

## Hydrogeochemistry of El-Negila basin, North Western Coast to delineate the best sites of water desalination for sustainable development

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**Abstract:** Egypt is one of many regions in the world that suffer from water shortage which impose constraints on economic, social and human development. The fast growing development in Egypt has required big movements of investments and people from the Nile Valley towards the west and fantastic North Western Coast of Mediterranean Sea. Although Egypt has already reached the water poverty limit, it possesses a high potential of brackish groundwater available from different aquifers. Brackish groundwater desalination is one of Egypt's most potentially significant water resources. Effective selection of desalination plant location depends on considering several factors concerning geomorphology, geology, hydrology, hydrogeochemistry and quality of groundwater resources. The groundwater is a wide variation in chemistry caused by pumping aquifers based on the local geology and hydrology parameters. Monitoring of these possible water chemistry studies should be accomplished prior to the final design of any desalination plant. Due to the complexity of groundwater chemistry; it is studied several factors, these factors will be studied based on the total dissolved solids (TDS), hardness, concentration of major, minor and trace components add to ion ratios and hypothetical salts. The results of the analysis of water samples collected from the study area show wide ranges of TDS (344-18063 mg/l), total hardness (100-6714 mg/l as CaCO<sub>3</sub>) and chloride concentration (67-8465 mg/l). Also, the presence of metals such as iron and manganese is observed. Moreover, according to chemical characteristics of the groundwater, best sites for possible desalination projects were selected.

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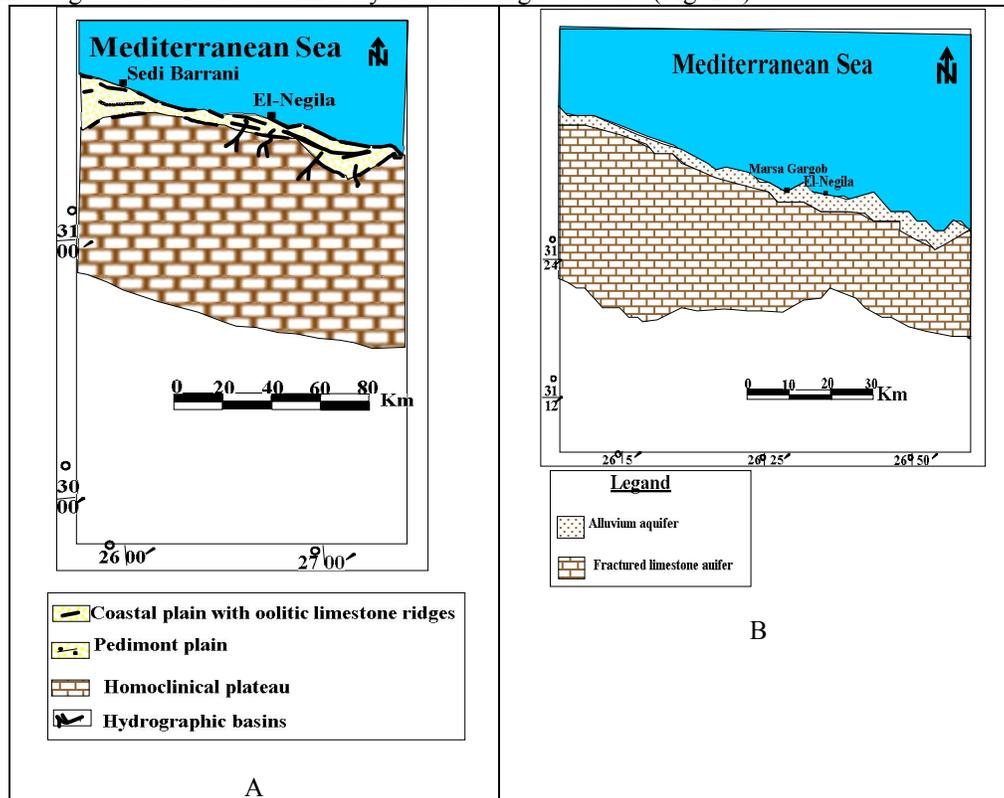
### 1. Introduction

Water is the most essential element for life. Not only it is vital for all organisms and ecosystems, but also constitutes the key for economic development. Many countries in the world suffer from a shortage of natural fresh water. Increasing the amounts of fresh water will be required in the future as a result of the rise in population rates and enhanced living standards, together with the expansion of industrial and agricultural activities. Available fresh-water resources from rivers and groundwater are presently limited and are being increasingly depleted at an alarming rate in many places. The oceans represent the earth's major water reservoir. About 97% of the earth's water is seawater while another 2% is locked in icecaps and glaciers. Available freshwater accounts for less than 0.5% of the earth's total water supply [1]. In the 21<sup>st</sup> century, the most crucial problem afflicting people around the world is global water scarcity. It is projected that by year 2030, the global needs of water would increase to 6900 billion. m<sup>3</sup> from current 4500 billion.m<sup>3</sup> [ 2].As a result, the present surface water resources will no longer be sufficient to meet the future need for mankind. Egypt is facing water

scarcity (especially in coastal areas) as a result of over population, industrialization, agricultural expansion and increasing conflict of the current Egyptian-Ethiopian's dam problems[3]. The rapid development of tourist resorts along the North Western Coast of Mediterranean Sea, which has exhausted water demand for tourist resorts. This had led to a wide spread need the development and management of regional water resources. In order to secure fresh water demand for this arid area, desalination concept has to be widely utilized. Desalination is one of the most important factors that can help in developing remote areas and the desert. Water desalination is the method by which brackish water can be changed to fresh water suitable for drinking and irrigation and other uses of people and animals. Desalination started in Egypt more than 100 years ago, its main objective at that time, was to produce fresh water for domestic use in the areas far from the public water network, however, Egypt began to apply advanced desalination technologies in the mid-seventies as a result of the continuous population growth and the urban expansion along the coastal zone and in remote areas,



The investigated area is characterized by the following landforms (Fig. 2A):



**Figure (2)** The main geomorphological units. (A) and Geological map, (B) along northwestern coastal zone. [7].

It acts as a major catchment area feeding the drainage lines during winter times. The plateau runs from the Qattara Depression southward to the piedmont plain northward with elevation varying from 100m at Fuka area to 160m at Baqqush area and it reaches 25m at Matruh escarpment [7].

