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COMPARATIVE STUDY OF WATER QUALITY OF THE QUATERNARY AQUIFERS IN WADI WATIR BASIN AND ITS DELTA, SOUTHEAST SINAI, EGYPT

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The objective of this paper, is to evaluate the hydrochemical data of groundwater in the alluvium aquifer of wadi Watir basin and its delta and to assess the hydrochemical processes affecting water quality in this area. Genesis, origin of mineralization and geochemical evolution have also been discussed in this study.

The obtained results of water salinity of alluvium aquifer reveal the dominance of fresh water in wadi Watir and brackish water in its delta. Based on ion relationships, the chemical composition of most groundwater from the wadi Watir shows a great resemblance to that of the inland rain water while most groundwater samples of delta Watir show a great resemblance to sea water.

The genetic diagrams show that most groundwater of wadi Watir is dominated by alkaline earth's and strong acid (secondary salinity) while most groundwater of its delta is dominated by alkalis and strong acid (primary salinity). On the other hand, most groundwater of wadi Watir is plotted on the sub-square sulfate-magnesium water while most groundwater of its delta is located near the end of the trend of major metasomatic changes of water quality (halite and bischofite subquadrants). This may confirm that the general flow of groundwater is from West to East, i.e. from the wadi to the delta and it is of meteoric origin.

Examination of Q-mode dendrogram reveals one groundwater facies in wadi Watir basin, which is affected by continental condition (three clusters) while two groundwater facies are found in delta wadi Watir; one affected by marine condition (three clusters) and the other is affected by continental condition (four clusters).

From the R-mode dendrograms in wadi Watir and its delta, it can be concluded that TDS (Total dissolved solids) is very highly significant, positively correlated with most major ions while being insignificantly correlated with most soluble minor elements. Highly significant positive correlations are also between (Cl^-, Br^-), (Cl^-, I^-) and (Br^-, I^-).

The correlations indicate that the groundwater acquires its quality from leaching and dissolution of salts in the aquifer matrix.

The main changes in groundwater chemistry in wadi Watir according to Back and Hanshaw (1979) are only of one reaction pathway R (recharge area) →D (down-gradient movement of groundwater) while in the delta, it is characterized by two pathways R→D and D→M (marine water type), the latter pathway (D→M) showed more influence by marine sediments in the delta than in the wadi.

Keywords: groundwater quality, Watir basin, Q-mode dendrogram, R-mode dendrogram.

Wadi Watir basin and its delta (3512 km^2) are located between long. 33° 53′ and 34° 42′ E. and lat. 28° 16′ and 29° 03′ N. The delta occupies an area of about 36 km^2 on the western side of the Gulf of Aqaba (Fig. 1). The local mean precipitation in the area is about 25.3mm/year, all of which falls within just few days, mainly during spring and autumn months. So, considerable temporary floods are noticeable during both seasons. The RIWR (1989) calculated seasonal floods through wadi Watir basin to be between 5 and 45 million m^3 per each period of flood.

MATERIALS AND METHODS

The present study depends on a number of 7 drilled wells to a depth of 80m, located at the outlet of wadi Watir; and a number of 29 hand dug wells to a depth of 3-13m located at the northern, western and southern parts of delta Watir, beside 17 hand-dug wells (total depth from 8 to 14 m) located at different subbasins of the wadi. Consequently, in this study, 17 hand dug wells and 36 wells tapping the alluvium aquifer in wadi Watir and its delta, respectively, are sampled during the year 2002 and investigated both hydrogeochemically and statistically, through the following:

1) Measurement of the depth to water during September (2002) for 29 wells and 17 wells representing the alluvium aquifer within the wadi and its delta, respectively.
2) Seventeen and thirty six groundwater samples of wadi Watir and its delta, respectively, as well as one sample of Ain Fortaga, two samples of rain

water (coastal and inland) one sample of Sea water at Nuweiba harbour were collected during September (2002),(Fig.1).

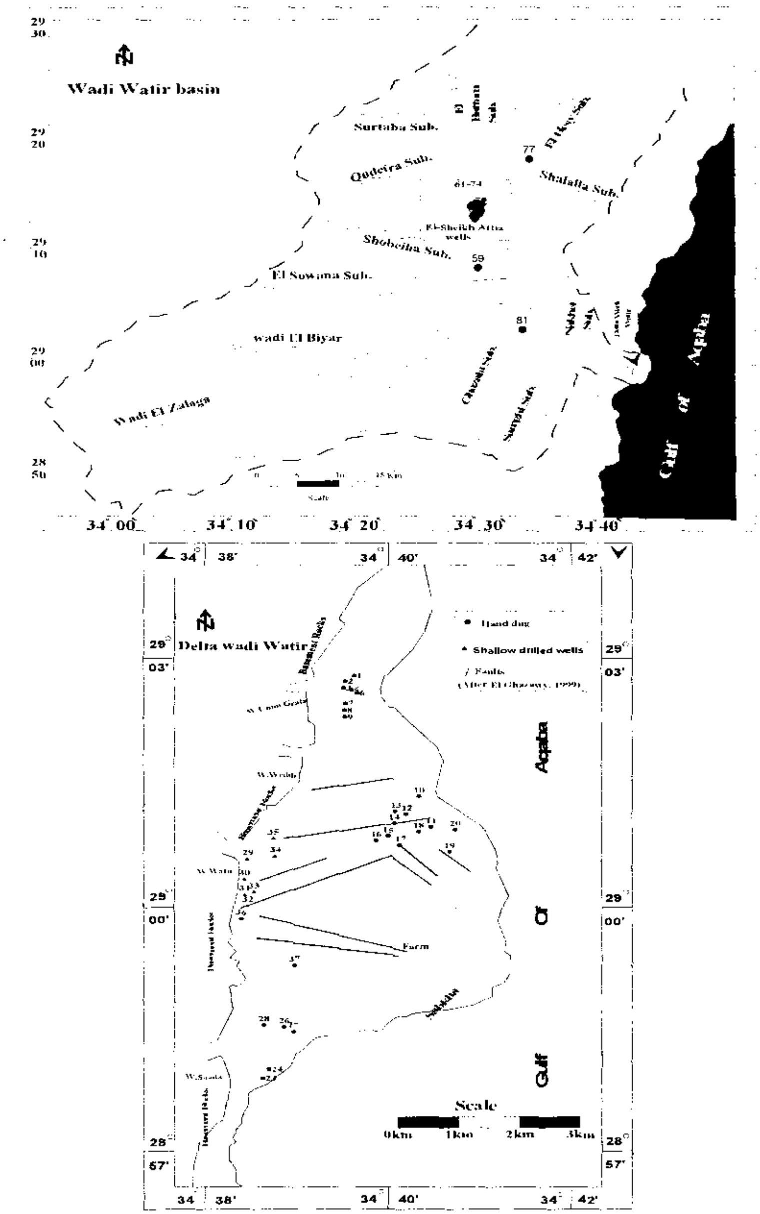


Fig. (1). Well location map of the groundwater samples of alluvium aquifer in wadi Watir and its delta.

