Water covers nearly three quarters of the earth's surface in oceans, lakes, snow and glaciers. It exists also in the atmosphere and under ground. Only a tiny portion (4.9 %) of this water is fresh and suitable for direct human uses. Groundwater represents two thirds of this fresh water. The groundwater of the Quaternary aquifer in the Nile Delta region represents an important source of water after the River Nile water. Greater demands for water with growing population in parallel with cultivation and industrial activities are increasingly needed. However, even in countries where surface water is abundant, the good quality of groundwater, its accessibility and its relatively low cost are factors that stimulate an increasing level of exploitation of this resource. Groundwater pollution due to agricultural and some non-agricultural activities could be particularly insidious because of its widespread character. A direct impact on the quality of groundwater by intensive agriculture is due to the excessive use of pesticides and chemical fertilizers. Not all of the nutrients in the fertilizers are used by the crops. The exact quantity used depends on many factors including the type of crop, climate and meteorological conditions as well as the amount of fertilizers spread per hectare. Part of these nutrients is percolated on the soil surface or infiltrated into groundwater. Intensive livestock farming generates similar problems because of high quantity of animal manure. Another source of pollutants that contaminate groundwater is the usage of sewage sludge instead of fertilizers in farming and use of drainage water for irrigation.

The eastern Nile Delta is an important part for agriculture in Egypt. Some problems appeared with decreasing Nile water, unfair usage of groundwater, and irrigation with drainage water. Many researchers devoted their efforts toward studying the sources and causes of these problems and consequences. Review of the previous work concerning the water pollution of groundwater and salt water intrusion problems in the study area is presented herein.

Quaternary and Tertiary aquifers are mostly of hydrological importance in the Nile Delta and its fringes. The deltaic deposits belonging to the Pleistocene represent the main aquifer, (Shata and El-Fayoumy, 1969). The main source of the groundwater of the aquifer is the Nile water seepage. The eastern Nile Delta aquifer is a rich one and could be utilized with considering a wise pumping policy and periodical control for water quality, (El-Dairy, 1980). Nada (1984), indicated that the recharge sources of the groundwater in the eastern Nile Delta involve a mixing between different sources of water: Nile water, Palaeowater, flood water and connate water in some wells. The hydrochemical characteristics of the groundwater in the eastern Nile Delta distinguished the aquifer into three zones with different water qualities. Ismailia Canal and Damietta branch (in some places) act as recharging streams for the adjacent aquifer. To the north, Damietta Branch acts as discharging stream for groundwater, (Khalil *et al.*, 1985). Total seepage from Ismailia Canal was estimated using the radioactive

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iodine-131. Where shallow wells were used for radioactive tracer experiments. The estimated filtration velocity values range between 0.021 and 0.137 m/day. Salem, 1996, applied the isotopic and hydrochemical techniques to study the recharge source of the groundwater in the eastern Nile Delta. The study area was classified into three main groups from the hydrochemical point of view. The southern group is mainly fresh water, indicating meteoric water influence, the middle group is characterized by brackish water, indicating leaching processes accompanying irrigation and the northern group is saline water, reflecting sea water intrusion. From the hydrochemistry and stable isotopes studies, the recharge sources were found to be: Fresh Nile water, saline water, precipitation, and irrigation water return.

Site description:

The investigated area (Fauqus and Hesinia) is located east of the River Nile north Cairo, between latitudes $30^{\circ} 45'$ and $31^{\circ} 00'$ N and longitudes $31^{\circ} 50'$ and $32^{\circ} 5'$ E. The study area is bounded at the west by the Nile River (Damietta Branch), Suez Canal at the east, Mediterranean Sea and Manzala Lake at the north and Ismailia canal at the south, Fig. (1). The relative humidity is moderate and active winds of intermediate speeds are recorded. The highest recorded value of relative humidity is 71.8 % in December. The mean annual precipitation ranges from 17.4 to 4.2 mm/year. Evaporation reaches up to 18.7mm/day in May and its minimum value of 2.3 mm/day recorded in December. The average daily temperatures vary from about 37.1°C in August to about 5°C in January. Mean annual precipitation increases northward from 20 to about 100 mm and daily evapotranspiration ranges between 1.5 mm in December to 7.5 mm in July (RIGW-IWACO (1992).

The overall objective of this hydrochemical study is to integrate geomorphology, geology, hydrology, hydrogeology and geochemical modeling in conjunction with their ionic data and hydrogeochemical indices to study groundwater salinity origin, the important hydrogeochemical reactions, groundwater mixing processes, controls on water quality, and further provide estimates of the anthropogenic contamination of the aquifer by TOC, COD, nitrate and ammonia ions. Such information will contribute to adequate land and water-planning strategies.

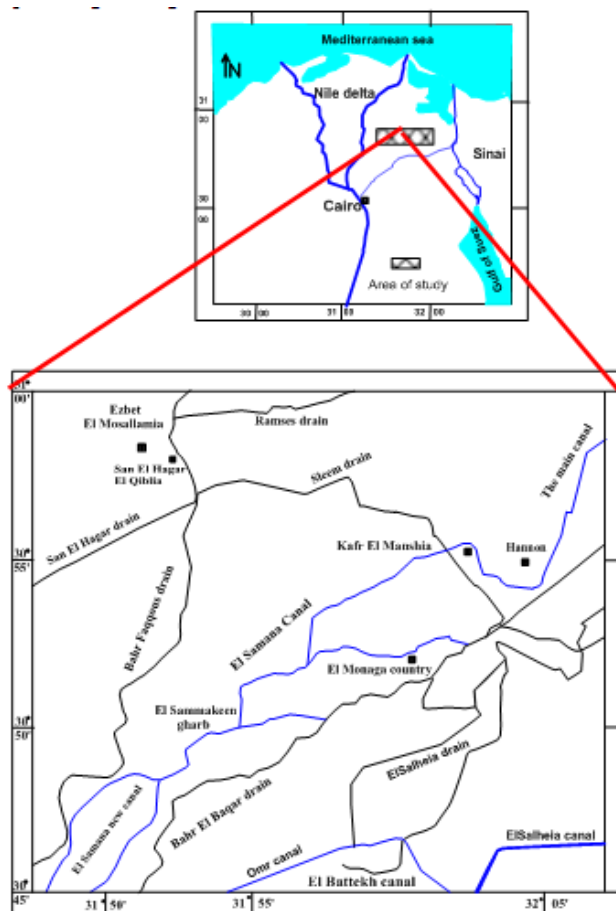


Fig. 1: Location map of the study area

Aquifer system:

The eastern region of Nile Delta is sloping regionally in a northward direction with a low relief. This area is characterized by sandy and gravelly sediments belonging essentially to the old Nile Delta, and shows good examples of deflation and peneplanation. The area includes the Nile Delta flood plain. The surface is formed of silt, clay and very fine sand resulting from the successive accumulation of the suspended matter in the Nile Delta during the flood seasons. This section is underlain by sandy and gravelly sediments deposited by the Nile during the Pleistocene times and having a thickness of about 300 m, (El Fayoumy, 1968). Geriesh, 1994, classified the East Nile Delta region into three geomorphologic units, as follow, Fig. (2):

- 1-El Salhiya Plain.
- 2-The Northern Low Lands.
- 3-The Eastern Nile Delta Flood Plain.

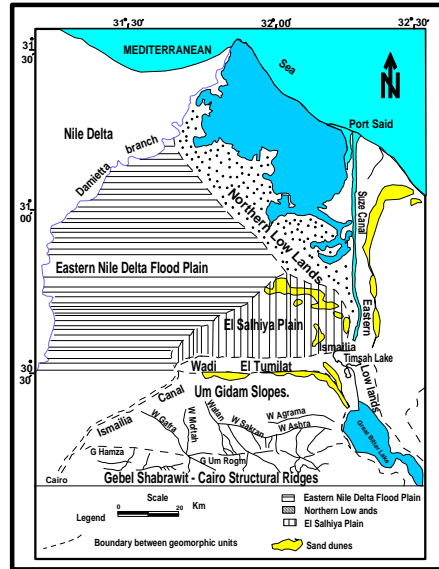


Fig. 2: Geomorphologic map of the study area, (after El Sayed, 2000).

Geologically, the study aquifer of the Eastern Nile Delta belongs essentially to the Quaternary Pleistocene deposits. The thickness of this aquifer increases seaward attaining 900-m thick close to the sea and gradually decreases southward to 100-m thick (Fig. 3). The southward thinning of the aquifer is attributed mainly to E–W faults (Shata and El-Fayoumy, 1970). On the other hand, the gravelly sand deposits have a marked thinning (about 150-m thick) toward the eastern fringes of the Quaternary aquifer. A gradual increase in the reservoir capacity is observed toward Damietta branch, where the water-bearing strata reach 400 m in thickness. In the cultivated area east of Damietta branch, the aquifer is overlain by a silty clay layer which displays semi-confined conditions.

In the remaining area, the water-bearing formation is exposed on the surface and the groundwater occurs under unconfined conditions. The groundwater body in the study area constitutes the eastern extremities of the huge convex lenses that occupy the whole delta region. The thickness of freshwater body is directly related to the water-bearing thickness. Its thickness decreases generally north and eastwards due to saltwater intrusion. A maximum reported fresh groundwater column of about 300 m is observed near Damietta branch at south, while, northerly the thickness of freshwater body decreases gradually toward the highly saline areas (Tantawi, 1998). The groundwater levels in the Quaternary aquifer slope generally from south to north (Fig. 4). Tracer experiments on direction of groundwater flow system approaches steady state conditions and direction from SW toward NE of the study area.

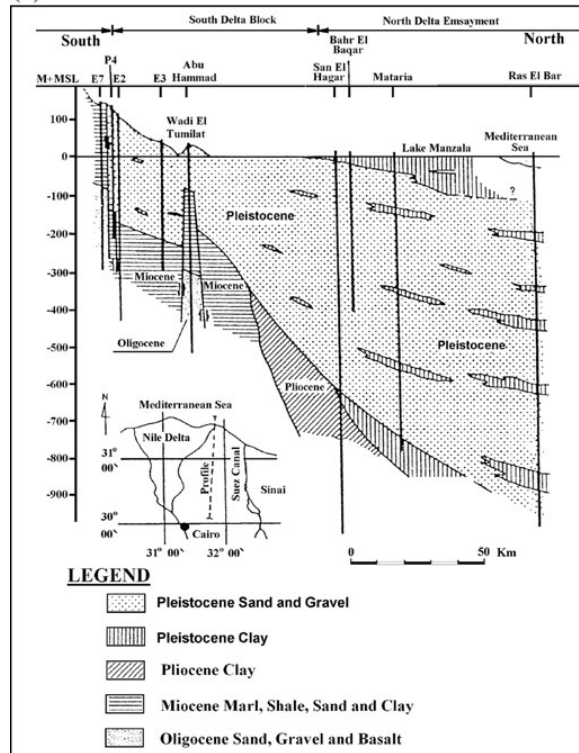


Fig. 3: Geological N–S profile (after RIGW-IWACO 1992)

The corresponding horizontal velocity is in the order of 2.3×10^{-6} m/s. Isotope-tagging technique is used to measure the infiltration velocity which was found to range between 3.1×10^{-8} and 5.8×10^{-8} m/s, (Mabrook *et al.*, 1983). Tantawi (1998) stated that the water table level in the north is about ~2 m, while being ~14 m in the south (Fig. 4).