The hydrological matrix material tends to control the type of chemical composition changes in the water yielded to the wells. Two aquifers are recognized in the study area as shown in (Fig. 3). The first is the Quaternary alluvium aquifer. It occupies the main trunk and the deltas of some drainage basins. It is composed mainly of loose pebbles, cobbles and gravel mixed together with fine sand and silt. These types of deposits have limited distribution and are unconfined to semi confined in the downstream of wadi channels. The main sources of groundwater recharge are precipitation and draining of wadis streams. The second aquifer is the fractured limestone; it is composed of limestone with few clay intercalations so certain amounts of rainwater percolate both through joints and solution channels as well as through the primary porosity to the top of the successive clay layers, which form the impervious media. Such occurrences of groundwater are in the form of separated thin sheets accumulated

above the contact with the impervious clays alternating with the porous limy strata [7].

### 3. Sampling and analytical techniques

In order to evaluate the variations in chemical compositions, sixty eight groundwater samples were collected during September 2013, (Fig. 1). The samples were preserved and analyzed according standard methods [8-12]. The analyses were carried out by the authors at the Central Laboratories, Water and Soil analysis unit, Desert Research Center (DRC). EC and pH were measured in the field immediately after the collection of the samples. Alkali metal ions ( $\text{Na}^+$  and  $\text{K}^+$ ) were measured using flame photometer (Jenway PFP 7). Total dissolved solids (TDSs) were computed by multiplying the EC (ds/m) by a factor of 640 [13].  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined titrimetrically using standard EDTA. Chloride was estimated by  $\text{AgNO}_3$  titration. Turbidimetric technique was used for the analysis of sulfate [14]. Standard solutions for the above analysis were prepared from the respective salts of analytical reagent grade. Heavy and trace metals were analyzed using inductively coupled plasma method. The obtained chemical data are expressed in milligram per liter (mg/l) or part per million (ppm). The results of all chemical analyses are listed in tables (1 & 2).

**Table (1) The hydrochemical results of groundwater samples of alluvium aquifer (2013)**

Well	pH	TDS	Unit	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	CO <sub>3</sub> <sup>--</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>--</sup>	Cl <sup>-</sup>
<b>Alluvium aquifer</b>											
1	8.1	1337	ppm	45.9	20.4	30	390	39.6	761.3	20	334.1
2	7.6	5549	ppm	310.8	118.3	72	1550	18	355.0	40	3192.8
3	7.3	14429	ppm	694.5	253.0	160	4250	10.8	135.4	400	8464.5
4	7.4	3958	ppm	377.2	161.2	86	742.66	14.4	424.6	28.6	2227.5
5	7.2	18063	ppm	1044.0	967.0	210	3800	Nil	172.0	6000	5816.3
6	7.8	439	ppm	50.6	46.9	15	24	Nil	311.1	34	66.8
7	6.7	3423	ppm	364.4	275.4	58	400	Nil	333.1	198	1782
8	7.6	3286	ppm	267.2	165.2	35	650	Nil	340.4	25	1819.1
9	7.7	962	ppm	86.0	79.6	16	150	Nil	322.1	7.14	420.8
10	7.4	1032	ppm	73.1	81.6	22	155	Nil	205	110	396
11	7.6	933	ppm	69.2	57.1	19	153.3	Nil	205	158	297
12	7.4	1207	ppm	100.6	34.7	25	260	Nil	333.1	80.0	495
13	7.6	2646	ppm	142.3	67.3	54	700	28.8	252.5	205	1274.6
14	7.9	4930	ppm	245.4	204	116	1250	14.4	179.3	100	2821.5
15	7.4	1331	ppm	73.9	104	24	250	Nil	303.8	140	507.4
16	7.7	2490	ppm	94.2	102	62	650	Nil	157.4	166.7	1237.5
17	8.0	2370	ppm	140.8	114.2	32	580	25.2	435.5	46.7	1163.3
18	7.9	4961	ppm	263.7	159.1	42	1350	18	380.6	240	2623.5
19	7.9	5110	ppm	320.2	191.8	43	1290	18	380.6	280	2722
<b>Fractured limestone aquifer</b>											
20	7.4	5424	ppm	207.2	222.7	1450	23	12	115.9	444.1	3006.9
21	7.6	4541	ppm	163.3	179.1	1250	21	27	131.2	316.8	2518.6
22	7.3	4874	ppm	155.4	191.2	1350	23	21	152.5	358.4	2698.5
23	7.4	4975	ppm	151.4	210.6	1400	23	33	152.5	253.8	2827
24	7.2	6929	ppm	211.2	244.5	1900	27	27	164.7	1250	3186.8
25	7.5	5985	ppm	143.4	208.1	1700	23	27	158.6	977.3	2827
26	7.0	8491	ppm	346.6	319.5	2250	32	Nil	167.8	1192.5	4266.2
27	7.3	6057	ppm	191.2	208.1	1800	28	24	155.6	721.3	3006.9
28	7.5	4641	ppm	175.3	142.8	1400	26	33	143.4	505	2287.3
29	7.1	7804	ppm	274.9	278.3	2150	35	9	149.5	1075.2	3906.4
30	7.6	7978	ppm	278.9	375.1	2050	33	15	106.8	906	4266.2
31	7.2	5903	ppm	223.1	232.3	1600	23	15	119.0	600	3150
32	7.2	5861	ppm	151.4	256.6	1600	25	15	158.6	675	3058.3
33	8.0	4797	ppm	151.4	198.5	1350	26	18	131.2	417.2	2570
34	7.6	5282	ppm	147.4	186.4	1500	23	27	119.0	640	2698.5
35	7.3	5565	ppm	199.2	198.5	1650	30	15	164.7	74.8	3315.3
36	7.8	4693	ppm	171.3	154.9	1350	26	18	125.1	237.9	2672.8
37	7.6	5910	ppm	223.1	186.4	1700	29	12	167.8	360	3315.3
38	7.5	5146	ppm	163.3	222.7	1400	26	24	140.3	340	2900
39	7.8	5100	ppm	227.1	183.9	1500	25	27	134.2	37.4	3032.6
40	7.6	6025	ppm	159.4	246.9	1750	30	21	128.1	490.1	3263.9
41	7.5	4929	ppm	159.4	186.4	1400	23	21	149.5	340	2724.2
42	7.7	6364	ppm	219.1	227.5	1800	26	24	134.2	600	3400
43	7.5	6477	ppm	334.7	150.1	1800	27	18	149.5	628.4	3443.8
44	7.6	4687	ppm	163.3	162.2	1300	23	27	122	600	2350
45	7.7	3550	ppm	85.6	83.4	1100	17	30	228.8	320.1	1799
46	8.3	5841	ppm	179.3	145.2	1750	32	0.0	51.9	650	3058.3
47	7.3	10140	ppm	262.9	350.9	2900	51	21	161.7	1230	5242.8
48	7.8	2945	ppm	97.0	141.4	780	17	33	207.4	179.5	1593.4
49	7.3	2700	ppm	103.6	107.5	720	15	21	200	382.8	1250
50	7.6	3759	ppm	94.0	133.6	1080	19	27	180	426.3	1889