3) The chemical analyses of groundwater samples were carried out according to the methods adopted by ASTM (2002).These analyses include the determination of total dissolved solids (TDS), pH, EC, cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe^{3+}, Mn^{2+}) and anions (CO_3^{2-} HCO_3^-, SO_4^{2-}, Cl^-, F^-, Br^-, I^-) as well as SiO_2, (Table 1).
4) The cluster analysis is carried out via statistical computer program "Statisical for Windows" (Statistics Multivariate Exploratory Techniques, 1984-2003) for 56 water samples (cases) of wadi Watir and its delta and 19 hydrochemical compositions (variables). The rain and sea water are used in the multivariate statistics, cluster and correlation analyses to classify the groundwater samples.
5) The saturation indices of carbonate minerals were computed by WATEQ program, (Plummer *et al.*, 1984) for 56 water samples of wadi Watir and its delta.

RESULTS AND DISCUSSION

Aquifer System

The Quaternary alluvium aquifer represents the main source of water in wadi Watir and its delta. The mountainous range bounding its southeastern part which is formed of highly fractured granites and granodiorites are dissected at some places by acidic and basic dykes.

Wadi Watir basin consists of twelve main hydrographic subbasins and several smaller ones that join the trunk channel from East and West at high acute angles. The main geologic units outcropping in wadi Watir range form highly permeable alluvium deposits, sandstone, clay, shale and fractured limestone which overly the basement rocks, (El Shazly *et al.*, 1974). The basement igneous rocks build up the wadi sides, while the main channel is filled with loose coarse sands mixed with pebbles and boulders of Quaternary ages, (Pavlov and El Ayuty, 1962). The rainfall passing through branches of this wadi has infiltrates through the permeable geologic units, open fractures and joints existed in the drainage area of the wadi.

The alluvium aquifer of wadi Watir and its delta is essentially composed of gravels, sand, boulders of carbonates and basement rock fragments embedded in silt and clayey matrix (El Refaei, 1992; Shalaby, 1997). The thickness of the clay and silt layers in the alluvium aquifer of delta Watir increases towards the southeastern part and the coastal area . In front of the outlet of wadi Watir, wadi El Saada and wadi El Samra, the alluvium deposits have a thickness varying between 35m(at the outlet of the southern wadi) and 60m (at the outlet of wadi Watir), while they are wedging out in the northern and southern directions. In wadi Watir basin, the alluvium deposits have a thickness changing between 30 and 90m. The depth to water in Watir delta ranges between 1.79m (well No. 4) and 40.10m (well

No.29) while the depth to water of wadi Watir basin changes from 6.7m (well No.81) to 12.6m(well No.71) from the ground surface due to local lithologic and topographic reasons.

Based on the results of several pumping tests in delta wadi Watir, the storativity of the water bearing horizon varies between 3.16×10^{-4} to 1×10^{-2} (Himida, 1997), which means that the aquifer is confined to unconfined. On the other hand, the results of several pumping tests in wadi Watir at El-Sheikh Attia and El-Ain subbasin, reveals that the storativity of the water bearing horizon is of the order of 4×10^{-3}, i.e. it lies within the limit of the unconfined aquifer (Ismail, 1998). The general groundwater flow is from west to east, i.e., towards the Aqaba Gulf. The recharging of alluvium aquifer in wadi Watir basin is from the subsurface infiltration of the runoff water (flash flood) as well as from the direct precipitation. Ain Fortaga is located at about 20km west Nuweiba town issues from the fractured granitic rocks and controlled by nearly vertical north-south dykes (El Ghazawi, 1999). The discharge of this spring was estimated as more than 3600m^3/day (Issar and Gilad, 1982) while being 1644m^3/day by RIWR (1989). El Ghazawi (1999) and El Sayed *et al.* (2002) mentioned that the aquifer in the concerned delta is recharged directly from the outlet of wadi Watir and the overflow water from Ain Fortaga spring.

El-Kiki *et al.* (1992) distinguished four hydrogeologic zones within the Quaternary aquifer of delta Watir, namely: Zone A is dry with an average thickness of about 30m; Zone B is saturated with groundwater (maximum 2.3m. thickness) and lies above the mean sea level. This zone produces the best water quality (900 mg/l) in the Quaternary aquifer; Zone C lies below the mean sea level where the groundwater salinity ranges from 900 to 6000 mg/l; Zone D is characterized by the high groundwater salinity.

The selected wells for the present study penetrate different zones of variable salinity. The pumped water from the alluvium in the delta is actually a mixture between the waters of zone B and the underlying zones C and D (Table 1). With regard to the present groundwater extraction rate from the alluvium aquifer at wadi Watir delta, it is estimated as 2460m^3/day (El Refaei, 1992) and 3054m^3/day (Shalaby, 1997). Worthmentioning, the estimated annual recharge to groundwater aquifer within the delta from the surface is 2212m^3/day (Ismail, 1998). However, this estimated recharge does not include the amount of direct infiltration of seasonal surface water flows over the delta region.

TABLE(1). Basic information and chemical results of groundwater samples of the alluvium aquifer in wadi Watir basin and its delta (mg/l).