The Quaternary aquifer is mainly recharged by downward vertical leakage of Nile water, subsurface flow from Damietta branch, Ismailia Canal and leakage from the net of irrigation canals and drains, as well as the minimal infiltration of the occasional rainfall. The discharge takes place by pumping wells for the irrigation and domestic uses and by seaward seepage into Manzala Lake and Mediterranean Sea. There is downward and/or upward vertical motion between both shallow (clay cap phreatic water) and deeper water in the Nile Delta aquifer according to the difference between the levels of the water table in the clay cap and the piezometric head in the aquifer.

The estimated total inflow into the aquifer is $2.71 \text{ km}^3/\text{year}$, while the total outflow from the aquifer is $2.365 \text{ km}^3/\text{year}$ (Arlt, 1995). The difference between the inflow and outflow rate of the groundwater balance leaves a shortage of $0.345 \text{ km}^3/\text{year}$. The present quantity of withdrawal does not allow any additional groundwater extraction potential to be exploited (Zaghoul, 1958; Farid, 1980 and Serag el Din, 1989). Generally, the aquifer is highly productive and shows good hydrodynamic characteristics, RIGW-IWACO (1992). The value of the effective porosity reaches 20 %. Horizontal and vertical hydraulic conductivity values are 75 and 25 m/day, respectively. Transmissivity values are in the range of $10,000\text{--}20,000 \text{ m}^2/\text{day}$.

According to Khalil *et al.* (1988) the aquifer to the south of Manzala Lake and near Bahr El-Bakar and El-Salhiya is characterized by a low specific yield (10 %), while in Wadi El-Tumylat, this yield ranges from 10 to 25 %. In the remaining area, it ranges between 25 and 35 % and the surface water is more effective upon groundwater.

Field measurement:

In situ measurements of water samples location were carried out in the field using GPS model (Magellan Nave 5000 pro.) for the determination of latitudes and longitudes. Some physical and chemical characteristics of the collected water were determined by electrical conductivity meter, Jenway, model (470) (EC in $\mu\text{s}/\text{cm}$) and pH is measured using pH meter Jenway, model (3150) for collected water samples

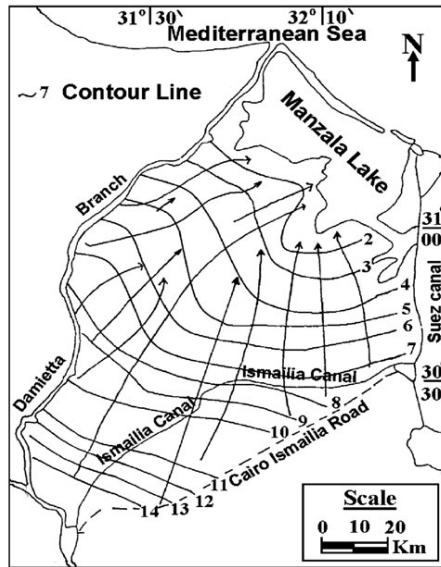


Fig. 4: Water-level contour map and groundwater flow of the Quaternary aquifer in the study area, (after Tantawi, 1998).

Laboratory measurement:

This work is based on the results of chemical analyses of sixty five groundwater samples from production wells in the study area, five surface canal samples and eleven surface drains samples collected in December, 2011, Fig.(5). Collected water samples were analyzed for major and minor dissolved chemical constituents (TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , Br^- , NH_3 , NH_4 , COD and TOC).

Laboratory measurements were carried out by EC meter (Orion model 150A+), pH meter (Jenway model 3510), flame photometer (Jenway model PFP7), ion-selectivity meter (Orion model 940) and uv/visible spectrophotometer (Thermo-Spectronic model 300). All the analyses were conducted in central lab., Desert Research Center (DRC), Egypt, following the methods of Rainwater and Thatcher (1960), Fishman and Friedman (1985), APHA (1998) and ASTM (2002). The results of the chemical analysis are illustrated in tables (1 and2).

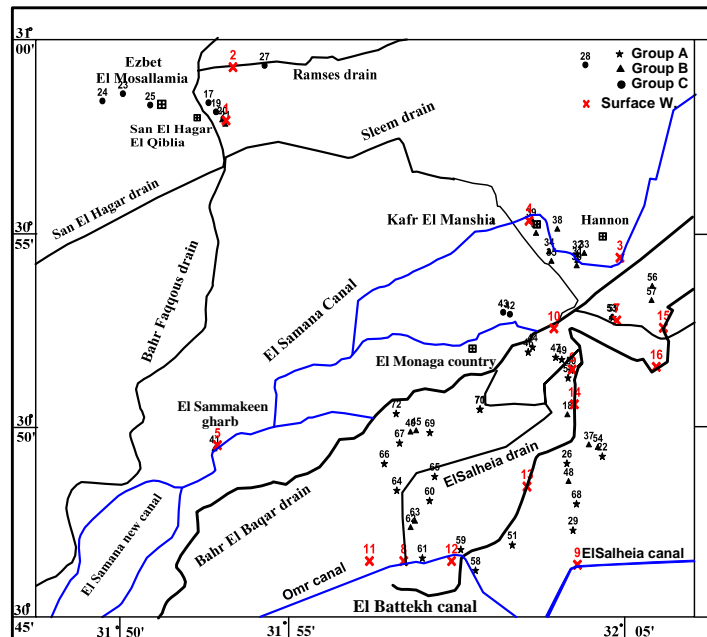


Fig. 5: Location map of the collected surface water and groundwater samples of Quaternary aquifer in the study area.

Table 1: Chemical characteristics of surface water and groundwater samples of the Quaternary aquifer, East of Nile Delta.

Sample No.	pH	EC ($\mu\text{S/cm}$)	TDS (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	Br (mg/l)
Canals water											
5	8.1	495	345	40	6.0	13.6	59.2	50.7	87.1	176.9	0.73
8	8.3	490	322	76	5.9	6.3	31.3	83.3	43.0	152.5	0.8
9*	8.4	1020	674	150	16.4	25.3	41.7	125.0	194.0	244.0	4.2
12*	8.2	420	290	32	5.9	19.0	44.1	70.9	34.0	167.8	1.1
13	8.4	500	349	70	4.7	25.3	20.8	83.3	76.0	137.3	2.1
mean	8.28		396	73.6	7.8	17.9	39.4	82.7	86.8	175.68	1.786
min	8.1		290	32	4.7	6.3	20.8	50.7	34.0	137.25	0.73
Max	8.4		674	150	16.4	25.3	59.2	125.0	194.0	244	4.2
Drain water											
1	7.6	3560	2180	520	12.0	70.0	140.0	824.0	500.0	207.1	10
2	8.1	4370	2497	620	16.0	82.6	149.7	950.8	507.3	319.9	16
3	8.4	3170	1844	460	17.0	66.0	91.6	600.0	450.0	292.4	12
4	7.8	2829	1701	340	18.0	71.0	150.0	583.2	350.0	339.0	8.3
6	8.6	2176	1300	290	14.0	38.9	110.0	375.2	300.0	310.6	6.5
7	7.8	1460	791	160	17.0	25.1	81.4	207.9	130.0	340.0	5.1
10*	8.1	3300	2022	524	24.6	82.3	62.5	375.0	840.0	197.8	15.2
11*	8.4	1790	1173	326	15.6	38.0	41.7	291.7	300.0	320.3	1.2
14*	8.2	1200	756	164	16.4	25.3	62.5	166.7	253.0	106.3	7.4
15*	7.9	1310	873	202	17.2	12.7	72.9	250.0	250.0	106.3	7.1
16*	8	2200	1305	310	18.8	44.3	83.3	333.3	440.0	121.5	10.1
mean	8		1494.7	356	17.0	50.6	95.1	450.7	392.8	241.9	8.9
min	7.6		756	160	12.0	12.7	41.7	166.7	130.0	106.25	1.2
max	8.6		2497	620	24.6	82.6	150.0	950.8	840.0	340	16
Group A (Fresh water)											
22*	7.48	1700	1056	213.7	23.1	38.0	104.2	291.8	225.0	320.3	4.6
26*	7.74	2300	1384	309.6	24.6	57.0	104.2	291.7	383.0	427.0	5.1
29*	8.33	1800	1019	300.1	4.7	12.7	41.7	250.0	288.0	244.0	3.9
32	8.4	2368	1434	310.0	14.0	55.6	112.2	390.5	326.5	404.9	7.4
44	8.4	1391	800	200.0	9.0	21.1	59.0	238.3	151.3	228.5	4.7
46	7.9	1190	781	140.0	16.0	27.0	86.2	142.0	210.0	289.3	3.1
47	7.5	2106	1194	210.0	31.0	47.0	144.9	329.6	180.4	475.4	6.3
49	7.7	1420	740	170.0	13.0	20.6	79.5	223.1	100.0	259.1	4.4
50	8	2030	1411	250.0	23.0	68.0	130.0	395.5	400.0	265.0	6.6
51*	8.54	1300	801	213.7	5.9	31.6	41.7	208.3	170.0	259.0	4.5
52	8	1006	615	125.0	6.0	26.0	55.1	162.3	140.0	201.3	2.7
55	8.2	2055	1064	270.0	7.0	38.5	82.7	329.6	140.0	371.8	6.4
58	8.3	947	579	170.0	6.0	9.4	31.8	78.6	140.0	252.6	2.9
59	8.2	716	392	84.0	5.0	11.0	45.0	58.3	68.0	225.5	1.7
60*	8.37	978	673	202.3	0.9	26.2	28.8	106.4	120.0	377.4	3.3
61	8.1	694	391	44.0	13.0	24.6	62.2	38.0	70.8	265.2	1.1
64	7.8	2415	1235	380.0	6.0	22.5	68.0	532.4	73.2	298.8	12.0
65*	8.06	669	271	70.0	2.3	9.7	16.0	27.2	65.0	162.1	1.4
66	7.9	804	425	48.0	17.0	19.6	74.0	50.7	78.4	268.3	2.0
67	7.9	1011	609	80.0	14.0	38.0	89.0	120.1	100.0	335.5	2.0
68*	8.16	1400	929	260.0	9.8	25.3	41.7	208.3	262.0	244.0	3.8
69	7.4	1305	741	125.0	8.0	66.3	53.8	152.1	110.0	451.4	3.3
70	7.9	1361	703	210.0	4.0	18.3	37.0	197.8	103.8	259.2	3.4
71	7.3	2629	1460	330.0	51.0	51.1	121.4	273.8	300.0	664.9	4.1
72	7.7	1850	1046	130.0	6.0	15.5	53.7	157.2	76.1	201.3	2.4
mean	7.9712	1497.8	870.12	193.8	12.8	31.2	70.5	210.2	171.3	310.0	4
min	7.3	669	271	44.0	0.9	9.4	16.0	27.2	65.0	162.1	1.1
Max	8.54	2629	1460	380.0	51.0	68.0	144.9	532.4	400.0	664.9	12
Group B (Brackish water)											
18*	7.84	3900	2617	626.0	12.5	113.9	166.7	1000.0	660.0	76.0	9.5
20	8.4	5520	3629	1100.0	48.0	63.0	81.7	1360.0	800.0	325.9	19.6
21	7.2	4980	3195	800.0	29.0	90.0	175.1	1166.0	800.0	268.4	14.3
30	7.5	3880	2200	480.0	37.0	82.6	168.8	685.0	500.0	481.7	10.0
31	8	2264	1510	320.0	22.0	60.2	110.0	355.0	420.0	426.7	8.9
33	8.6	3610	2112	450.0	19.0	90.3	151.5	697.0	513.1	322.3	9.5
34	8.2	3270	2020	480.0	17.0	85.8	120.0	558.0	440.0	606.4	9.2
35	8.4	2387	1520	340.0	7.0	79.1	78.8	390.0	420.0	359.1	7.6
36	7.9	7500	4233	1100.0	24.0	150.0	190.0	1800.0	740.0	407.9	33.0
37*	8.11	4100	2726	700.0	61.4	69.6	72.9	750.0	920.0	305.0	6.4
38	8.2	3210	2018	460.0	48.0	80.0	120.0	593.0	460.0	465.9	7.7