51	8.4	344	ppm	31.9	4.8	86	4	Nil	97.6	40	128.5
52	7.6	6902	ppm	139.4	251.7	2100	33	18	219.6	1217.3	3032.6
53	7.5	13110	ppm	302.8	416.3	3900	76	21	164.7	1115.4	7196
54	7.6	3039	ppm	137.1	146.2	740	18	24	152.5	420	1477.8
55	7.7	1621	ppm	95.6	82.3	370	7	18	170.8	238.0	724.7
56	9.0	2470	ppm	74.9	115.2	650	17	21	183	400	1100
57	7.5	3687	ppm	82.9	169.4	1020	18	9	207.4	343.7	1940.4
58	7.5	5629	ppm	231.1	171.8	1550	24	3	219.6	712	2827
59	7.6	5329	ppm	219.1	186.4	1450	24	12	173.9	575	2775.6
60	7.2	4341	ppm	171.3	145.2	1200	32	Nil	237.9	540	2133.1
61	7.6	4681	ppm	171.3	208.1	1250	28	21	143.4	129.2	2801.3
62	7.4	7755	ppm	262.9	278.3	2200	46	18	173.9	390.7	4471.8
63	7.8	5018	ppm	179.3	145.2	1500	23	Nil	70.2	205.2	2929.8
64	8.1	2044	ppm	78.1	101.7	520	9	27	173.9	290.8	930.3
65	8.2	2361	ppm	95.6	135.5	580	11	39	112.9	81.7	1362.1
66	7.9	3497	ppm	106.0	123.6	1000	15	15	131.2	270	1901.8
67	7.0	5651	ppm	402.4	193.6	1300	17	Nil	216.6	1240	2390.1
68	7.5	7797	ppm	219.1	305.0	2350	36	21	140.3	530	4266.2
Sea water	8.1	42203	ppm	597.6	1415.9	12750	230	21	94.6	4525	22616
Rain water	7.9	68	ppm	15.1	1.5	7	1	Nil	27.5	6.4	23

Table(2) Heavy metals analysis for groundwater samples

No.	B	Cd	Cu	Fe	Mn	Pb	Sr	Zn
<b>Alluvium aquifer</b>								
1	3.614	<0.002	<0.02	2.011	0.0384	<0.01	0.0316	0.0203
2	1.325	<0.002	<0.02	1.002	0.3385	<0.01	0.1215	0.0218
3	2.799	<0.002	<0.02	1.352	0.0663	<0.01	0.1342	0.0092
4	1.948	<0.002	<0.02	4.366	0.6879	<0.01	0.1214	0.0898
5	7.544	<0.002	<0.02	1.128	0.186	<0.01	0.1242	0.0457
6	0.2755	<0.002	<0.02	0.5909	0.4712	<0.01	0.1123	0.0057
7	0.7801	<0.002	0.0444	6.624	1.227	<0.01	0.1213	0.098
8	1.418	<0.002	<0.02	1.922	0.0751	<0.01	0.1123	0.0279
9	0.3238	<0.002	<0.02	2.58	0.3763	<0.01	0.1203	0.0405
10	0.5299	<0.002	<0.02	1.525	0.0482	<0.01	0.052	0.0453
11	0.47	<0.002	<0.02	1.127	0.0427	<0.01	0.0221	0.0198
12	1.041	<0.002	<0.02	0.5617	0.0353	<0.01	0.0124	0.0237
13	1.361	<0.002	<0.02	1.209	0.0387	<0.01	0.162	0.012
14	0.9709	<0.002	<0.02	0.7482	0.0352	<0.01	0.0152	0.0043
15	0.4289	<0.002	<0.02	0.5451	0.0919	<0.01	0.0421	<0.002
16	0.4947	<0.002	<0.02	0.0986	<0.003	<0.01	0.0421	<0.002
17	0.7761	<0.002	<0.02	1.48	0.2893	<0.01	0.0421	0.0186
18	1.162	<0.002	<0.02	4.605	0.3035	<0.01	0.0241	0.0335
19	1.145	<0.002	<0.02	0.9309	0.444	<0.01	0.0421	0.0046
<b>Fractured limestone aquifer</b>								
20	0.8233	<0.002	<0.02	<0.01	<0.002	<0.01	6.343	<0.002
21	0.9511	<0.002	<0.02	<0.01	<0.002	<0.01	6.07	<0.002
22	1.045	<0.002	<0.02	1.279	0.0488	<0.01	6.74	<0.002
23	1.101	<0.002	<0.02	2.83	0.0309	<0.01	7.627	<0.002
24	1.264	<0.002	<0.02	1.899	0.2152	<0.01	9.504	<0.002
25	1.114	<0.002	0.0402	3.809	0.0345	<0.01	7.978	<0.002
26	1.068	<0.002	<0.02	0.0506	0.32	<0.01	9.178	<0.002
27	1.17	<0.002	<0.02	0.5278	0.1068	<0.01	6.008	<0.002
28	1.02	<0.002	<0.02	<0.01	<0.002	<0.01	4.615	<0.002