Well No.	Total depth (m)	Depth to water (m)	Ground-water Zone	pH (Lab.)	EC (dSm^{-1})	TDS	Total Hardness	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO$_3^{2-}$	HCO$_3^{-}$	SO$_4^{2-}$	Cl^{-}	Class	Br^{-}	I^{-}	F^{-}	Fe^{3+}	Mn^{2+} × 10^{-3}	SiO$_2$
Rain1	-----	-----	-----	7.0	50	30	0.2	7.1	0.6	2.3	-----	-----	14.5	6.4	5.5	II	0.08	0.002	0.00	----	----	0.00
Rain2	-----	-----	-----	7.0	200	128	73.6	25.8	2.2	8.0	-----	-----	34.6	39.6	13.8	II	-----	-----	-----	-----	-----	-----
Ain	-----	Flowing	----	8.0	1840	1205	6.9	156.6	72.8	150	19	12.33	158.7	446	269.6	II	1.89	0.006	1.23	0.310	3.73	23.4
Wadi Watir basin																						
Fresh water class (TDS <1500 mg/l and μ < 0.03)																						
59	10.15	9.25	----	8.0	1770	1296	769	152.9	94.0	130	9.5	4.1	192.2	5.65	245.1	II	1.35	0.005	0.93	0.38	9.5	14.3
61	11.65	10.70	----	7.7	2150	1412	744	145.1	92.7	190	9.0	4.1	179.6	490	392.1	II	1.57	0.011	0.63	0.23	6.6	11.9
62	11.70	9.50	----	8.0	1795	1279	783	158	94.3	140	9.0	0.0	196.3	510	269.6	II	1.35	0.009	1.00	0.17	2.9	16.0
63	10.60	9.53	----	8.0	1763	1365	796	171.4	89.5	155	9.5	4.1	183.8	550	294.1	II	1.33	0.008	0.92	0.25	5.2	19.1
64	10.45	10.10	----	8.0	1880	1155	698	147	80.3	140	9.0	4.1	162.9	400	294.1	II	1.40	0.008	0.95	0.39	6.5	21.1
65	11.65	10.40	----	8.0	1797	1338	856	180.6	98.5	125	9.0	4.1	183.8	560	269.6	II	1.23	0.007	0.94	0.20	2.1	18.8
68	9.70	8.35	-----	7.9	1870	1322	783	162.2	91.8	155	8.5	4.1	183.8	515	294.1	II	1.36	0.008	0.89	0.39	5.8	19.9
69	9.15	7.80	-----	8.0	2110	1392	703	162.2	72.3	200	9.5	8.2	171.3	590	264.4	I	1.55	0.008	0.91	0.19	0.4	21.7
71	14.20	12.60	-----	8.2	1030	739	479	106.8	51.5	65	7.0	8.2	129.5	330	105.8	I	0.73	0.005	0.79	0.31	5.7	9.0
72	13.55	12.10	----	8.1	1047	769	469	110.5	47.0	80	7.0	4.1	150.4	275	170.0	II	0.75	0.005	1.35	0.24	3.3	5.4
73	12.35	11.05	-----	8.2	1305	804	470	114.2	44.8	95	8.0	4.1	121.1	290	187.9	II	1.10	0.006	0.91	0.41	8.8	15.0
74	12.35	11.45	-----	8.2	1289	936	562	125.3	60.4	100	8.5	4.1	104.4	380	196.1	II	0.87	0.005	0.80	0.87	13.6	16.5
77	9.80	9.45	-----	8.0	1046	554	282	27.2	52.1	105	7.0	8.2	249.7	50	184.4	II	1.52	0.048	0.78	0.42	11.6	18.0
81	7.65	6.70	-----	8.3	1496	995	516	120.9	25.1	155	8.0	4.1	112.8	280	318.6	II	2.45	0.014	0.76	0.49	13.5	30.8
Brackish water class (TDS = 1500-5000mg/l and μ = 0.03-0.1)																						
66	10.45	10.25	----	7.9	2960	1832	1078	218.4	129.5	220	11.0	0.0	309.2	820	278.7	I	1.63	0.008	1.08	0.39	3.7	15.5
67	10.83	8.90	----	7.8	2120	1699	1022	210.1	120.9	180	9.5	0.0	213.1	680	392.1	II	1.60	0.008	0.94	0.18	1.7	16.8
70	10.60	9.60	-----	7.8	2190	1776	1041	232.2	111.9	180	10.5	0.0	200.5	750	392.1	II	1.54	0.007	0.90	0.27	3.9	21.0

TABLE (1). Cont.