Table 1: Cont.

Sample No.	pH	EC (μ S/cm)	TDS (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	Br (mg/l)
40*	7.95	6200	4364	702.0	390.9	215.2	270.8	1542.0	1175.0	137.3	12.0
41	8.9	2490	1604	470.0	4.0	26.8	82.0	220.0	400.0	693.6	6.1
45*	8.3	2890	2002	619.3	9.0	31.6	52.1	625.0	582.0	167.5	9.3
48*	8.26	2400	1630	336.1	34.0	69.6	93.8	292.0	660.0	289.8	5.4
53	8.3	2980	1550	460.0	9.0	41.9	74.7	431.0	257.0	493.1	11.0
54	7.97	3000	1918	484.0	71.1	63.3	62.5	500.0	600.0	274.5	6.9
56	8.4	3870	2852	800.0	27.0	65.2	140.2	1300.0	300.0	410.0	14.0
57	7.7	3710	2039	470.0	14.0	87.4	137.9	735.0	330.0	504.0	13.0
62	7.6	3890	2049	520.0	8.0	60.2	175.8	786.0	177.0	584.6	16.0
63	7.7	3190	1744	550.0	3.0	31.7	100.8	583.0	150.0	603.1	15.0
mean	8.06	3773.38	2358.7	584.2	42.6	78.9	125.1	779.5	538.3	390.5	11.63
min	7.2	2264	1510	320.0	3.0	26.8	52.1	220.0	150.0	76	5.38
max	8.9	7500	4364	1100.0	390.9	215.2	270.8	1800.0	1175.0	693.6	33
Group C (Saline water)											
17	6.7	21670	15598	4000	80	460.2	900.0	7606.4	2500.0	103.7	106.0
19	6.6	28770	19587	5000	48	729.7	1050.0	10395.4	2300.0	128.1	153.0
23	7.3	27820	18942	4400	29	800.0	1300.0	10344.7	2000.0	124.9	150.0
24	7.4	24030	16479	4100	31	704.2	848.4	8519.1	2200.0	152.5	140.0
25	7.5	22230	12861	3400	16	300.0	814.2	6500.0	1800.0	61.0	140.0
27	7	28050	15364	4500	32	268.6	768.8	8200.0	1500.0	189.1	210.0
28	8.9	27630	17360	5400	90	250.0	581.7	9000.0	2000.0	67.0	190.0
39	6.9	28550	20224	5200	66	810.0	900.0	10500.0	2600.0	286.6	190.0
42	7.8	24100	15375	4500	110	490.0	320.0	7800.0	2000.0	277.0	150.0
43	7.8	17180	11749	3200	90	450.0	400.0	6085.1	1233.4	490.0	110.0
mean	7.39	25003	16354	4370	59	526.3	788.3	8495.1	2013.3	187.9	153.9
min	6.6	17180	11749	3200	16	250.0	320.0	6085.1	1233.4	61	106
max	8.9	28770	20224	5400	110	810.0	1300.0	10500.0	2600.0	490	210
Rain water	7.0	50	29.1	2.3	00	7.1	0.6	5.5	6.4	14.5	--
Damietta, branch	8.1	440	282	26	5.5	10	30	37.3	17.4	148	
Ismailia canal	7.8	711	455	33	4	15	31	27	25	160	
Sea water	8.2	59700	14171	12000	380	1343	439	21568	2300	155	175
Manzala	7.7	5130	1180	885	24	140	131	1257	648	287	

Table 2: Ion ratios, sodium adsorption ratio (SAR), total hardness (TH) and some pollutant parameters of Quaternary aquifer East Nile delta, Egypt

Sample No.	TOC (mg/l)	COD (mg/l)	NO ₃ ⁻ (mg/l)	NH ₄ ⁺ (mg/l)	TH (mg/l)	SAR (meq/l)	Br/Cl	Na/Cl	SO ₄ /Cl	HCO ₃ /Cl	Ca/Mg	Ca/SO ₄
Canals water												
5	580.0	8.9	3.4	1.8	203.8	1.2	0.014	1.2	1.3	2	2.6	1.6
8	1400.0	9.7	24.31	2.46	104.1	3.2	0.01	1.4	0.4	1.1	3	1.7
9*	2046.0	58.3	3.5	2.4	208.2	4.5	0.034	1.9	1.1	1.1	1	0.5
12*	1723.0	58.3	4.5	3.61	188.2	1	0.016	0.7	0.4	1.4	1.4	3.1
13	1508.0	136.1	37.61	1.2	156.2	2.4	0.025	1.3	0.7	1	0.5	0.7
mean	1451.4	54.3	14.7	2.3	172.1	2.5	0.02	1.3	0.8	1.3	1.7	1.5
Min	580.0	9.7	3.5	1.2	104.1	1	0.01	0.7	0.4	1	0.5	0.5
max	2046.0	136.1	37.61	3.61	208.2	4.5	0.034	1.9	1.3	2	3	3.1
Drain water												
1	32.0	200.0	30.4	6.5	637.8	9	0.01	1	0.45	0.16	1.2	0.67
2	48.0	435.0	5.1	3	713.9	10.1	0.02	1	0.39	0.21	1.1	0.71
3	16.0				500.4	9	0.02	1.2	0.55	0.31	0.8	0.49
4	129.0	750.0	16.7	14.4	666.9	5.7	0.01	0.9	0.44	0.38	1.3	1.03
6	16.0				434.9	6.1	0.02	1.2	0.59	0.53	1.7	0.88
7	16.0	98.3	81.4	18.9	306.8	4	0.02	1.2	0.46	0.95	2	1.5
10*	2428.0	155.5	3.56	5	494.7	10.3	0.04	2.2	1.65	0.35	0.5	0.18
11*	1292.0	165.2	20.2	2	260.4	8.8	0	1.7	0.76	0.64	0.7	0.33
14*	331.0	648.0	18.2	10.02	260.3	4.4	0.04	1.5	1.12	0.48	1.5	0.59
15*	3972.0	155.5	17.2	10.5	234.2	5.7	0.03	1.3	0.74	0.32	3.5	0.7
16*	1986.0	64.8	25.2	7.21	390.5	6.8	0.03	1.4	0.97	0.27	1.1	0.45
mean	933.2	296.9	24.22	8.61	445.5	7.25	0.02	1.3	0.74	0.42	1.4	0.69
min	16.0	64.8	3.56	2	234.2	3.97	0	0.9	0.39	0.16	0.46	0.18
max	3972.0	750.0	81.4	18.9	713.9	10.25	0.04	2.15	1.65	0.95	3.49	1.5
Group A (Fresh water)												
22*	882.8	99.0	43.39	1.6	416.4	6.4	0.02	1.2	0.6	0.6	1.7	1.1
26*	4524.1	29.7	60.21	1.2	494.6	8.6	0.02	1.7	1	0.9	1.1	0.7
29*	1938.5	79.2	31.47	1.6	156.2	14.8	0.02	1.9	0.9	0.6	2	0.4
32	49.0	1000.0		0.47	509	8.5	0.02	1.3	0.6	0.7	1.2	0.8
44				1.83	234.1	8	0.02	1.3	0.5	0.6	1.7	0.9
46				1.02	326.6	4.8	0.02	1.6	1.1	1.3	1.9	1