29	1.039	<0.002	<0.02	0.4723	0.0293	<0.01	8.657	<0.002
30	0.9773	<0.002	<0.02	0.0314	<0.002	<0.01	10.85	<0.002
31	1.04	<0.002	<0.02	0.168	<0.002	<0.01	10.12	<0.002
32	0.912	<0.002	<0.02	1.008	0.1907	<0.01	8.179	<0.002
33	0.9274	<0.002	<0.02	0.1371	0.0212	<0.01	4.092	<0.002
34	1.013	<0.002	<0.02	0.4732	0.0092	<0.01	4.191	<0.002
35	1.198	<0.002	<0.02	<0.01	<0.002	<0.01	5.106	<0.002
36	0.8143	<0.002	<0.02	0.9337	0.0275	<0.01	3.365	<0.002
37	1.086	<0.002	<0.02	0.1407	<0.002	<0.01	4.487	<0.002
38	1.034	<0.002	<0.02	0.1648	<0.002	<0.01	4.545	<0.002
39	0.95	<0.002	<0.02	0.0465	<0.002	<0.01	4.359	<0.002
40	1.023	<0.002	<0.02	0.2796	<0.002	<0.01	3.75	<0.002
41	1.194	<0.002	<0.02	1.158	0.1065	<0.01	4.575	<0.002
42	1.332	<0.002	<0.02	<0.01	<0.002	<0.01	5.493	<0.002
43	1.185	<0.002	<0.02	0.045	<0.002	<0.01	5.551	0.1339
44	0.9438	<0.002	<0.02	0.1806	<0.002	<0.01	3.761	<0.002
45	1.349	<0.002	<0.02	0.7943	0.0184	<0.01	1.798	<0.002
46	1.267	<0.002	<0.02	0.3546	0.0044	<0.01	3.885	<0.002
47	1.887	<0.002	<0.02	0.5638	0.0076	<0.01	5.808	<0.002
48	0.7748	<0.002	<0.02	0.3116	0.0581	<0.01	2.441	<0.002
49	0.6953	<0.002	<0.02	1.991	0.2841	<0.01	2.288	<0.002
50	1.008	<0.002	<0.02	0.2425	0.0583	<0.01	3.012	<0.002
51	0.0909	<0.002	<0.02	0.3954	0.0341	<0.01	0.2855	<0.002
52	1.248	<0.002	<0.02	0.1705	0.0943	<0.01	4.476	<0.002
53	1.767	<0.002	<0.02	<0.01	<0.002	<0.01	5.695	<0.002
54	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
55	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
56	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
57	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
58	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
59	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
60	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
61	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
62	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
63	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
64	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
65	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
66	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
67	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
68	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002
Sea water	0.4269	<0.002	<0.02	0.2452	0.0049	<0.01	1.687	<0.002
Rain water	0.4069	<0.002	<0.02	<0.01	<0.002	<0.01	4.954	<0.002

## 4. Results and discussion

### 4.1. Groundwater chemistry

The chemistry of groundwater is strongly related to the physical, chemical and mineralogical properties of lithofacies, and controlled by recharging sources in addition to the geochemical processes during water movement.

#### 4.1.1. Chemical characteristics

TDS is the main factor affecting desalination process. Low TDS value is favorable in the desalination process. This means that, the slightly brackish or

brackish water sites, (43% in the area of study), are the best localities for the desalination projects upon the other sites. Based on the TDS levels, the water salinity in the study area are classified into 11 % fresh, 43 % brackish, and 46 % saline [15]. Most of freshwater samples are found within the alluvium aquifer and one sample in the fractured limestone aquifer (No.51) while all brackish and saline samples are found in the fractured limestone aquifer. High TDS concentration is attributed mainly to the leaching and dissolution of some marine sediments.

**Hardness** is an important factor affecting the performance of desalination process, where the increase in  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and,  $\text{SO}_4^{-2}$ ,  $\text{HCO}_3^{-}$  ions concentrations give high scaling, which reduces the water flux. So, when we choose the water points, the samples must have low concentration of  $\text{Ca}^{+2}$  and  $\text{HCO}_3^{-}$  or before desalination process these ions must be removed by soften in pretreatment.

According to the chemical analysis, (Table 1), it is clear that the mean values of total, permanent and temporary hardness attains 1453, 1178 and 275 mg/l as  $\text{CaCO}_3$  respectively, in alluvium groundwater samples. On the other hand, in the fractured limestone groundwater samples, the mean values of total, permanent and temporary hardness attains 1254, 1096 and 157 mg/l as  $\text{CaCO}_3$ , respectively. These data indicate an increase in total and permanent hardness as water salinity increase. This is mainly attributed to the effect of leaching and dissolution of soluble salts leading to the increase of hardness with particular importance to the effect of NaCl concentration (effect of ionic strength) on increasing solubility of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  [15,17]. Also, the results of the total hardness indicated that, all groundwater samples are very hard and need pretreatment before desalination process to avoid the membrane from the effect of scaling, which decreases the water flux [18].

#### 4.1.2. Ionic relations and sources of major components in groundwater

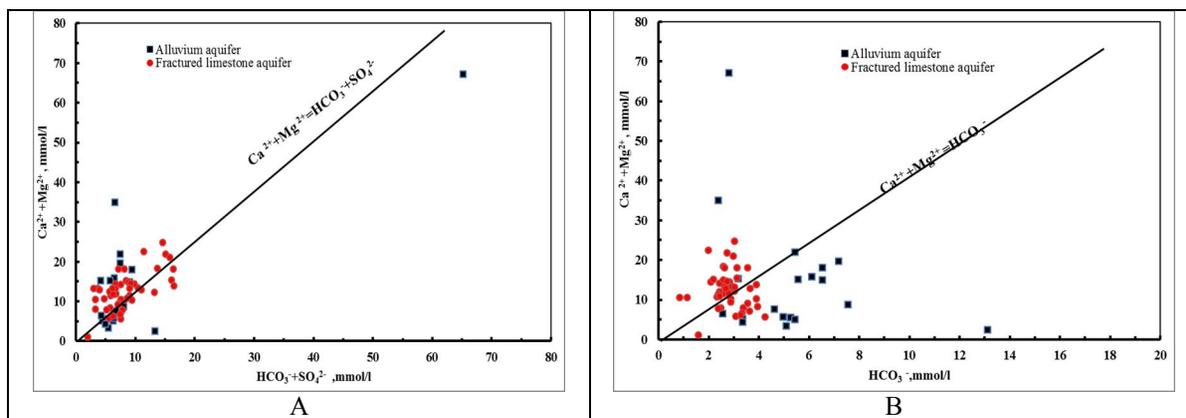
The groundwater salinity could be caused by several factors. Thus, it is necessary to use the characteristic ion relations of potential source to discriminate between them. Scatter diagrams for the most significant parameters are presented in (Fig. 3 A-E) [19].