Well No.	Total depth (m)	Depth to water (m)	Ground-water Zone	pH (Lab.)	EC (dSm^{-1})	TDS	Total Hardness	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	Class	Br^{-}	I^{-}	F^{-}	Fe^{3+}	Mn^{2+} $\times 10^{-3}$	SiO_2
Delta wadi Watir																						
Brackish water class (TDS = 1500-5000mg/l and μ = 0.03-0.1)																						
1	4.65	4.28	C	7.8	4350	2828	1255	297.6	124.3	550	21.5	---	162.0	485	1268	III	15.9	0.063	2.23	0.377	13.21	19.0
2	5.10	3.76	C	7.1	3930	2678	1092	241.8	118.6	500	17.0	---	137.8	760	972	II	11.3	0.033	1.98	0.206	2.35	20.9
3	4.00	3.55	C	7.2	3630	2526	999	260.4	84.7	480	18.5	8.22	100.2	690	929	II	11.5	0.023	2.17	0.201	3.56	17.0
4	2.29	1.79	C	7.1	5130	3492	1301	251.1	163.8	775	25.5	8.22	146.2	700	1495	II	16.4	0.032	2.2	0.171	2.09	16.6
5	3.30	2.85	C	7.3	5250	3494	1185	279	118.7	810	24.5	8.22	129.5	680	1507	II	16.6	0.033	2.09	0.178	2.06	16.3
6	4.95	4.25	C	7.4	3630	2557	1069	232.5	118.6	480	15.5	4.11	112.8	620	1029	II	11.4	0.023	2.2	0.177	2.77	20.8
8	4.95	3.85	C	7.4	3530	2469	1091	204.6	141.2	440	15.0	4.11	112.8	480	1089	II	12.8	0.026	2.2	0.182	0.55	14.9
9	7.75	6.45	C	7.4	4190	3570	1324	251.1	169.5	780	21.0	4.11	129.5	760	1519	II	19.2	0.058	1.94	0.243	3.60	22.9
10	2.45	2.20	C	7.6	3030	2460	1230	241.5	152.5	385	15.5	8.22	125.3	1040	637	II	6.01	0.018	1.94	0.191	0.11	16.6
11	6.65	6.27	C	7.6	3900	2691	1045	213.9	124.3	520	17.0	8.22	137.8	740	989	II	12.8	0.026	2.12	0.174	0.59	18.8
12	6.85	6.07	C	7.7	2840	1908	854	171.1	103.8	340	13.5	8.22	116.9	520	689	II	9.7	0.019	1.99	0.131	1.17	20.7
13	6.20	5.97	C	7.7	2910	2060	901	171.1	115.2	360	13.5	8.22	129.5	600	727	II	10.0	0.020	1.98	0.178	0.70	33.0
14	9.05	8.60	C	7.8	2630	1901	900	182.2	108.3	310	10.5	8.22	108.6	620	607.6	II	8.7	0.017	2.13	0.241	3.22	9.9
15	11.05	10.50	C	7.8	2660	1549	910	190.0	106.0	320	11.5	4.11	125.3	520	735	II	9.0	0.018	1.93	0.246	2.66	18.9
16	14.75	13.83	C	7.6	2720	1862	1080	201.0	88.0	330	19.0	8.22	175.4	506	621.9	II	9.2	0.018	1.4	0.382	16.36	15.0
17	10.95	9.22	C	7.9	2810	2038	826	174.8	94.9	380	13.5	4.11	125.3	629.2	679.4	II	9.4	0.019	1.82	0.220	2.29	9.4
18	8.60	7.95	C	7.9	2990	2111	919	182.2	113	380	15.5	----	146.2	620	727.2	II	10.2	0.020	1.95	0.209	2.44	12.3
22	5.10	4.70	C	8.0	6190	4368	1672	372.0	180.8	900	42.0	4.11	79.3	700	2129	III	28	0.028	1.75	0.310	3.34	25.4
23	5.02	4.63	C	7.9	7390	4559	1486	390.6	124.3	1050	26.5	8.22	108.6	586	2319	III	28.6	0.029	1.71	0.313	1.62	23.9
25	12.85	12.15	C	8.2	4540	3094	1184	279.0	118.7	640	20.0	----	71.0	580	1421	III	16.0	0.032	1.72	0.228	2.20	15.9
29	75.00	40.10	C	8.1	3990	2799	1277	316.2	118.6	480	17.0	8.22	108.6	700	1105	II	13.3	0.027	1.47	0.238	4.36	23.8
30	70.00	37.20	C	8.0	2950	2048	901	245.6	70	350	13.0	8.22	112.8	540	761	II	9.8	0.020	1.51	0.225	21.00	14.7
33	75.00	38.82	C	8.0	3910	2454	1207	312.5	103.9	440	16.5	12.33	104.4	430	1086	III	13.9	0.028	1.27	0.024	2.97	19.4
34	75.00	37.25	C	8.0	2460	1477	799	223.2	58.8	200	11.5	8.22	108.6	403.9	516.7	III	7.2	0.014	1.34	0.215	4.60	17.1
35	80.00	33.07	C	8.1	5190	3567	1695	446.4	141.2	575	15.5	8.22	104.4	800	1528	III	18.6	0.037	1.55	0.227	2.52	18.8
36	21.50	20.90	C	7.9	3530	1737	825	193.5	83.9	310	13.5	4.11	100.2	440	641.8	II	7.5	0.015	2.15	0.424	2.30	22.4
37	11.85	10.65	C	8.0	4250	2925	1242	248.8	151	530	19.0	8.22	125.3	820	1085	II	11.4	0.023	1.95	0.200	0.62	22.8

TABLE (1). Cont.

Well No.	Total depth (m)	Depth to water (m)	Ground-water Zone	pH (Lab.)	EC (dSm^{-1})	TDS	Total Hardness	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	Class	Br^-	I^-	F^-	Fe^{3+}	$Mn^{2+} \times 10^{-3}$	SiO_2
Delta wadi Watir																						
Saline to extremely saline water classes (TDS >5000 >1000 mg/l and μ >0.1 >0.2)																						
7	4.90	4.30	D	7.5	7790	6147	2200	488	238.9	1325	53.5	----	41.7	1240	2702	I	27.9	0.084	1.13	0.287	2.12	10.4
19	5.50	5.00	D	7.5	10690	9613	4505	799.9	610.2	1540	41.5	----	100	3200	3325	I	34.6	0.035	1.57	0.626	14.99	36.9
20	5.48	4.46	D	7.5	7980	6038	3112	483.6	463.3	900	42	8.22	142	1750	2320	I	28	0.028	2.10	0.122	0.50	19.2
24	5.40	5.30	D	7.7	7540	5623	1997	502.2	180.8	1200	51	4.11	146.2	1100	2512	II	29.9	0.030	1.57	0.170	0.38	27.9
26	3.55	3.03	D	7.4	15280	12733	5388	967	723	2400	132	----	75.7	2600	5873	I	60.5	0.24	1.42	0.432	6.45	32.5
27	2.90	2.65	D	7.9	12520	10525	4133	892.9	463.3	2100	64	12.33	83.5	3100	3851	I	36.3	0.073	1.68	0.248	0.94	14.5
28	5.65	5.15	D	7.8	11780	9927	4272	1005	429	1700	48.5	8.22	104.4	3000	3684	I	35.1	0.070	1.99	0.320	1.03	31.0
31	80	28.49	D	7.6	28200	23825	5203	848	751	6700	150	4.11	125.3	2350	12950	I	100	0.20	1.39	0.334	0.59	19.2
32	74	37.20	D	8.0	19150	12418	3437	632.5	452	3300	61	---	58.4	1900	6044	I	69	0.14	1.20	0.913	39.64	6.6
Sea	-----	-----	D	7.6	51700	42232	7806	390.6	1661	12600	461	32.8	116.9	3500	23528	I	172	0.48	1.37	0.306	0.77	4.1

Rain 1 = Coastal rain, Rain 2 = Inland rain. Groundwater, Zone = Groundwater,
Zone (A or B or C or D according to the classification of El-Kiki *et al.*, 1992),
Class = Assemblage of hypothetical salt combinations, where assemblage, I: NaCl, Na_2SO_4 , $MgSO_4$, $CaSO_4$, Ca $(HCO_3)_2$,
II: NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, Ca $(HCO_3)_2$, III: NaCl, $MgCl_2$, $CaCl_2$, $CaSO_4$, $Ca(HCO_3)_2$.