47				1.23	555.4	5.5	0.02	1.1	0.4	0.9	1.9	1.9
49				4.05	283.3	6.2	0.02	1.2	0.3	0.7	2.4	1.9
50				nil	604.6	6.3	0.02	1	0.8	0.4	1.2	0.8
51*	1184.6	19.8	20.52	2	234.3	8.6	0.02	1.6	0.6	0.8	0.8	0.6
52				2.04	244.6	4.9	0.02	1.2	0.6	0.7	1.3	0.9
55				0.26	365.1	8.7	0.02	1.3	0.3	0.7	1.3	1.4
58				0.17	118	9.6	0.04	3.4	1.3	2.1	2.1	0.5
59				0.17	157.8	4.1	0.03	2.3	0.9	2.4	2.5	1.6
60*	1721.4	153.9	337.6	0.5	180	9.3	0.03	3	0.8	2.3	0.7	0.6
61			20.4	0.04	256.4	1.7	0.03	2.1	1.4	4.2	1.5	2.1
64			5.1	0.02	262.6	14.4	0.02	1.1	0.1	0.3	1.8	2.2
65*	1324.1	92.6	243.1	0.5	80	4.8	0.05	4.1	1.8	3.7	1	0.6
66				3.89	265.4	1.8	0.04	1.8	1.1	3.2	2.3	2.3
67			535.7	0.23	378.7	2.5	0.02	1.1	0.6	1.6	1.4	2.1
68*	1400.0	69.3	14.66	2.4	208.3	11.1	0.02	2	0.9	0.7	1	0.4
69			28.6	0.03	407.3	3.8	0.02	1.3	0.5	1.7	0.5	1.2
70				0.09	167.7	10	0.02	1.7	0.4	0.8	1.2	0.9
71			267.8	0.63	513.5	9	0.01	2	0.8	1.4	1.4	1
72				0.33	197.9	5.7	0.02	1.3	0.4	0.7	2.1	1.7
mean	1628.0	234.6	80.5	1.1	304.7	7.2	0.02	1.7	0.7	1.4	1.5	1.2
min	49.0	19.8	5.1	0.02	80	1.7	0.01	1	0.1	0.3	0.5	0.4
max	4524.1	1000.0	337.6	4.05	604.6	14.8	0.05	4.1	1.8	4.2	2.5	2.3
Group B (Brackish water)												
18*	3089.7	48.6	3.77	3.2	885.1	9.2	0.01	1	0.49	0.05	0.9	0.61
20	16.0			1.785	463.3	22.2	0.014	1.3	0.43	0.15	0.8	0.25
21	16.0			2.718	807.8	12.2	0.012	1.1	0.51	0.13	1.2	0.53
30				0.328	761.4	7.6	0.015	1.1	0.54	0.42	1.2	0.81
31				5.445	522.5	6.1	0.025	1.4	0.87	0.73	1.1	0.63
33	16.0			1.798	750	7.1	0.014	1	0.54	0.32	1	0.71
34	16.0			0.837	652.7	8.2	0.017	1.4	0.58	0.67	0.8	0.65
35				0.185	522.5	6.5	0.02	1.4	0.79	0.61	0.6	0.45
36				0.087	1092	14.5	0.018	1	0.3	0.15	0.8	0.62
37*	1655.2	89.1	52.9	8.81	468.6	14.1	0.009	1.5	0.9	0.24	0.6	0.19
38				0.034	629	8	0.013	1.3	0.57	0.5	0.9	0.63
40*	2692.3	46.2	47.45	14.82	1562	7.7	0.008	0.9	0.56	0.05	0.8	0.55
41				4.008	315.1	11.5	0.028	3.3	1.34	2.13	1.9	0.49
45*	2046.2	29.7	0.1	3.2	260.3	16.7	0.015	1.5	0.69	0.17	1	0.21
48*	1292.3	69.3	48.9	2.003	520.7	6.4	0.019	1.9	1.67	0.58	0.8	0.34
53			81.4	0.68	358.9	10.6	0.026	1.7	0.44	0.75	1.1	0.7
54*	2537.9	9.9	59.52	21.63	416.6	10.3	0.014	1.6	0.89	0.32	0.6	0.25
56	15.0			1.203	618.5	14	0.011	1	0.17	0.2	1.3	1.12
57	15.0			0.023	704.2	7.7	0.018	1	0.33	0.42	1	1
62				0.008	686.8	8.6	0.02	1	0.17	0.48	1.8	2.38
63	19.0	1607.0		0.06	382.4	12.2	0.026	1.5	0.19	0.65	1.9	1.61
mean	1032.8	271.4	42	3.47	637.2	10.5	0.017	1.4	0.62	0.46	1.1	0.7
min	15.0	9.9	0.1	0.008	260.3	6.1	0.008	0.9	0.17	0.05	0.6	0.19
max	3089.7	1607.0	81.4	21.63	1562	22.2	0.028	3.3	1.67	2.13	1.9	2.38
Group C (Saline water)												
17	65.0			3.013	4142	38.2	0.014	0.82	0.24	0.008	1.19	0.86
19	65.0			0.218	5626	41	0.015	0.75	0.16	0.007	0.87	1.1
23	81.0			0.626	6540	33.5	0.015	0.66	0.14	0.008	0.99	1.56
24	81.0	416.6	5.1	0.077	5017	35.6	0.016	0.75	0.19	0.01	0.73	0.93
25	48.0			0.327	3268	36.6	0.022	0.81	0.2	0.005	1.65	1.09
27	48.0			0.286	3026	50.3	0.026	0.85	0.13	0.013	1.74	1.23
28	81.0			0.056	2482	66.7	0.021	0.93	0.16	0.005	1.41	0.7
39			16.7	0.073	5582	42.8	0.018	0.77	0.18	0.016	0.67	0.83
42	32.0			1.941	2816	52.2	0.019	0.9	0.19	0.023	0.4	0.38
43	32.0			0.617	2851	36.9	0.018	0.82	0.15	0.056	0.54	0.78
mean	59.2	416.6	10.9	0.723	4135	43.4	0.018	0.81	0.18	0.015	1.02	0.94
min	32.0	416.6	5.1	0.056	2482	33.5	0.014	0.66	0.13	0.005	0.4	0.38
max	81.0	416.6	16.7	3.013	6540	66.7	0.026	0.93	0.24	0.056	1.74	1.56

Samples * Hussein,(2010).

Results and Discussion

The chemical characteristics of surface and groundwater samples from the Eastern Nile Delta are compiled together with some ionic ratios (expressed in mg/l and me/l), tables (1 and 2). Analysis of rain water, Seawater, Dameitta branch, Ismailia Canal and Manzala lake are also added as possible sources of recharge of the Quaternary aquifer. All the sampled wells are tapping the Quaternary alluvium aquifer in the Eastern Nile Delta.

The results of chemical analyses show wide variations in chemical compositions and also indicate high salinity of some groundwater samples. In general, the groundwater samples exhibit pH values between 6.6 and 8.9 (neutral to alkaline) and electrical conductivity (EC) 669–28770 $\mu\text{S}/\text{cm}$, and total dissolved solids (TDS) values 271–20224 mg/l. Moreover, very wide ranges are easily recognized for most parameters (Table 1). In particular, the ranges of Na^+ and Cl^- concentrations are wide; 44–5400 and 27.2–10500 mg/l, respectively. Also, Ca^{2+} and Mg^{2+} concentrations range from 16 to 1300 mg/l and from 9.4 to 810 mg/l, respectively. The sulfate concentration varies from 65 to 2600 mg/l, while bicarbonate values range between 61 and 693.6 mg/l. Such wide ranges of solute concentrations suggest that multiple sources and/or complex hydrochemical processes act to generate the chemical composition. The very high TOC (up to 4524 mg/l), COD (up to 1607 mg/l), nitrate (up to 337.5 mg/L) and ammonium (up to 21.6 mg/l) concentrations in some groundwater wells can be attributed to anthropogenic sources such as sewage effluent through seepage from septic tanks, agricultural activity, and the use of organic manure and nitrogen fertilizers. This reflects a considerable degradation of groundwater characterized by high TOC, COD, NO_3^- and NH_4^+ concentrations due to the presence of agricultural influences coupled with the traditionally applied flood irrigation that introduce a long-term risk of groundwater pollution by excess fertilizers and pesticides leached downward.

Based on the differences in the water facies, the groundwater samples are grouped according to their TDS values. The broad range of TDS values differentiates three types of groundwaters in the system, each having somewhat unique chemical characteristics: fresh water (group A), brackish water (group B), and saline water (group C). According to, (Chebotarev, 1955), twenty five groundwater samples, accounts for 45 % of the whole groundwater samples, come under group A, 21 samples (37 %) in group B, and ten samples (18 %) are in group C. This classification helps to understand profoundly the processes that regulate mineralization of groundwater. These results reveal the relatively polluted nature of groundwater recharged from surface and subsurface run off through general flow path from south to north, Fig. (6). To suffice, the chemical characteristics of each groundwater group are summed up as follows,

Group A:

Group A includes 25 fresh groundwater samples practically of low salinity (TDS < 1500 mg/l). The samples of this group are located mainly at the southern part of the region. These samples have relatively low ionic concentrations and have the lowest EC values among the three groups (mean 1498 $\mu\text{S}/\text{cm}$), and Cl^- concentration is 27.1–532.4 mg/l (mean 210.1 mg/l). This group has mainly Na–Cl water type with seven samples exhibiting Na– HCO_3^- and three other samples have Ca– HCO_3^- water type. Groundwater of this group is largely suitable for most uses according to their TDS (mean 870 mg/l), TH (79.9–604 mg/l) and SAR (1.7–14.8 me/l) values (Table 1).

This group is characterized by the highest Na^+/Cl^- ratio (1.02–4.04), which is higher than that of water in the hydrological cycle (0.86–1). This may probably be as a result of cationic exchange between sodium and both calcium and magnesium (Hem, 1992). The ratios of $\text{HCO}_3^-/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{Cl}^-$ and Br^-/Cl^- are also high (mean 1.36, 0.74 and 0.022, respectively). Moreover, this group is characterized by higher $\text{Ca}^{2+}/\text{Mg}^{2+}$ (mean 6.08) and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ (up to 1.18) ratios accompanied by a low $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio (mean 0.68).

Group B:

This group includes 21 groundwater samples characterized by an intermediate TDS values (1510 to 4364 mg/l) brackish water type and represent mixed water types. The group occupies, in terms of EC, ionic concentrations, and ionic ratios, an intermediate position between group A and group C. The water facies are dominantly Na–Cl, Na– HCO_3^- , and Na– SO_4 facies based on their salinity levels and ionic ratios.

Also, this group is characterized by Cl^- concentrations between 220–1800 mg/l and EC mean value of 3773 $\mu\text{S}/\text{cm}$, relatively high $\text{SO}_4^{2-}/\text{Cl}^-$, $\text{HCO}_3^-/\text{Cl}^-$ and Br^-/Cl^- ratios (mean 0.61, 0.46 and 0.016, respectively), and a low $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio 0.7. In addition, the samples of this group are characterized by a relatively lower $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio (mean 0.7) and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio (mean 1.05) than group A. The SAR values (6.1–22.2 me/l) are relatively high compared to group A, and TH values ranged from 260 to 1562 mg/l (Table 1). This type of water was sampled mainly from the central part of the study area.