The  $\text{HCO}_3^{-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in investigated groundwater may be derived from rock weathering. The plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus  $(\text{HCO}_3^{-} + \text{SO}_4^{-2})$

shows that most of data falls below the 1:1 trend, reflecting the requirement of cations exchange from weathering of minerals of carbonate silicate rocks as shown in (Fig. 3A). The plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus  $\text{HCO}_3^{-}$  makes the upper limits of  $\text{HCO}_3^{-}$ , input from weathering of carbonates [20]. This ratio increases with salinity;  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are added to solution at greater rate than  $\text{HCO}_3^{-}$ . If  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  originate only from the dissolution of carbonates in the aquifer materials and from the weathering accessory pyroxene or amphibole minerals, this ratio would be about 0.5 [21]. The plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus  $\text{HCO}_3^{-}$  in (Fig. 3B) shows that most of data falls below the 1:1 trends, although some points approach this line. The low  $(\text{Ca}^{2+} + \text{Mg}^{2+}) / \text{HCO}_3^{-}$  ratios ( $<0.5$ ) could be the result of either  $\text{Ca}^{2+} + \text{Mg}^{2+}$  depletion by cation exchange or  $\text{HCO}_3^{-}$  enrichment. However, high ratios cannot be attributed to  $\text{HCO}_3^{-}$  depletion, under the existing alkaline conditions,  $\text{HCO}_3^{-}$  does not form carbonic acid [22]. High ratios suggest that, the excess of alkalinity of these waters balance by alkalis ( $\text{Na}^{+} + \text{K}^{+}$ ). The excess of alkaline earth elements ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) over  $\text{HCO}_3^{-}$  in some samples reflects an extra source of  $\text{Ca}^{2+}$  and is balanced by the  $\text{Cl}^{-}$  and  $\text{SO}_4^{-2}$ . Further, the plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus total cations show that the data is far below the 1:1 trend, reflecting a high contribution of  $\text{Na}^{+}$  and  $\text{K}^{+}$  as TDS increase (Fig. 3C).

From (Fig. 3D), the increase in alkalis corresponds to a simultaneous increase in  $\text{Cl}^{-} + \text{SO}_4^{-2}$ , suggesting a common source for these ions depicting the contribution of cations via silicate matrix in the aquifer to some extent and the presence of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in the soils [23,24].

In (Fig. 4E), the plot of  $(\text{Na}^{+} + \text{K}^{+})$  versus  $\text{Cl}^{-}$  shows that, the data is below 1:1 trend reflecting the dominance of  $\text{Cl}^{-}$  over  $(\text{Na}^{+} + \text{K}^{+})$  due to the leaching and dissolution of marine deposits.



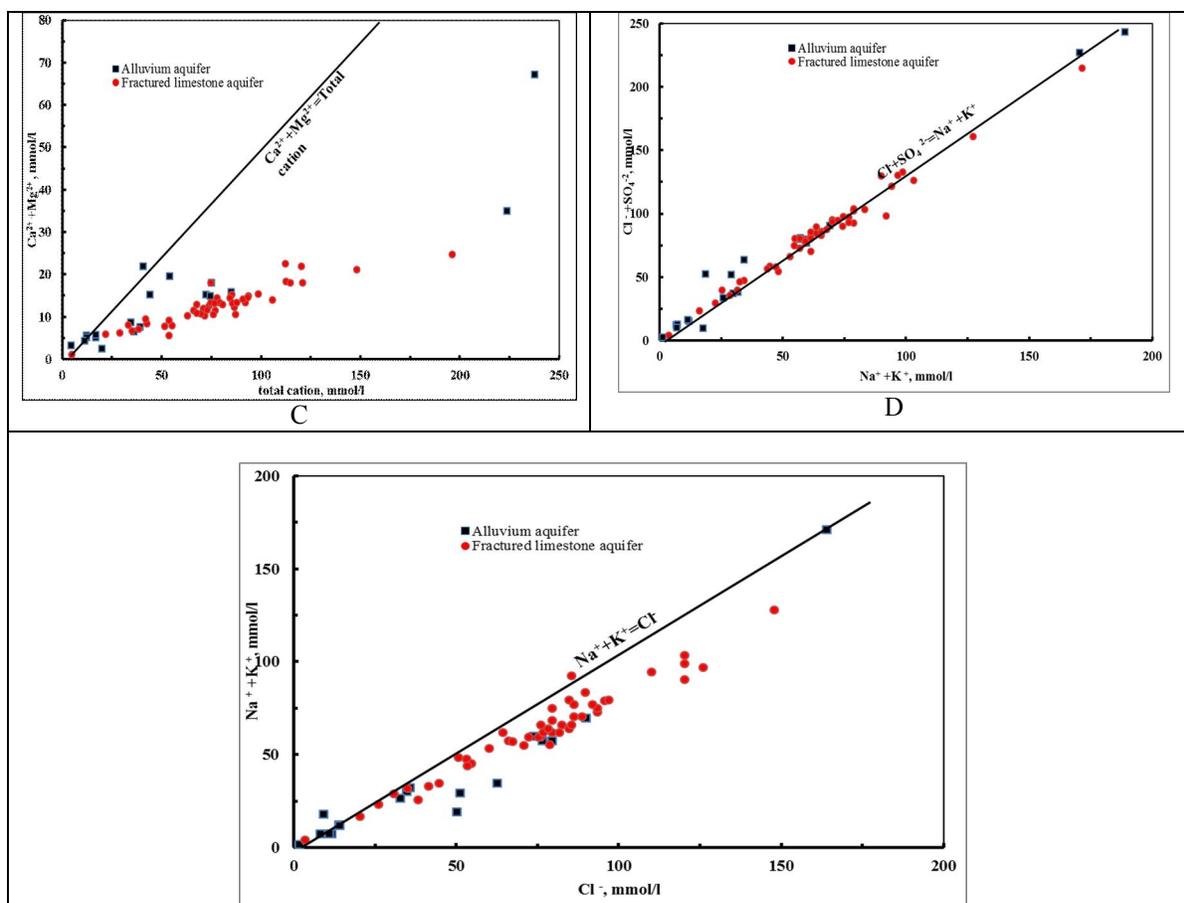


Figure (3) Ions scatter diagrams of the investigated groundwater

#### 4.1.3. Minor and heavy metals

##### 1-Iron and manganese

Iron and manganese concentrations of alluvium aquifer range between 0.09 & 6.6mg/l and less than 0.04 & 1.2 mg/l, respectively, while in the fractured limestone aquifer, they range between 0.03& 3.8 mg/l and less than 0.002&0.32 mg/l respectively, ( Table 2). The sources of iron can be attributed to the dissolution of iron ores within aquifers matrices as ferruginous gypseous limestone member and the clayey gypseous limestone member, also high manganese content is due to the dissolution of dolomitic and calcareous deposits encountered within the aquifer matrices [7]. So, the chance of water points suitable for desalination is in low limit < 1 ppm or a pretreatment process for high iron and manganese must be done [25].

##### 2- Strontium

For groundwater samples of alluvium aquifer, the strontium concentrations are ranging between 0.01 & 0.16 mg/l and in the fractured limestone aquifer it ranges between 0.29 & 10.8 mg/l. The concentrations of strontium in all samples have a wide variation. This could be explained by the effect of leaching and dissolution of strontium minerals within water bearing

formation, Sr is always associated with calcium scales over the full range of proposed water types in spite of the concentration of Sr, which is above the saturation level in many cases. Such observation is in full agreement with the geochemical affinity concept of mineral formation theory [25]. At pH 10 precipitation of all of carbonate, bicarbonate and sulfate of Ca, Mg and Sr, in addition to a limited part of  $MgCl_2$  took place, so the choose of samples close to this value should be considered [26].