Hydrochemical Aspects

A-Water salinity

According to Chebotarev (1955), the natural water is classified into three main categories of total salinity; fresh water (TDS up to 1500 mg/l); brackish water (1500 to 5000 mg/l) and saline water (TDS more than 5000 mg/l).

The frequency distribution of water salinity in wadi Watir basin (559 – 1833 mg/l), is characterized by the abundance of fresh water which constitutes about 82% of the investigated samples while the brackish water is less pronounced and the saline water is absent, (Table 2). The relatively low water salinity values are true reflection of flushing of the integrated recharge of surface and subsurface runoff waters to the basin, indicating the meteoric origin of groundwater. The presence of slightly brackish water is due to moderately low infiltration of surface runoff water of the middle part at El-Sheikh Attia locality (Ismail, 1998).

In the delta, there are two water salinity zones, one is the brackish water (75%, zone C) which occupies the western parts of delta and the second is the saline to extremely saline water (25%, zone D) which dominates the coastal plain and southeastern part. The salinity ranges between 1467mg/l to 12733mg/l with a mean value of 4640 mg/l. The two drilled wells of samples Nos. 31 and 32 that exist at the apex of the fan have salinities, from 11999 to 23691 mg/l, higher than the surrounding hand dug and drilled wells. This is attributed to over-pumping processes and depth of pumping where these water points reached the hydrogeologic zone D of extremely saline water. The low salinity values (brackish water, zone C) encountered at the west parts are true reflection of the integrated recharge of subsurface infiltration of the runoff water through a bypass along the dense fracture system crossing the basement rocks. This is in agreement with the main recharge sources, since the groundwater flow is from west to east, i.e., towards the Aqaba Gulf. The high values of water salinity (extremely saline water, zone D) in the coastal area and southeastern part are due to the following reasons:

1- Salt water intrusion due to over-pumping activities.
2- The evaporation from the shallow water table (less than 2m near the sea) leads to an increase in water salinity.
3- The presence of some saline deposits such as sabkhas and carbonate deposits in the catchment area and within the aquifer matrix, where the saline deposits in water zone D is more than that in water zone C leads to an increase in water salinity of zone D (Said, 2004).

TABLE (2). Frequency distribution of water salinity of the alluvium aquifer in wadi Watir and its delta.

Locality	Total water samples	Water salinity					
		Fresh TDS up to 1500 mg/l, μ^* up to 0.03		Brackish 1500 <TDS up to 5000 mg/l, $0.03 < \mu'$ up to 0.1		Saline to extremely saline 5000 <TDS >10000 mg/l, $0.1<\mu' > 0.2$	
Delta	36	No.	%	No.	%	No.	%
		---	---	27	75	9	25
Wadi	17	14	82	3	18	---	---

μ^*= Ionic Strength.

Comparing the distribution of water salinity of alluvium aquifer, one can find that fresh water dominates in wadi Watir basin while brackish water dominates in its delta. This confirmed that the groundwater of wadi Watir is more flushed by fresh runoff water than that of the delta.

B- Geochemical Classification Based on Ion Relationships

B-1-Ions dominance

Based on ion relationships of the groundwater of alluvium aquifer in wadi Watir basin, two main hydrochemical facies are distinguished, namely: (1) $SO_4^{2-} > Cl^- > HCO_3^-$ and Na^+, Ca^{2+} or Mg^{2+} (76 %); and (2) $Cl^- > SO_4^{2-} > HCO_3^-$ (24 %). The dominance of Na^+, Ca^{2+} or Mg^{2+} is a matter of cation exchange activity on the surface of clays and fine materials. Such condition has resulted in the formation of Ca-SO_4, Mg-SO_4, Na-SO_4 Ca-Cl and Na-Cl types (Table 3). The chemical composition of most groundwaters (76%, hydrochemical facies 1) shows a great resemblance to the inland rain water while the chemical composition of some groundwater (24%, hydrochemical facies 2) shows a great resemblance to the sea water. These chemical composition and water types reflect leaching and dissolution of terrestrial (assemblage of hypothetical salts I) and marine salts (assemblage of hypothetical salts II) through downward infiltration of the surface and subsurface runoff waters and within aquifer matrices.

On the other hand, one main hydrochemical facies is distinguished on basis of ion relationships in the alluvium aquifer of delta Watir, namely: (2) $Cl^- > SO_4^{2-} > HCO_3^-$ (97%) and $Na^+ > Ca^{2+}$ or Mg^{2+}, $Ca^{2+} > Na^+ > Mg^{2+}$ with Na-Cl (94%) and Ca-Cl (3%) chemical types. The chemical composition of most groundwaters (97%) shows a great resemblance to that of the sea water. This is probably attributed to the metamorphism and development of mineralization of the recharging water (surface runoff water) through the dissolution of the soluble salts found in the basement and marine carbonate rocks. This is confirmed by assemblages of hypothetical marine salts II and III.

Finally, based on ion relationships of the groundwater of alluvium aquifer, it is clear that the hydrochemical facies 1, characterize most groundwater samples (76%) of wadi Watir basin while the hydrochemical facies 2 characterize most groundwater samples (97%) of wadi Watir delta. Thus, the genesis and formation of groundwater mineralization in wadi Watir is subjected to continental condition more than marine one and vice versa in case of the groundwater of delta wadi Watir.

The hydro-chemical aspects of these hydrochemical facies in wadi Watir and its delta dictate that, the groundwater is of meteoric origin, affected by terrestrial and marine salts contamination as well as cation-exchange activities. This is confirmed by both assemblages of hypothetical salt combinations I (18%) and II (82%) in case of wadi Watir and II (78%) and III (22%) in case of delta Watir. Consequently, there is one main geo-chemical class of groundwater in the alluvium aquifers of the study area, viz.: - The groundwater which acquires its quality from leaching and dissolution of soluble salts found in the catchment area of wadi Watir and the aquifer sediments through the subsurface infiltration of the runoff water (flash flood) and the overflow water from Ain Fortaga spring as well as cation exchange processes.