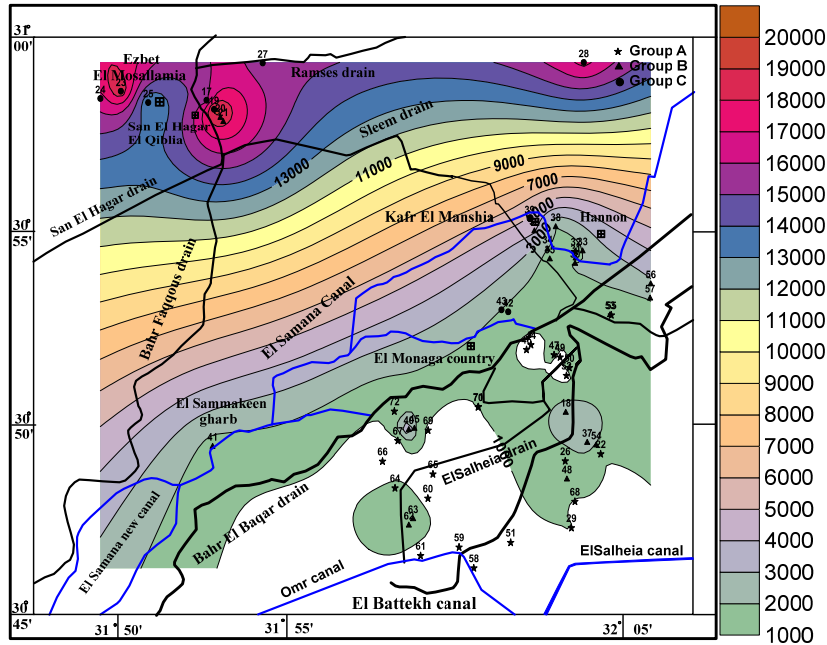


Fig. 6: iso salinity contour map of the groundwater in study area

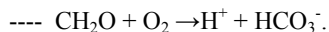
Group C:

This group includes 10 groundwater samples of highly saline water type (TDS, 11749 to 20224 mg/l) that was observed only in the northern section of the Eastern Nile Delta. Groundwater from this group has EC values (17180–28770 $\mu\text{S}/\text{cm}$) and is not recommended for domestic use and irrigation. The Cl^- concentrations of this saline groundwater vary from 6085 to 10500 mg/L. Concentrations of Mg^{2+} , Ca^{2+} and SO_4^{2-} are also high, whereas alkalinity is relatively low. Group C is characterized by the lowest Na^+/Cl^- ratio (0.6–0.93), Br^-/Cl^- ratio of 0.013–0.025, $\text{HCO}_3^-/\text{Cl}^-$ ratio (0.005–0.6) and $\text{SO}_4^{2-}/\text{Cl}^-$ ratio (0.13–0.24). The highest $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio (1.1–2.9), SAR (33.5–66.7 me/l), as well as TH (2481–6539 mg/l) were recorded in this group. While $\text{Ca}^{2+}/\text{Mg}^{2+}$ and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ mean values (1.01 and 0.94, respectively) are almost similar to the previous groups (Table 1). Overall the Na^+/Cl^- , $\text{CO}_3^{2-}/\text{Cl}^-$ and $\text{SO}_4^{2-}/\text{Cl}^-$ ratios decrease with the increasing salinity of the groundwater.

In general, the average values for each group show a continuous increase of TDS and EC with Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , Mg^{2+} , K^+ and Br^- concentrations from groups A to group C. Similarly, SAR and TH values exhibit the same behavior. In addition, ion/ Cl^- ratios decrease and ion/ HCO_3^- ratios increase with increases the salinity of groundwater. The progressive salinity increases from group A to group C with the movement of groundwater from south to north.

Surface-water hydrochemistry:

The surface-water samples in the Eastern Nile Delta were collected from five different canals and eleven different drains (agricultural drains or mixed drains water). The surface water facies display HCO_3^- mixed cations ($\text{Ca}^{2+}/\text{Na}^+$) in the canals water, whereas, Na–Cl facies characterize all mineralized drain water. Dissolution of carbonate minerals by CO_2 dissolved in meteoric water and soil water produces HCO_3^- and Ca^{2+} . Therefore, surface water samples contain relatively higher bicarbonate and calcium concentrations than drain water (Table 1). The pH value changes little between 8.1 and 8.4 in the canals water, and it was even wider (7.6–8.6) in the drain water. The increase of pH value could be explained by the consumption of dissolved CO_2 gas by the aquatic plants (Livingstone, 1963), whereas the decrease of this parameter is primarily due to oxidation of organic matter, which could lead to further amounts of HCO_3^- and H^+ species, according to the following reaction (Kempfe, 1984):



The surface water of canals is fresh (TDS, 290 to 674 mg/l) while being fresh to slightly brackish (TDS, 756–2497 mg/l) in drains water, (Tables 1 and 2). The average concentrations of Ca^{2+} , K^+ , HCO_3^- , SO_4^{2-} , Cl^- ,

Na^+ , TH, SAR and Mg values of the drain water are greater compared with canals water. Also, the mean values of NO_3^- concentrations are 17.5 and 24.2 mg/l in canals and drains water, respectively, indicating that these waters did not exceed the allowable level given for domestic uses (45 mg/l), except for the sample 7 at Bahr El-Baker drain (81.4mg/l). On the contrary, the concentration of TOC in canal water is considerably low being up to 2046mg/l while rises up to 3972mg/l for drain water. likewise, COD concentration in canal water is 136mg/l and rises up to 750mg/l for drain water, ammonium concentrations of surface water (is 8.6mg/l) for drains water while reduced about 4 times in the canals water (2.41mg/l) exceeding the maximum limits of WHO for drinking water (10, 10 and 0.5 mg/l) respectively. This behavior could be interpreted by the microbiological consumption of nitrate, with the presence of organic matter, according to the following reaction (Kempe, 1984):



Surface water is characterized by high Na^+/Cl^- ratio (>1) with small change between ~ 1.29 in canals water and ~ 1.32 in drain water. For canals water, the ratios of $\text{HCO}_3^-/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{Cl}^-$, $\text{Ca}^{2+}/\text{Mg}^{2+}$ and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ are also high (mean 1.31, 0.76, 1.71 and 1.53 respectively) compared to drain water (mean 0.42, 0.74, 1.4 and 0.69 respectively). Conversely, the value of Na^+/K^+ ratio is higher in drain water (mean 36.97) with respect to canals water (mean 16.76) whereas, the $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ ratio is similar for both canals and drain water (~ 0.8).

In general, the water chemistry of group A and group B is nearly similar to that of canals and drain water, and largely reflects mixing of groundwater with surface water in the southern and central region. whereas, group C reflects further modifications that may be due to recycling, evaporation, ion exchanges and precipitation of carbonates or saline water intrusion in the northern region of the study area.

Water type, hydrochemical relations and origin of solutes:

The dissolved species ratio were studied in an attempt to identify the origin of salinity and to separate mixing mechanisms of freshwater and saline water from the main geochemical processes occurring in the aquifer, such as ion-exchange processes.

Piper diagram, (1953) provides a convenient method to classify and compare water types based on the ionic composition of different water samples (Keenan, 1994) Piper trilinear diagram shows that the groundwater is characterized by four chemically different groundwater facies, namely Na– HCO_3 (14.3 %), Na–Cl (78.6 %), Ca– HCO_3 (5.3 %) and Na– SO_4 (1.8 %) (Fig.7).

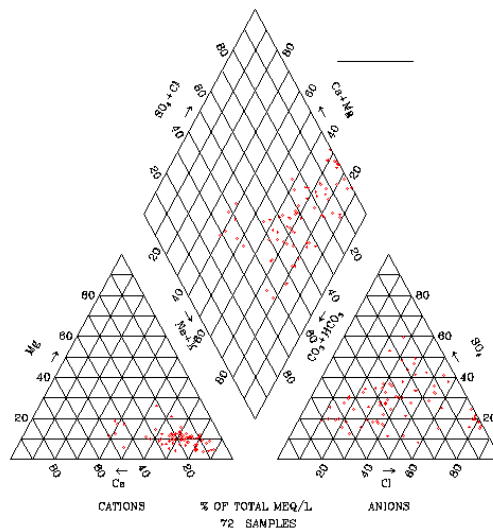


Fig. 7: Piper diagram of the groundwater in Quaternary aquifer of the study area.

Also, most of the ions (Na^+ , Br^- and Mg^{2+}) are positively well correlated indicating that such ions are derived from the same source of saline waters. Sodium increases linearly with chloride (Fig. 8, A) with high correlation coefficient ($R^2 = 0.98$). In particular, the groundwater samples of group A and 76% of group B falls on or above 1:1 halite dissolution line and show Na^+/Cl^- ratios up to 4.1, respectively (Fig. 8,B). This value reflects an increase of sodium relative to chloride. Conversely, group C samples lie below the 1:1 line. These samples, at the northern part of the study area, have Na^+/Cl^- ratio lower than 1.0 close to or slightly below the

seawater ratio of 0.86. The decrease of sodium relative to chloride as well as increasing of $(Ca^{2+}+Mg^{2+})/(HCO_3^- + SO_4^{2-})$ ratio (Table 1 and 2) likely predominates the effects of reverse cation exchange activity of Na^+ for Ca^{2+} and Mg^{2+} on clay fraction of the aquifer material, rather than seawater intrusion. In addition, leaching of salt precipitated through evaporation of surface water and soil moisture can be another dominant process in this context of semi-arid lands.

Since Br^- and Cl^- are ubiquitous solutes in hydrological systems, both species have often been used as a reliable indicator of the origin of salinity due to its specific composition in various saline sources. In general, the content of bromide in groundwater is low (Hitchon *et al.*, 1999). Nevertheless, high concentrations of this element sometimes occur in groundwater by pollution, interaction with seawater or reaction with evaporite deposits.

A contribution of evaporate dissolution leads to a low Br^-/Cl^- molar ratio (Cartwright *et al.*, 2006 and Ghabayen *et al.*, 2006) whereas anthropogenic sources give a ratio around 0.0005 for wastewater seepages or around 0.02 for agriculture return flows (Andreasen and Fleck, 1997; Ghabayen *et al.*, 2006 and Vengosh *et al.*, 1999). Finally, seawater has a Br^-/Cl^- molar ratio around 0.00015 in Mediterranean countries (Jones *et al.*, 1999 and Vengosh *et al.*, 1999). In water located south and middle of the study area, bromide concentration is as low as 0.145 meq/l (group A and group B); on the contrary, its content in waters of group C is high (up to 1.92 meq/l). Plot of Br^- and Cl^- concentrations, (Fig. 8,C) shows Br^- excess relative to Cl^- with a strong correlation coefficient ($R^2 = 0.95$). The bromide content increases gradually according to the following sequence: group A \rightarrow group B \rightarrow group C along groundwater flowpath suggesting that Br^- is released in the direction of groundwater flow. The Br^- increase for the most saline samples could be explained by the degradation of organic matter which is known to be a source of Br^- (Richter and Kreitler, 1993). Accordingly, intensive agricultural activities and irrigation-water returns to the aquifer are expected to be one of the major salinization sources to the aquifer.