##### 3- Boron content

For humans boron can represent reproductive dangers and has suspected teratogenic properties. WHO has set a preliminary limit of 0.5 mg/L for drinking water [27].

In groundwater samples of alluvium aquifer, boron concentration ranges between 0.28 & 7.5 mg/l and in the fractured limestone groundwater it ranges between 0.09 & 1.9 mg/l.

##### 4.1.4. Hypothetical salts assemblages

The combination between major anions and cations reveals the formation of five main groups of hypothetical salts in the investigated groundwater.

Such groups of hypothetical salts are arranged according to water evolution as following:

I- NaCl, MgCl<sub>2</sub>, MgSO<sub>4</sub>, CaSO<sub>4</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub> (66% of total samples).

II- NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, CaSO<sub>4</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub> (18% of total samples).

III- NaCl, MgCl<sub>2</sub>, MgSO<sub>4</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub> (12% of total samples)

IV- NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, CaSO<sub>4</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub> (3% of total samples).

V- NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>, CaSO<sub>4</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub> (1% of total samples).

Most of groundwater samples of alluvium aquifer (95%) and the fractured limestone aquifer (94%) are characterized by the assemblages (I, 21%, II, 37% & III, 37%) and (I, 18% & II, 76%), respectively, presence of two and three chloride salts, reflect the effect of leaching and dissolution of marine salts (marine facies groundwater) with some contribution of cation-exchange phenomenon. On the other hand, the rest of the groundwater samples of alluvium (5%) and the fractured limestone aquifers (6%) are characterized by the assemblages (V, 5%) and (III, 2% & IV, 4%), respectively, which have two or three carbonate salts due to leaching and dissolution of terrestrial salts or rain water recharge.

In general, aggradation in chemical evolution starts from the dominant HCO<sub>3</sub><sup>-</sup> salts in assemblage (V), which changed to SO<sub>4</sub><sup>-</sup> salts and ended by dominant chlorides salts (II).

#### 4.2. Geochemical classification of groundwater

Different graphs have been proposed to study groundwater evolution based on the constituents of both cations and anions. This approach can help in the identification of the mixing, leaching and other chemical processes during water circulation as following:

The tri-linear diagram has proved to be a useful tool in the study of the chemical character of natural waters [28,29]. Piper trilinear diagram (Fig. 4) shows that groundwater samples of alluvium aquifer (79%) and fractured limestone aquifer (94%) are located in sub-area 7 {Non carbonate alkali (Na<sup>+</sup>+K<sup>+</sup>)Cl and {(Na<sup>+</sup>+K<sup>+</sup>)<sub>2</sub>SO<sub>4</sub>}, where the groundwater are dominated by alkalis and strong acids (Primary salinity). This is due to the recharge sources, rainwater, surface and subsurface runoff waters which dissolve the terrestrial and marine salts from the aquifer matrix and catchment area. Some of groundwater samples (11%) of alluvium aquifer and (4%) of fractured limestone aquifer are located in sub-area 9, where no one cation- anion pair exceeds 50 percent. These groundwater have a marine and continental facies as a result of leaching and dissolution of marine and terrestrial salts, while (5%) of alluvium aquifer samples and (2%) of the fractured limestone aquifer samples are located in sub-area 6 (non-carbonate hardness secondary salinity) exceeding 50-percent. Only (5%) of alluvium groundwater samples are located in sub area 5 (carbonate hardness or temporary hardness or secondary alkalinity) exceeding 50 percent, that is chemical properties of the groundwater are dominated by alkaline earths and weak acids {CaMg(HCO<sub>3</sub>)<sub>2</sub>}.

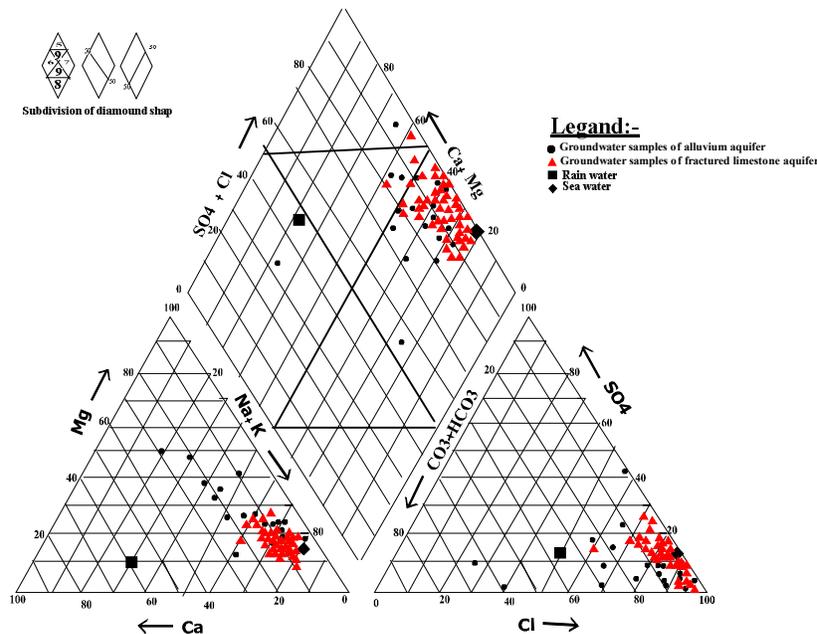


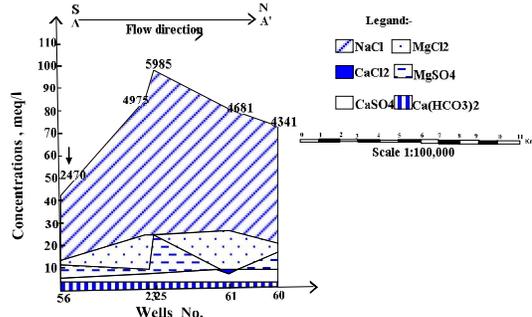
Figure (4) Groundwater classification (piper, 1944)

### 4.3. Spatial variations in groundwater chemistry

In the study area, the groundwater chemical composition has some changes from south due north, passing through different rock types. The main changes in groundwater chemistry during its movement from South to North are illustrated by one hydrochemical profile (Profile 1), (Fig. 5A). On the other hand, the probable changes in water chemistry from West to East, i.e., parallel to the coast due to changes in aquifer types are also considered and illustrated by one hydrochemical profile (Profile 2), (Fig. 5B) [30].