TABLE (3). Classification of groundwater of the alluvium aquifer in wadi Watir basin and its delta based on ion relationships.

Area	Hydrochemical facies	Water Type	% of the water samples	*Assemblages of hypothetical salts and umber of water sample	
				Assemblage	No. of samples
Wadi Watir basin	(1): $SO_4^{2-} > Cl^- > HCO_3^-$ and Na^+, Ca^{2+} or Mg^{2+}	Ca, Mg, Na-SO_4(64, 6, 6 %)	%76	I II	3 10
	(2): $Cl^- > SO_4^{2-} > HCO_3^-$ and Na^+or $Ca^{2+} > Mg^{2+}$	Na, Ca-Cl (18, 6%)	24%	II	4
Delta wadi Watir	(2): $Cl^- > SO_4^{2-} > HCO_3^-$ and Na^+or $Ca^{2+} > Mg^{2+}$	Na, Ca-Cl (94, 3%)	97%	II III	10 25
Coastal rain	$HCO_3^- > Cl^- > SO_4^{2-}$ and $Ca^{2+} > Na^+ > Mg^{2+}$	Ca- HCO_3	----	II	1
Inland rain	$SO_4^{2-} > HCO_3^- > Cl^-$ and $Ca^{2+} > Na^+ > Mg^{2+}$	Ca-SO_4	-----	II	1
Sea water	$Cl^- > SO_4^{2-} > HCO_3^-$ and $Na^+ > Mg^{2+} > Ca^{2+}$	Na-Cl	-----	II	1

*Assemblages of hypothetical salts I: NaCl, Na_2SO_4, $MgSO_4$, $CaSO_4$ and Ca (HCO_3).
II: NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$ and Ca (HCO_3).
III: NaCl, $MgCl_2$, $CaCl_2$, $CaSO_4$, and Ca $(HCO_3)_2$

B-2- Piper's tri-linear diagram (1944)

The chemical data were plotted on Piper's diagram (Fig.2) which shows that:

1- All water samples of wadi Watir and its delta are plotted in area 4 of the diamond-shaped field where strong acids exceed weak acids, i.e.(SO_4^{2-} +Cl^-)>(CO_3^{2-}+HCO_3^-).

2- Most groundwater samples (82%) of wadi Watir and some groundwater samples (25%) of delta Watir lie in the sub-area 6 (secondary salinity, alkaline earth's and strong acid dominance). Therefore, such water is shown to be more influenced by leaching and dissolution of non-carbonate hardness salts ($MgSO_4$, $CaSO_4$, $MgCl_2$ and $CaCl_2$).

3- Some groundwater samples of wadi Watir and its delta (18 and 31%, respectively) and Ain Fortaga spring occupy the sub-area 9. This reflects that such water is more affected by meteoric water.

4- None of the groundwater samples of wadi Watir is enclosed in sub-area 7 while 44% of the groundwater samples of delta Watir are located within the sub- area 7 (primary salinity, alkalis and strong acid dominance). Consequently, such water of delta Watir are shown to be more influenced by marine sediments than that of wadi Watir basin (Fig. 2).

In conclusion, alkaline earth's and strong acid (secondary salinity) dominate most groundwater samples of wadi Watir. This reflects the dissolution of soluble salts by fresh water of surface and subsurface runoff from the aquifer matrices and catchment area of wadi Watir, which is characterized by the Cenomanian carbonate rocks (marine environment) and the basement rocks (rich in mafic minerals). On the other hand, most groundwater samples of delta Watir have dominant alkalis and strong acid (primary salinity). This is due to dissolution of soluble salts especially sodium chloride salt either derived from marine deposits or salt lagoon (dry–wet) which is surely responsible for increasing salinity.

B-3- Modified Durov's diagram (1948)

From the modified Durov's diagram for groundwater samples (Fig.3), it can be concluded that:

i- Almost all water samples (97%) of the alluvium aquifer in the delta is related to the subsquares of bischofite (magnesium-chloride water, 55% of total samples) and halite (chloride-sodium water, 42%). In contrast, some groundwater samples (6%) of the alluvium aquifer in wadi Watir is located in the subsquare of bischofite (magnesium-chloride water). Consequently, most of the plotted data of groundwater (97%) of delta wadi Watir and some groundwater (6%) of wadi Watir are located near the end of the trend of major metasomatic changes of water quality (halite and bischofite subquadrants). So, this means that these investigated samples displayed chemically more developed stage of mineralization, where the dominant anion is chloride, i.e. they are subdued to different processes of metasomatism until they reach the present quality

ii- On the other hand, most water samples (94%) of the alluvium aquifer in wadi Watir, very few water samples (3%) in delta wadi Watir and Ain

Fortaga spring are plotted on the sub-square sulfate-magnesium water which displays chemically less advanced stage of mineralization, where the dominant anion, is sulfate. This indicates that the effect of dissolution process of sulfate minerals is accompanied by cation exchange process. Noteworthy to mention that the rainwater occupies the same position of wadi samples, sub-square gypsum (calcium-sulfate water), while the normal seawater is plotted at the sub-square of halite (sodium chloride-water) which reveals that of the delta.

In conclusion, most of water samples of wadi Watir basin showed that chemically less developed stage of mineralization while most water samples of wadi Watir delta displayed chemically more advanced stage of mineralization. This confirms that the general flow of groundwater is from west to east direction, which has been, hydrologically, proved by other authors in previous studies. Consequently, ions dominance, Piper's and modified Durov's diagrams suggest that the groundwater samples of alluvium aquifers in the study area have meteoric origin of mineralization and is possibly subjected to infiltration of pure meteoric water affected by marine and continental deposits from the catchment area and aquifer matrices. This conclusion is not in agreement with that achieved by Shalaby (1997) and Ismail (1998) who stated that the groundwater has a mixed origin between meteoric and paleowater while Abd El Hafez (2001) reported that the groundwater in the area has a mixed origin between meteoric and seawaters.