Magnesium, among the major elements in groundwater, can be taken as representative of salt water occurrence, as it is seldom found with similar concentrations in groundwater (Hem, 1992).

In the study area, all magnesium contents are far below those of seawater (110.5 me/l), ranging from 0.88 to 66.6 me/l. The Mg^{2+} versus Cl^- graph (Fig. 8, D) indicates an excess of Mg^{2+} in the more saline water (group C). This excess may be linked to the flushing of marine formations in the northern part of the study area.

Ca^{2+}/Mg^{2+} values (Table 1) were all higher than the seawater ratio (0.2). The lowest value of 0.49 and the highest value of 2.4 were found in the group A (south region), whereas, the values of the more saline water, in the northern region, are close to 1.0. According to the interpretation of this index, the water in the study area appears to be of inland origin, because groundwater under marine influence would have values of about 0.2 (Morell *et al.*, 1986) except where other processes such as cationic exchange intervene when the values could be >0.25 .

The examination of the relationship between $(Ca^{2+} + Mg^{2+})$ with respect to $(HCO_3^- + SO_4^{2-})$ can reveal the importance of carbonate, sulfate and silicate minerals in the dissolution processes. The 1:1 stoichiometry ratio for $[Ca^{2+} + Mg^{2+}]$ to $[HCO_3^- + SO_4^{2-}]$ should exist if these ions are derived from simple dissolution of calcite, dolomite and gypsum, then a charge balance should exist between the cations and the anions. As indicated in Fig. 8, E, a deficiency of $(Ca^{2+} + Mg^{2+})$ relative to $(HCO_3^- + SO_4^{2-})$ exists in group A and 91% of group B groundwater samples. Therefore, the excess negative charge of SO_4^{2-} and HCO_3^- must be balanced by Na^+ , the only other major cation, whereas, all the samples of group C are falling below the 1:1 trend, reflecting the requirement of cations from weathering of silicate rocks.

The HCO_3^-/Cl^- values (Fig. 8, F), ranged from 0.005 in group C (northern region) to 4.2 in group A (southern region). Values of this hydrogeochemical index given for inland waters are between 0.2 and 10 and for seawater between 0.05 and 0.02 (Custodio, 1987). Thus, the value less than 0.05 for the northern region (0.0152), (Table 1) might be explained as the case of marine origin sediments that had not been completely flushed by the water initially saturating them rather than the effect of seawater.

Hydrochemical process controlling groundwater chemistry:

Gibbs diagram (Gibbs, 1970) represents anionic $[Cl^-/(Cl^- + HCO_3^-)]$ and cationic $[Na^+/(Na^+ + Ca^{2+})]$ relations as a function of the Log (TDS) in the groundwater samples of the Quaternary aquifer. This diagram is widely used to assess the functional sources of dissolved chemical constituents, such as precipitation dominance, rock dominance and evaporation dominance. Figure 9 indicated that groundwater samples for all groups were individually scattered in the rock and evaporation dominance fields. Group A, (fresh water) and group B, (brackish water) show rock dominance, whereas group C shows more evaporation dominance.

Evaporation of water in the unsaturated zone is the main process in the evolution of groundwater chemical composition. It greatly increases the concentration of ions formed by precipitation and deposition of evaporates that are eventually leached into the saturated zone, leading to high salinity of groundwater.

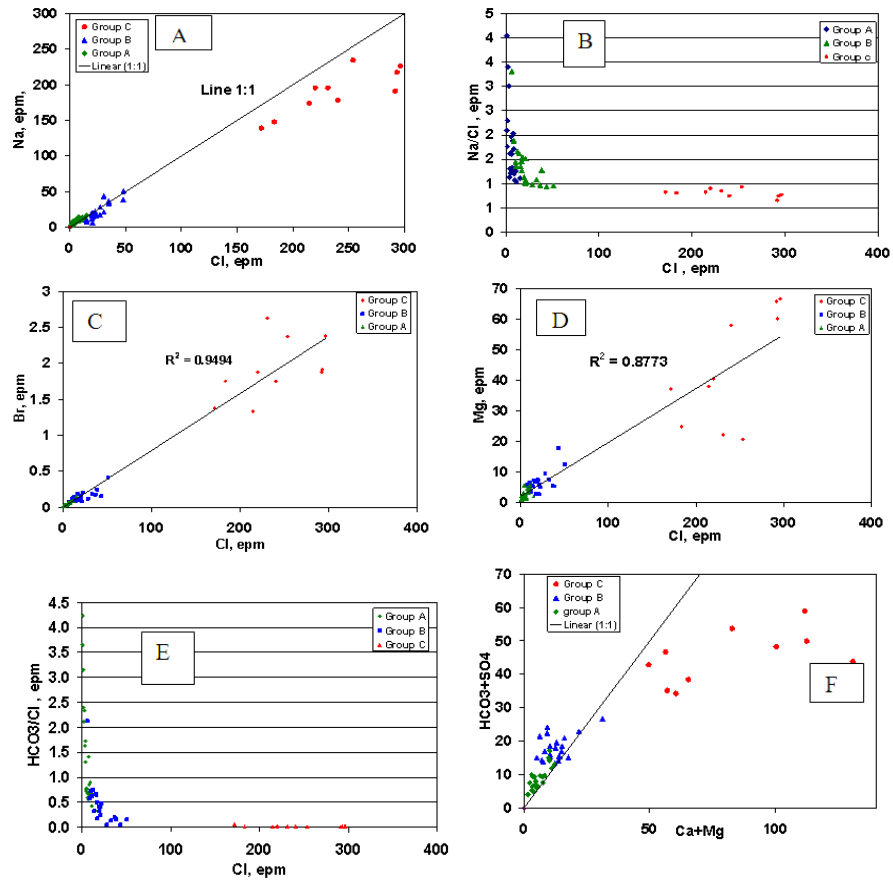


Fig. 8: Relationships between major and minor ions and their ionic ratios for groundwater.

Ion exchange is another important process occurring in aquifer that responsible for the concentrations of ions in groundwater, and therefore, plays a temporary buffer role when ionic concentrations are variable. The evidence for cation exchange is provided by a diagram of $(Ca^{+2} + Mg^{+2}) - (HCO_3^- + SO_4^{-2})$ as a function of $(Na^+ - Cl^-)$ in meq/l, as shown in Fig. 10. The $(Na^+ - Cl^-)$ represents the amount of Na gained or lost relative to that provided by gypsum, calcite and dolomite dissolution. If cation exchange was an important composition-controlling process, the relation between these two parameters would exhibit an inverse proportional evolution, (Mc Lean *et al.*, 2000). The groundwater samples plot is along a straight line ($R^2 = 0.988$) indicating that ion exchange has taken place in the groundwater. Moreover, Fig. 10 indicates an increase in Na^+ related to a decrease in $(Ca^{2+} + Mg^{2+})$ or an increase in $(HCO_3^- + SO_4^{2-})$ with respect to group A and group B. This indicates that almost all Na^+ , Ca^{2+} and Mg^{2+} participate in the ion-exchange reaction and may be considered as the dominant process that would explain the less mineralized Na/Ca-HCO₃ water type (Garcia *et al.*, 2001). It is also noteworthy that samples of group C implies that the cation exchange sites preferentially adsorb Na^+ and discharge Ca^{2+} and Mg^{2+} .

Sources of salinity in groundwater:

The salinization process is often linked to cation-exchange reactions (Appelo and Geinaert, 1991; Appelo and Postma, 2005 and Andersen *et al.*, 2005). These ion-exchange processes account for the increase or decrease of the cations involved in the reactions. To understand and differentiate the sources of salinity and other geochemical processes that take place in the aquifer during fresh/salt water mixing, ionic delta (Δ) and saturation index (SI) were calculated. According to (Appelo and Postma, 2005) the ionic deltas were calculated based on the theoretical mixing of fresh/ salt water, and comparing the theoretical concentrations calculated from the chloride concentration of the sample with the actual concentration of each constituent found in the studied groundwater samples. The concentration of each ion (i) in the theoretical mixing of fresh/salt water ($m_{i,mix}$) is:

$$m_{i,mix} = f_{sea} \times m_{i,sea} + (1 - f_{sea}) \times m_{i,fresh}$$

Where $m_{i,sea}$ and $m_{i,fresh}$ (in me/l) are the concentrations in seawater and freshwater of the species (i) and f_{sea} is the fraction of seawater in mixed freshwater-seawater. The seawater fraction is normally calculated based on chloride (in me/l) since chloride is assumed to be a conservative tracer (Tellam, 1995) and it not usually removed from the system due to its high solubility (Appelo and Postma, 2005):

$$f_{sea} = (m_{Cl,sample} - m_{Cl,fresh}) / (m_{Cl,sea} - m_{Cl,fresh})$$

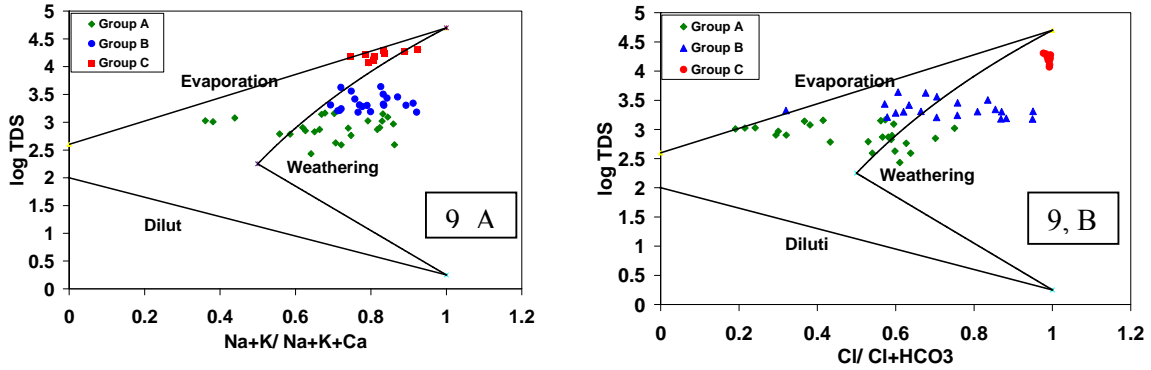


Fig. 9: Gibbs plots for cations (A) and anions (B).