#### 4.3.1. Hydrochemical profile along South to North direction

Profile (1) extends from south to north for about 9.6 Km and passes through five wells tapping the fractured limestone aquifer (The main aquifer in the study area). In this profile the structure plateau



represents the main catchment area feeding the drainage lines during winter times. This fractured limestone aquifer is recharging from rainwater which percolate both through joints and channels as well as through the primary porous of the fractured limestone to form the groundwater. This hydrochemical profile is developed along the fractured limestone aquifer in the studied area from South to North, where the general flow of groundwater is in the same direction. The total dissolved solids of groundwater are obviously low southwards (well No. 56) due to fresh water recharge from the hydrographic basin. Then the total dissolved solids and the ionic composition rise rapidly northwards to reach their maximum values (well No.25) then decrease slightly (wells Nos.61 and 60) near sea coast.

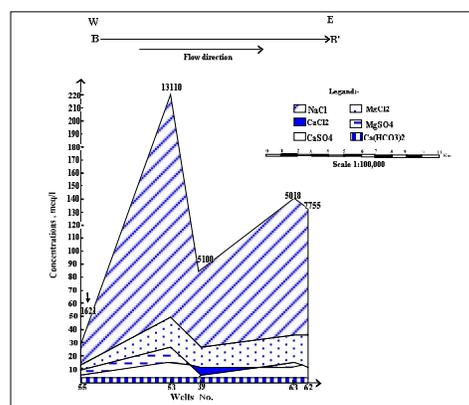


Figure (5) Hydrochemical profiles of groundwater along South to North, A and from West to East, B. in El Negila area

#### 4.3.2. Hydrochemical profile along West to East direction

Profile (2) extends from west to east for about 14.8 Km and passes through five wells tapping fractured limestone aquifer. The total dissolved solids of groundwater are obviously low westward (well No. 55) due to rain water recharge then the total dissolved solids and the ionic composition rise rapidly due east to reach their maximum values (well No.53) then decreases (wells Nos.39,68 and 62) due to local recharge from the seasonal rain water.

From these profiles, it is clear that:

1. The superiority of  $\text{Cl}^-$  over  $\text{Na}^+$  in groundwater from south to north and from west to east is due to marine salts dissolution.

2. It is obvious that these profiles start with a grade of metasomatic,  $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$  (more advanced stage of hydrochemical evolution) then it changes from south and west into  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$  (less advanced stage of hydrochemical evolution). Then ended with a grade of metasomatic,  $\text{Cl}^- > \text{SO}_4^{2-} >$

$\text{HCO}_3^-$  (more advanced stage of hydrochemical evolution).

3. There are two assemblage salts (I and II) dominating the two profiles,

**Assemblage I:**  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{HCO}_3)_2$

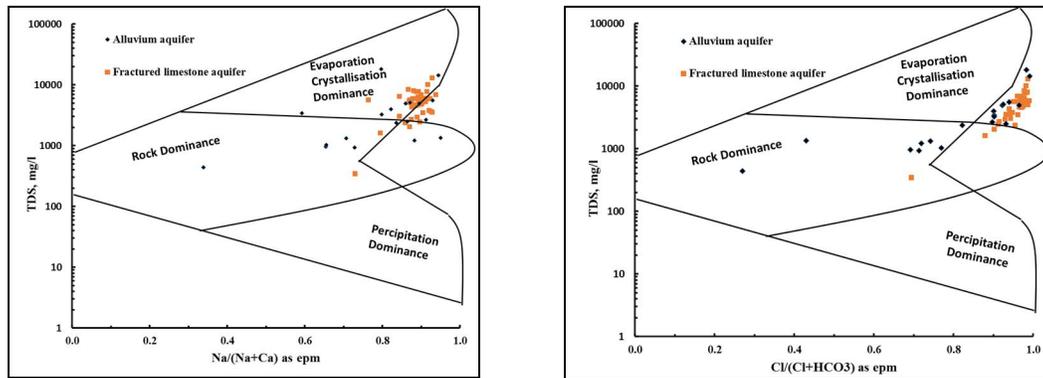
**Assemblage II:**  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{HCO}_3)_2$

The presence of the two or three chloride salts indicates that the groundwater is strongly affected by marine salts.

**Finally,** This indicates a local meteoric water recharge to the aquifers with some contribution of leaching and dissolution of terrestrial and marine sediments.

#### 4.4. Evaporation, precipitation, leaching and dissolution processes

Ratios of  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  and  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$  with a function of TDS is illustrated to indicate that the chemical weathering of the rock-forming minerals. From Gibbs plot (Fig. 6) [31], evaporation concentrates the remaining water and leached to precipitation and deposition of evaporates that are eventually leached into the saturated zone [19].



Figure(6)Mechanisms governing groundwater chemistry(Gibbs,1970)

Most groundwater samples of alluvium and fractured limestone aquifers are located near the upper end of the boomerang and they are affected primarily by slight to moderate progressive evaporation and precipitation of calcite that increases the TDS value and enriched the water by  $\text{Na}^+$  while depletes it by  $\text{Ca}^{2+}$ . Some groundwater samples lie in the center of the boomerang, are influenced by rock weathering, where the alluvium matrix contains weathered fractured limestone transported from southern tableland and oolitic ridges.[7].

#### 4.5. Evaluation of groundwater quality for human drinking

According to TDS values, 88% of total samples are unsuitable for human drinking. The concentration of iron and manganese in the investigated groundwater samples exceeds the maximum recommended limits (0.3 and 0.05 mg/l, respectively) and most of the samples in the study area have values of boron concentration higher than the permissible limit for drinking water (0.5 mg/l). With regards of heavy metals,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  concentrations are less than the permissible limit <0.005, <1.0, 3.0 and <0.05 mg/l respectively, for all investigated groundwater samples.

#### 4.6. Evaluation of groundwater quality for drinking of livestock and poultry

Comparing the chemical analysis data of the groundwater samples of the studied aquifers (table1) with the permissible limits [32] and based on TDS values, the suitability of the collected samples for livestock drinking are given as: 6% of the total samples have excellent class at El Negila and Marsa Gargoob areas, 19% very satisfactory, 29% satisfactory and 45% have risk class, where waters have TDS concentrations more than 5000 mg/l.

#### 5. Best sites for groundwater desalination

The possibility of producing drinking water from brackish and saline groundwater depend on different parameters as total dissolved salts (TDS), type of hypothetical salts, bicarbonates type  $\text{B}^{3+}$  and  $\text{Sr}^{2+}$  concentration as following, (Figs. 7 & 8)[3].