4- Statistical analyses of the chemical data of groundwater in wadi Watir and its delta

The analysis of variance (ANOVA) of the data sets with Alpha-level of 0.05 was carried out. The multivariate statistics, cluster analysis (Q-mode) and correlation analysis (R-mode) were carried out using the computer program (Statistics Multivariate Exploratory Techniques, 1984-2003). According to the analysis of variance (Table 4) for Q-mode of wadi Watir and its delta, the linear regression between variables is significant since the critical values of F (1.63 and 4.59, respectively) are less than the estimated values (6.24 and 4.59, respectively).

On the other hand, the analysis of variance for R- mode of wadi watir and its delta, the linear regression between variables is significant since the critical values of F (1.63 and 1.62, respectively) are less than the estimated values (1.67 and 15.06, respectively).

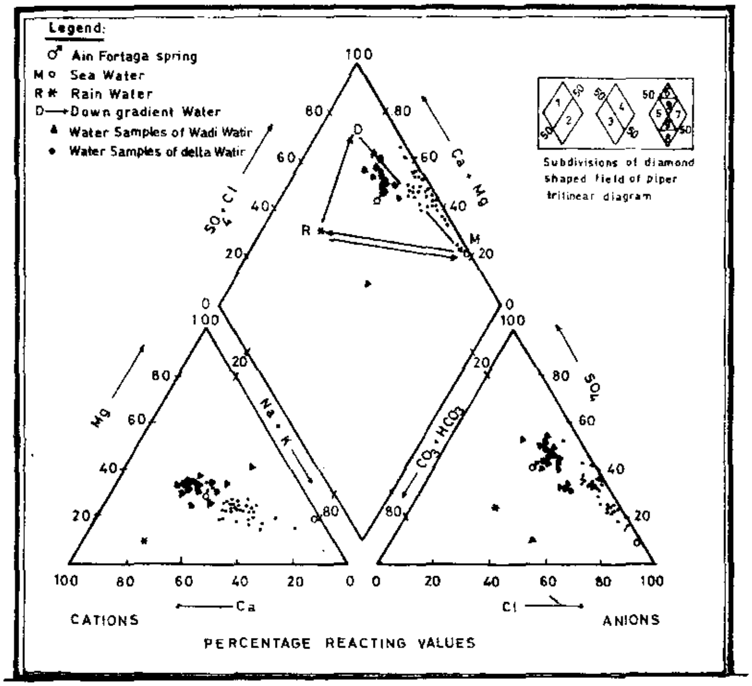


Fig. (2). Piper's diagram for the groundwater samples of alluvium aquifer in wadi Watir and its delta.

The cluster analysis was carried out on the non transformed input data matrix of 39 water points (cases) of delta and 19 water points (cases) of wadi Watir and 10 hydrochemical compositions (variables) for each of wadi and its delta (Table 5). The rain and sea waters are used in the multivariate statistics, cluster and correlation analyses to classify the groundwater samples.

The results are given as Q-mode dendrogram and R-mode with amalgamation rule of complete linkage and euclidean distance of 1-Person (r) method for both wadi and its delta. From the examination of Q-mode dendrogram at similarity level with a distance of 0.068, it is clear that there is one groundwater facies in wadi Watir basin, which is affected by continental more than marine condition and the wadi exhibits three clusters (groups) (Fig. 4).

The Q-mode dendrogram of the groundwater samples are discussed in details as follows: -

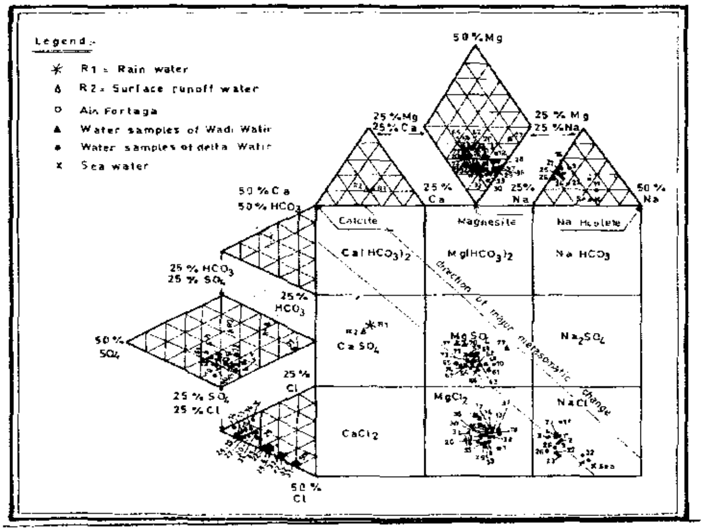


Fig. (3). Durov's diagram of the groundwater samples of alluvium aquifer in wadi Watir and its delta.

TABLE (4). The results of regression statistics and analysis of variance (ANOVA) of the groundwater samples of alluvium aquifer in wadi Watir and its delta.

Cases of wadi (Q-mode)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1596925202	18	88718066.8	**6.24**	2.8E-13	**1.63**
Within Groups	4859342015	342	14208602.38			
Total	6456267217	360				

Cases of delta (Q-mode)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2133204387	38	56136957.56	**4.58**	7.79E-17	**1.42**
Within Groups	8594229795	702	12242492.59			
Total	10727434183	740				

Variable of wadi (R-mode)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	520592046.9	18	28921780.38	**1.66**	4.35E-11	**1.63**
Within Groups	5935675170	342	17355775.35			
Total	6456267217	360				

Variable of delta (R-mode)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2928196868	18	162677603.8	**15.05**	2.71E-39	**1.61**
Within Groups	7799237314	722	10802267.75			
Total	10727434183	740				

SS=sum of squares
MS=mean squares
df=degrees of freedom

Clusters (first class) affected by continental condition in wadi Watir basin at similarity level with a distance of 0.068.

The first cluster (I) domains four cases of water points (59, 65), (63, 67), (62, 68) and (66, 71). It reflects fairly fresh to slightly brackish water salinity (739-1832 mg/l or 1030-2960 dSm^{-1} at 25 °C), according to Chebotarev (1955) and low bromide and iodide (0.73-1.63 and 0.005-0.009 mg/l).