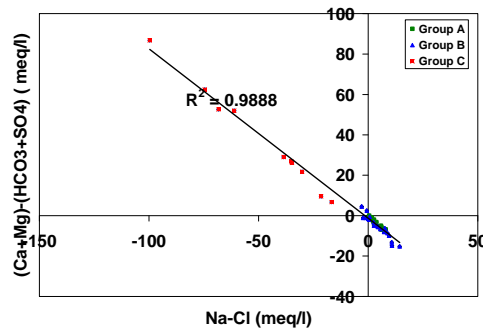


Fig. 10: plot of Na-Cl versus (Ca+mg)-(SO₄+HCO₃).

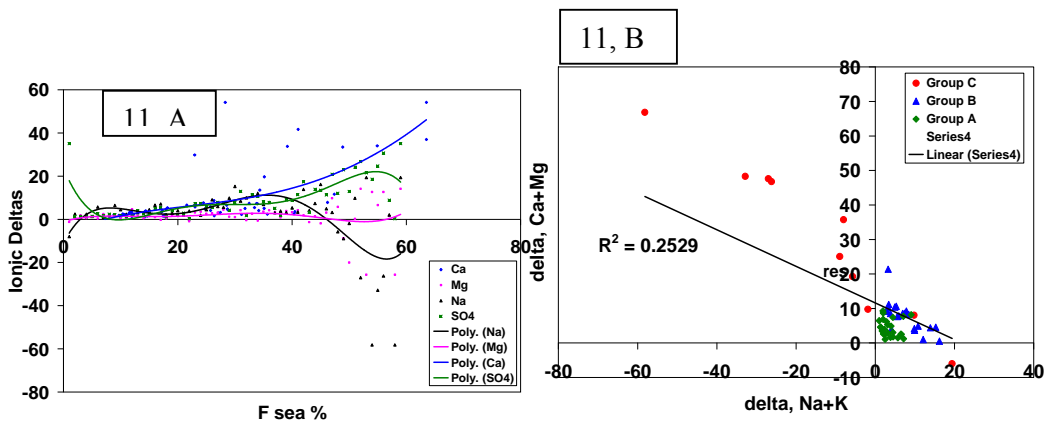


Fig. 11: Plots of ionic deltas versus percentage of sea water function A and delta(Na+K) versus delta (Ca+Mg) B.

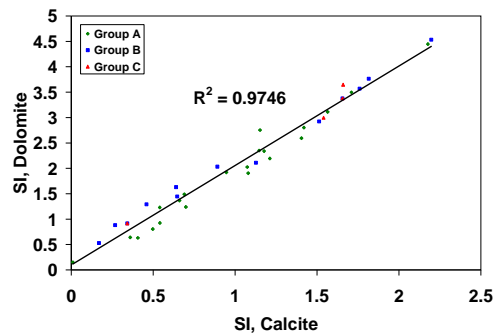


Fig. 12: Plot of saturation index of calcite versus saturation index of dolomite.

For each ion i , the difference between the concentration of the theoretical mixing and the measured one simply represents the concentration resulting from any chemical reaction occurring with mixing:

$$Dm_i = m_{i, \text{sample}} - m_{i, \text{mix}} :$$

percentage of seawater fraction (f_{sw} %) and A positive Δm_i indicates the groundwater to be increased for species i , and a negative Δm_i indicates decrease compared to a simple non-reactive mixing. In this study, the

ionic delta (Δm_i) of $\text{Na}^+ + \text{K}^+$, Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} were calculated for all groundwater samples in the study area (Table 3). The various geochemical processes that occur in the groundwater indicated that the process of hydrogeochemical changes in the Quaternary aquifer was complex and displayed a heterogeneous pattern in the studied ions.

The results show high saltwater contribution (Table 3). The aquifer contains high saltwater (up to 63.5 %) in its northern part, whereas the saltwater proportion ranged from 7.3 to 63.5% (mean 26.3%). It has been found that the fractions of saltwater are (mean 16.2 %) for group A, about double 31.2 % for group B and up to about four folds 63.5 % for group C. The most marked pattern could be observed in major cations. Overall, as the percentage of saltwater increases, the water becomes increasingly in Ca^{2+} and Mg^{2+} while Na^+ is decreased; ΔCa and ΔMg behave in analogous trend, and reveal opposite trend to $\Delta \text{Na}^+ + \Delta \text{K}^+$, Figure 11, A. The cation evolution shows two different trends according to the increase of salinity. For the samples containing up to 31.2% saltwater (group A and group B), Ca^{2+} , and Mg^{2+} are slightly variable (2.9 to 5.1 and -1.5 to 2.5 me/l, respectively) and are accompanied with Na^+ increase from 3.7 to 7.7%. This reveals an increase of cation exchange processes along the flowpath. Nevertheless, the increase of Na^+ is more evidenced than the Ca^{2+} and Mg^{2+} and suggests that another process affects the Na^+ content such as halite dissolution. These observations imply that mineral dissolution is the predominated process in group A and group B water. Samples containing more than 31.2 % salt water (group C) shows high decreases in $\text{Na}^+ + \text{K}^+$ (up to -58.1 %) according to the increase of salinity. This variability could be linked with higher increase in Ca^{2+} up to about 54.1 % according to the increase salinity. For the most saline group (C), high calcium enrichment is accompanied by high sodium depletion. The heterogeneous patterns shown by these cations are most probably due to the direct contact between Na^+ highly enriched water (seawater/saline) with Ca^{2+} highly enriched water (fresh groundwater).

In general, the anions decrease or increase seems to be limited and less important. To clarify the positive trend of ΔCa and ΔMg , the $\Delta \text{Ca} + \Delta \text{Mg}$ is plotted against $\Delta \text{Na} + \Delta \text{K}$ for all groundwater samples. (Figure 11, B exhibits quite obvious negative relationship ($R^2 = 0.92$) and firmly confirmed the effect of reverse ion exchange reactions. This could explain the different types of exchange that can occur between groundwater and the clay matrix, (Robertson, 1991).

Saturation indices for equilibrium states of the groundwater:

To better understand the chemical changes that can occur in water as it moves through the ground during its percolation, movement and storage in the aquifers represent, the key factors in the groundwater chemistry, the chemistry of the water and aquifer materials and the interactions between them are examined. One aspect of such geochemical interactions is the dissolution and precipitation of minerals along flow paths in the groundwater system. The saturation indices (SI) is a measure of the departure from equilibrium of the water with respect to various minerals phases as $\text{SI} = \log (\text{KIAP} / \text{KSP})$, where KIAP is the ionic activity product,

Table 3: Percentage of seawater fractions, ionic deltas and saturation indices of groundwater

Sample No.	f_{sw} (%)	$\Delta Na^+ \Delta K$	ΔCa	ΔMg	ΔSO_4	ΔHCO_3	Calcite	Dolomite
Group A (Fresh water)								
22*	17.92	2.86	4.562	1.603	3.917	4.983	0.01	
26*	28.74	7.07	4.562	3.165	7.204	6.732	1.42	1.28
29*	17.43	7.15	1.485	-0.264	5.320	3.736	1.08	0.94
32	24.77	4.43	4.864	2.545	5.810	7.121	1.41	1.26
44	12.29	3.20	2.359	0.490	2.502	3.737	0.41	0.26
46	17.32	3.10	3.815	1.474	3.936	4.995	1.18	1.03
47	21.58	1.98	6.557	2.154	2.906	7.977	0.95	0.80
49	11.90	2.36	3.401	0.524	1.469	4.139		
50	23.01	1.92	5.747	3.541	7.327	4.472	1.15	1.00
51*	14.67	4.44	1.527	1.512	2.958	4.240	1.21	1.07
52	10.71	1.70	2.243	1.284	2.436	3.045	1.15	1.01
55	17.13	3.98	3.453	1.454	2.065	6.178	0.54	0.40
58	14.26	5.68	1.162	0.348	2.621	4.451	0.66	0.57
59	9.71	2.41	1.843	0.586	1.168	3.704		
60*	17.96	6.49	0.986	1.591	2.143	6.747	0.54	0.4
61	11.46	1.36	2.721	1.803	1.271	4.306	0.7	0.55
64	10.38	3.83	2.515	-0.901	0.226	4.710	0.50	0.35
65*	7.28	2.48	0.427	0.639	1.174	2.557	0.36	0.22
66	11.61	1.33	3.298	1.329	1.401	4.255		
67	14.38	0.97	3.977	2.488	1.697	5.248		
68*	17.68	6.55	1.527	0.991	4.871	3.740	1.07	0.93
69	17.81	2.00	2.188	4.651	1.834	7.145	0.69	0.55
70	11.95	4.49	1.304	0.469	1.603	4.091	1.71	1.57
71	33.42	9.06	5.440	2.774	5.517	10.633	2.18	2.03
72	8.83	2.04	2.180	0.443	1.117	3.045	1.57	1.42
Mean	16.17	3.715196	2.966	1.468	2.980	5.040		
min	7.28	0.967083	0.427	-0.901	0.226	2.557		
max	33.42	9.061394	6.557	4.651	7.327	10.633		
Group B (Brackish water)								
18*	27.13	3.38	6.972	4.212	11.398	1.167	0.17	0.02
20	35.68	16.19	2.372	-1.824	13.513	5.432	0.34	0.20
21	33.96	7.34	7.227	1.392	13.942	4.051	1.66	1.51
30	32.50	5.29	7.394	3.253	8.768	7.795	1.76	1.62
31	28.68	5.92	4.790	3.107	7.833	7.025		
33	28.57	3.22	6.518	3.824	9.013	5.993	2.20	2.05
34	35.11	7.85	5.086	4.168	7.800	10.205		
35	27.46	5.55	3.199	4.480	7.755	6.471	0.27	0.12
36	33.77	4.93	7.337	3.073	11.292	7.140	0.89	0.75
37*	40.34	13.89	2.544	1.853	17.359	4.690	0.64	0.5
38	31.76	6.91	5.050	3.512	8.138	8.152		
40*	47.39	3.23	11.629	9.757	20.911	1.866		
41	40.48	15.25	3.527	1.054	7.716	12.934		
45*	26.38	12.07	1.630	-0.628	10.605	2.701		
48*	34.16	8.46	4.042	4.206	12.965	4.482		
53	27.09	9.84	2.950	1.211	4.274	8.817	1.82	1.63
54*	31.16	10.80	2.274	2.616	11.256	4.213	0.46	0.32
56	18.19	4.06	5.352	-1.334	3.246	6.867		
57	25.71	3.04	5.802	3.392	5.119	8.358	0.65	0.50
62	24.48	3.84	7.642	0.894	1.825	10.283	1.51	1.37
63	25.73	9.92	4.103	-0.405	1.712	10.403	1.13	0.98
mean	31.23	7.665916	5.116	2.467	9.354	6.621		
min	18.19	3.041127	1.630	-1.824	1.712	1.167		
max	47.39	16.18675	11.629	9.757	20.911	12.934		
Group C (Saline water)								
17	63.51	-8.02	36.960	-1.228	35.052	0.751		
19	41.05	-32.83	41.656	6.616	24.721	0.891		
23	28.30	-58.18	54.182	12.657	18.593	1.045		
24	48.87	-27.01	33.473	14.152	26.793	1.466		
25	39.18	-8.98	33.785	-8.722	22.940	0.154		
27	22.95	-1.87	29.820	-20.033	12.939	2.095	1.54	1.40
28	35.14	19.39	19.684	-25.670	21.569	0.171		
39	54.90	-26.21	34.067	12.682	30.730	3.630	1.66	1.52
42	46.21	9.80	7.825	0.228	24.224	4.131	0.34	0.20
43	34.35	-5.75	13.531	5.744	12.073	8.746	1.66	1.51
mean	41.45	-13.9670	30.498	-0.357	22.963	2.308		
min	22.95	-58.1804	7.825	-25.670	12.073	0.154		
max	63.51	19.3870	54.182	14.152	35.052	8.746		