The TDS value increases from south to north in the same direction of groundwater flow, so the best sites are inland or in west and east coast sites which have low TDS value, (Fig. 7).

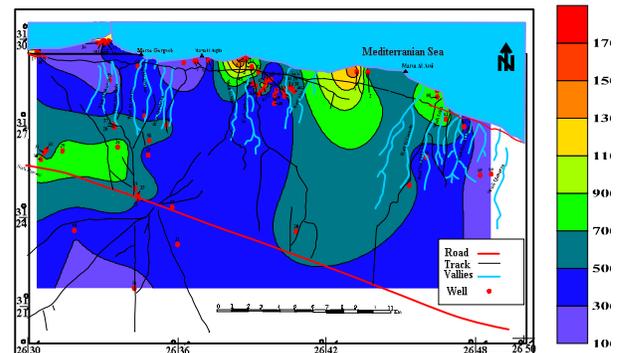
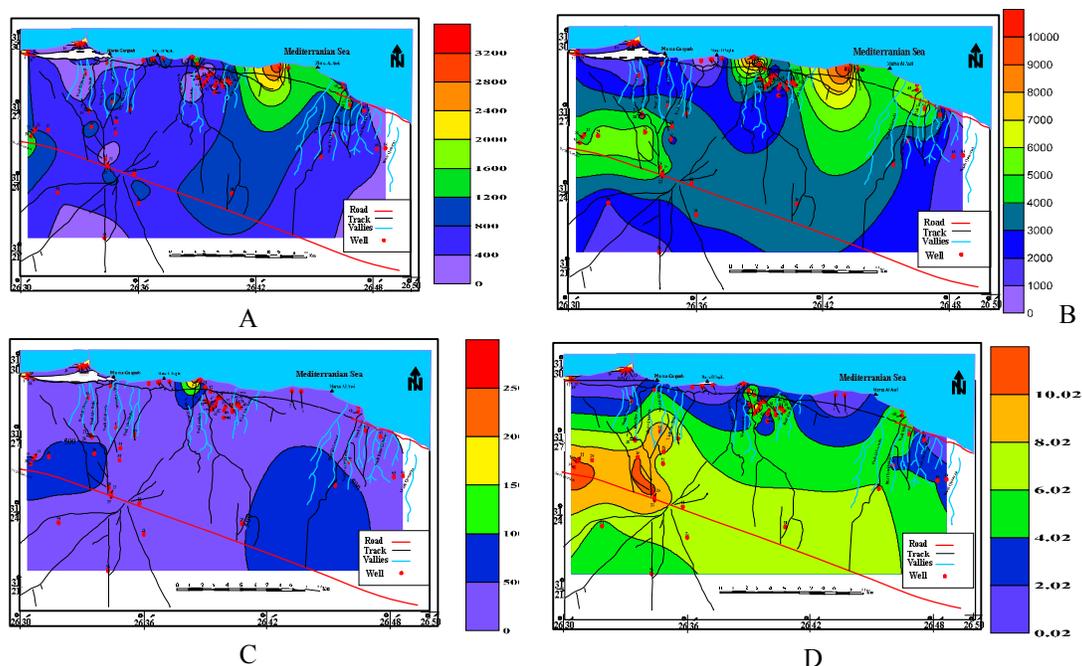


Figure (7) Iso salinity contour map for groundwater in El Negila area.

The high rejection of  $\text{MgCl}_2$  and  $\text{CaCl}_2$  salts relative to  $\text{NaCl}$  salt is due to two factors; the first is the diffusivity (diffusion coefficient) of salts, where  $\text{NaCl}$  salt has diffusivity of  $1.48 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  more than that of  $\text{MgCl}_2$  and  $\text{CaCl}_2$ ,  $1.04$  and  $1.11 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively. The second factor is based on the Donnan exclusion theory; a high co-ion valence causes a higher salt rejection [33]. So, the samples have a high concentration of  $\text{MgCl}_2$  and  $\text{CaCl}_2$  than  $\text{NaCl}$  in two hypothetical salts of chloride (I and II) are favorable for desalination process (fig.8A & B).



**Figure (8) Iso contour map of  $MgCl_2$  salt, (A),  $NaCl$  salt, (B),  $CaSO_4$  salt, (C) and Boron and strontium, (D) in groundwater in El Negila area**

In brackish and saline groundwater samples, which contains three salts such as  $MgSO_4$ ,  $CaSO_4$  and  $Ca(HCO_3)_2$ , the sequence rejection is  $CaSO_4 > Ca(HCO_3)_2 > MgSO_4$ , i.e., calcium salts are more rejected than magnesium salt (fig.8C).

Also, boric acid has trigonal structure, uncharged in addition to its small size. Therefore, boric acid is nonpolar, which causes it to interact very differently with membrane materials relative to charged salt ions and polar water molecules [3]. So, the water point should be selected have low Boron concentration. On the other hand, the prepared membranes have high rejection percent for strontium because it is similar to  $Ca^{2+}$  and  $Mg^{2+}$  metals, (Fig. 8D).

According to TDS,  $MgCl_2$ ,  $CaCl_2$ ,  $NaCl$ ,  $CaSO_4$ ,  $MgSO_4$ ,  $Ca(HCO_3)_2$ , Boron and strontium salts, the water points in Mersa El Negila and Gargoob due west and Mersa El-Assy due east are the best sites for sustainable development due to low TDS,  $NaCl$ ,  $MgSO_4$  and boron concentrations,

### Conclusion and recommendations

Groundwater in El-Negila basin is the only source for drinking and irrigation purposes. Nowadays, due to the increase of the population, the groundwater development in the study area becomes of great necessity; especially that area is of tourist attraction. The groundwater chemistry in El-Negila is studied to detect the quality of water. The main problem affect the development of study area is the higher concentrations of sodium and chloride (salinity). Reverse osmosis

desalination is the essential solution to overcome this problem. With regard to the previous discussion, and to select the best sites for the desalination process, the following items should be taken into consideration:

- 1- Low with constant TDS and type of hypothetical salts around the pumping of groundwater points are favorable.
- 2- Low depth to water is favorable in economic study for selected groundwater sites.
- 3- High production wells of the feed water ( $m^3/h$ ) are needed.
- 4- Water points have a high concentration of  $MgCl_2$  and calcium salts and low concentrations of TDS and  $NaCl$  with low iron, boron and strontium concentrations are suitable sites for desalination process to sustainable development in El Negila basin.

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