KSP is the solubility product, and SI is the saturation index of the concerned mineral. When the saturation indices of minerals are equal to zero, the solution is considered saturated with these minerals. Positive values indicate super-saturation with minerals (precipitation is possible) and negative values indicate under-saturation conditions (dissolution of the mineral is possible). The saturation indices SI of the major mineral phases in the investigated groundwater samples were calculated using the software package NETPATH for windows, (El-Kadi *et al.*, 2010). The obtained results (Table 2 & Figure 11) reflect that:

Except for 77 and 88 % of group A and group B samples, the SI of calcite and dolomite are close to or above zero confirming that the Ca^{2+} and Mg^{2+} increase is due to cation exchange and not to carbonate dissolution. Dolomite or calcite precipitation is likely to occur in the Quaternary aquifer. The most saline group(C) also show calcite supersaturation ($\text{SI}_{\text{Calcite}} \sim +1$). The evolution of calcite and dolomite saturation indices shows a similar trend when plotted against the percentage of seawater fraction along groundwater flowpath (Fig. 12). Such trend shows the usual distribution in groundwater, where mineral saturation is gradually attained along the flowpath as a function of water residence time within the aquifer (Plummer *et al.*, 1990).

Surface water-Groundwater pollution:

From surface water seepage to groundwater, the anthropogenic environmental impacts of sewage water irrigation on the general groundwater quality will be evaluated according to the variations of these items:

- 1- Total organic carbon (TOC)
- 2- Chemical oxygen demand (COD)
- 3- Nitrate NO_3^-
- 4- Ammonia (NH_4)

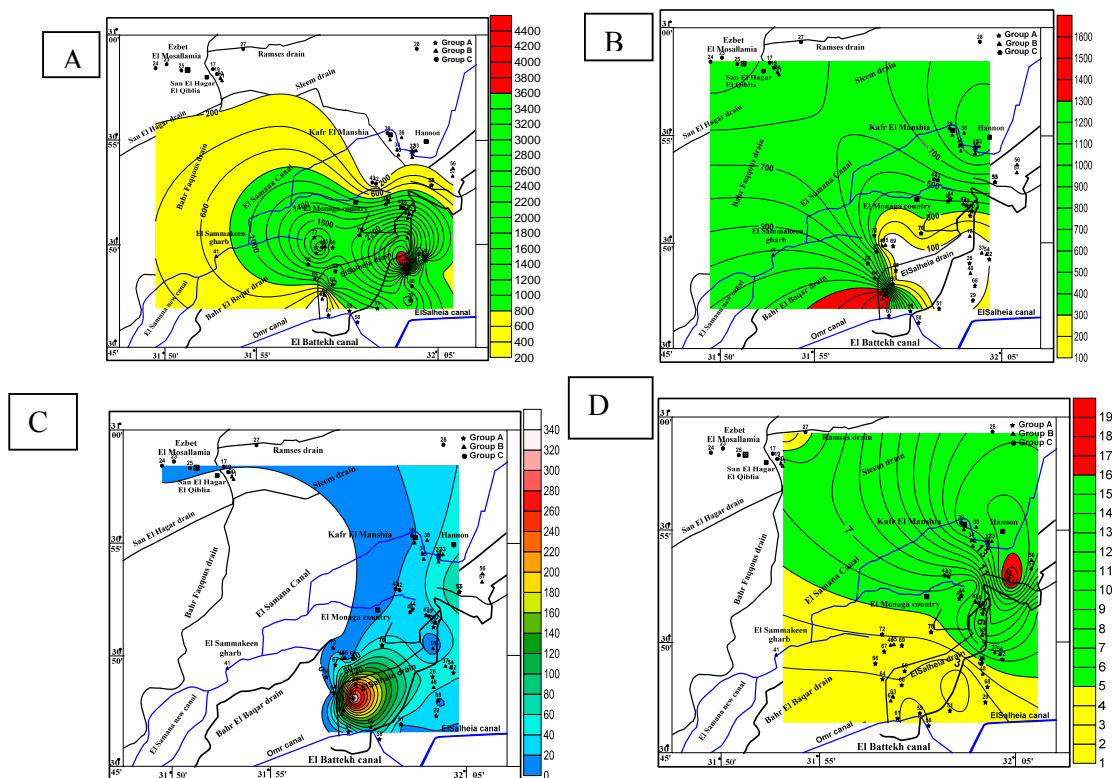


Fig. 13: Iso contour maps of (A)TOC, (B) COD, (C) NO_3^- and (D) NH_4 of groundwater in study area.

1- Total Organic Carbon (TOC):

Results in Table (2) revealed that in the representative water samples of canal, drain and groundwater in study area, the concentration of TOC varies widely from 15.0 to 4524mg/l, indicating polluted water according to the acceptable limit 10mg/l for fresh water . The high value of TOC is related to disposal of sanitary

wastewater in agricultural canals and drains that infiltrate to such aquifer as well as downward infiltration of excess amount of irrigation water containing fertilizers man used and pesticides, Fig.(13, A)

In canal water, TOC varies from 580 to 2046mg/l with a mean of 1451mg/l while in drain surface water, is changed from 16 to 3972mg/l with a mean of 933mg/l. Also, the concentration of TOC in group A (fresh water) ranges from 49 to 4524mg/l and in group B (brackish water) ranges from 15 to 3089mg/l with a mean of 1032mg/l. On the other hand, in the group C (saline water) TOC ranges from 32-81mg/l with a mean of value 59.2mg/l. This means that, the water of groups A and B are more affected by the seepage of surface water than group C.

2- Chemical Oxygen demand (COD):

The results of the representative waters samples of canal, drain and groundwater have COD values that vary from 9.7 mg/l to very high values of COD (1607 mg/l) with a mean value of 237mg/l. This means that, all samples have more than the acceptable level of pollution for fresh water (10 mg/l) except Nos. 5 and 8 from canal water, table 2. All water samples of fresh and brackish groundwater have the concentration greater than the saline groundwater due to the intensive drain ago of waste polluted water. This is attributed to excess amount of irrigation water containing organic manures fertilizers and pesticides beside the sewage wastewater and many industrial activities in the city, Fig. (13, B)

3- Nitrogen compounds:

The nitrogen compounds play an important role in many processes that takes place in natural water. Nitrogen is also one of the basic components of proteins, so it can enter surface water in sewage and industrial wastewater from the breakdown of proteins and other nitrogenous compounds. Nitrogen fertilizers are used extensively in agriculture, and the excess overcrop requirements is mostly leached into drainage water.

A-Nitrate content:

The concentration of NO_3^- in the water samples of the study area, (canal, drain and groundwater) varies widely. For instances, its content in the groundwater samples ranges from 0.1 to 337.6mg/l with a mean of 47.8mg/l. In canal water samplers, low nitrate concentrations (3.5-37.6 mg/l) with a mean of 14.7mg/l are recorded except for samples Nos. 8 and 13 which have relatively high concentrations (24.3 and 37.6mg/l) but still below the level of pollution (45 mg/l) as in table (2). But, in drain water, the concentration ranges from 3.56- 81.4mg/l with a mean value of 24.2mg/l. On the other hand, the nitrate ion concentration in group A varies from 5.1-337.6mg/l with a mean of 80.5mg/l and in group B ranges from 0.1-81.4mg/l with a mean value of 42mg/l. Conversely, in group C, the concentration of NO_3^- in the representative groundwater samples is low, Fig. (13, C).

B- Ammonia content:

The concentration of NH_4^+ in water samples, (canal, drain and groundwater) ranges from not detected to 21.6mg/l with a mean of 2.8mg/l. In canal water samples, NH_4^+ ions have low concentration (1.3-3.6mg/l) with a mean of 2.3mg/l, table (2). But in drain water, the concentration ranges from 2.0- 18.9mg/l with a mean value of 8.6mg/l. The relatively high concentration of NO_3^- and NH_4^+ compared to that of canal water is referred to the excess amount of nitrogen fertilizer and manures used in this cultivated area. On the hand, the NH_4^+ ions concentration in group A varies from 0.02- 4.05mg/l with a mean of 1.1mg/l and in group B ranges from 0.008-21.6mg/l with a mean value of 3.47mg/l. Also, in group C, the concentration of NH_4^+ ranges from 0.056-3.01mg/l with a mean value of 0.72mg/l. The increases of concentration are confirmed to the groundwater flow from southwest to northeast, Fig. (13, D).

Generally, the high concentration of nitrate ions and ammonia are due to the excess nitrogen manusing and fertilization, seepage of irrigation canals and drains as well as the disposal of sanitary wastewater rich in nitrate content in canals and drains water in some localities.

Conclusion:

To improve groundwater quality of the quaternary aquifer of the Eastern Nile Delta and to avoid water salinization and pollution problems, we recommend that:

- (1) Drilling of wells in the northern portion of the study area should be minimized, controlled or even forbidden to avoid highly saline groundwater supply.
- (2) Treatment processes must be used for sewage and drainage water before irrigation.

(3) Fertilizers use and additives in the agriculture areas, management must be reduce to prevent or minimized groundwater pollution. So, connecting an advanced sanitary drainage network in the urbanizing areas can solve this problem.

(4)Monitoring both surface and groundwater to detect and prevent the transport of pollution.

In short, the results obtained can help in planning, protection and decision- making regarding the groundwater management of the Quaternary aquifer in the Eastern Nile Delta.

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