The independent cases involve the water points 70 (with respect to the second case 63,67) and 74 and 69 (with respect to the third case 62, 68). The independent case 70 shows the highest values of water salinity (1776 mg/l or 2190 dSm^{-1}) with respect to the second case (1296 – 1338 mg/l or 1770 – 1797 dSm^{-1}). The independent case 74 has water salinity (936 mg/l or 1289 dSm^{-1}) less than the third case (1279 – 1322 mg/l or 1795 – 1870 dSm^{-1}) and vice versa in the bromide content (1.55 mg/l) with respect to the same case (1.35- 1.36 mg/l). On the other hand, the independent case 69 has water salinity (1392 mg/l or 2110 dSm^{-1}) more than the third case and vice versa in the bromide and iodide contents (0.87 and 0.005 mg/l) with respect to the same case (1.35-1.36 and 0.008 – 0.009mg/l). Also, the water points of independent case 69 is characterized by cations dominance in the descending order: $Na^+ > Ca^{2+} > Mg^{2+}$ and continental facies (assemblage of hypothetical salts I) where rNa / rCl is more than unity.

The second cluster (II) involves one case of water points (64, 73), which exhibit the low values of water salinity (804-1155mg/l or 1305-1880 dSm^{-1}), fairly fresh water, and low bromide and iodide contents (1.1-1.4 and 0.006-0.008 mg/l).

The independent cases involve the water points 61, 72 and 81 (with respect to the case 64, 73). This case (61) has water salinity, bromide and iodide contents (1412, 1.57, 0.011 mg/l, respectively) more than that such case while the independent case 72 has water salinity, bromide and iodide (769, 0.75 and 0.005 mg/l, respectively) less than such case. On the other hand, the independent case 81 is considered as the average values of water salinity (995 mg/l or 1496 dSm^{-1}) in respect to such case while this independent case has the highest values of bromide and iodide contents (2.45 and 0.014 mg/l) with respect to the same case. Also, both independent cases 61 and 81 have more advanced stage of mineralization where the dominant anion is chloride ($Cl^- > SO_4^{2-} > HCO_3^-$) and the dominant cation is sodium.

Most water points of these clusters are characterized by less advanced stage of mineralization where the dominant anion is sulfate ($SO_4^{2-} > Cl^- > HCO_3^-$) and the dominant cation is calcium. This is rendered to the integrated recharge of subsurface infiltration of the runoff water from the hydrographic basin of wadi Watir. The majority of water points of these clusters have marine facies (assemblages of hypothetical salts II and III).

The third cluster (III) contains one case (77, rainwater) which exhibit the lowest values of water salinity (30-554 mg/l or 50-1040 dSm^{-1}), ultra-fresh water to fresh water, and low bromide and iodide contents (0.08-1.52 and 0.002 -0.048 mg/l). This cluster is characterized by cations dominance in the descending order: $Na^{+} > Mg^{2+} > Ca^{2+}$ and has less advanced stage of mineralization ($Cl^{-} > HCO_3^{-} > SO_4^{2-}$).

Generally, the water points of cluster III is affected by meteoric water more than the water points of clusters II and I in a descending order. On the other hand, the independent case involves marine water (sea water) with respect to all clusters considered as independent case when interpreted at similarity level with a distance 0.15 (Fig. 4). This reflects the metamorphism and development of mineralization of the recharging water (surface runoff water) through the dissolution of the marine soluble salts found in the catchment area and aquifer matrices.

The Q-mode dendrogram of delta wadi Watir exhibits seven clusters (groups) when interpreted at similarity level with a distance 0.15 (Fig. 4). Examination of this dendrogram revealed two groundwater facies, one affected by marine condition and the other is affected by continental condition. The Q-mode dendrogram of the groundwater samples are further discussed in details as follows: -

Clusters (first class) affected by marine condition in delta wadi Watir basin at similarity level with a distance 0.035.

The Q-mode dendrogram of wadi Watir delta exhibits groundwater which is affected by marine condition (first class) containing three clusters (groups) when interpreted at similarity level with a distance of 0.035.

The first cluster (I) domains four cases of water points (1, 33), (4, 5), (8, 25) and (6, 29). This cluster reflects slightly brackish to brackish water salinity, (2454-3492mg/l or 3900-5250 dSm^{-1}) and relatively low bromide and iodide (11-17 and 0.02-0.06 mg/l). The independent case involves water point 35 with respect to case (6, 29), which shows the highest values of water salinity and iodide content (3567mg/l or 5190 dSm^{-1} and 0.04mg/l) relative to case of water pionts (6, 29).

The second cluster (II) domains two cases of water points (7, 24) and (22, 23, representing saline water zone D). It is characterized by definitely brackish to extremely saline water, (3569-12733 mg/l or 4190-19150 dSm^{-1}), and high bromide and iodide (19.2-69.2 and 0.035-0.245 mg/l). The independent cases involve water points 9, 26 (with respect to case 7, 24) and 32 (with respect to case 22, 23).

The independent case 9 has water salinity, bromide and iodide less than that of (7, 24) and vice versa in the independent case of 26 with respect to the same case. The independent case 32 has water salinity, bromide and iodide more than that of (22, 23).

The third cluster (III) involves one case of water points (31 and sea) representing saline water. Extreme water salinity (13128 - 42232 mg/l) or (28200 – 51700 dSm-1) and high bromide and iodide (172 -0.55 mg/l) characterize this cluster.

Generally, the water points of cluster III is affected by marine conditions more than that of the water points of both clusters I and II. On the other hand, the case involves 31, sea water with respect to clusters I and II which are considered as dependent cases, i.e. the chemical composition of water samples of cluster one and two depends on the variation in chemical composition of water sample No.31 and sea water (independent case) when interpreted at a similarity level with a distance of 0.035 (Fig. 4). This independent case (cluster III, 31 and sea) shows very high values of water salinity, bromide and iodide. The chemical similarities between the different zones of groundwater of clusters I, II, III and the Gulf water (sea water) are probably attributed to the metamorphism and development of mineralization of the recharging water (surface runoff water) through the dissolution of the marine soluble salts found in the catchment area and aquifer matrices. However, the sea water intrusion is not confirmed. Therefore, the water points of clusters I, II and III are affected by marine conditions more than continental conditions.

Clusters (second class) affected by continental condition in delta wadi Watir area at similarity level with a distance of 0.022.

The Q-mode dendrogram of wadi Watir delta when interpreted at similarity level with a distance of 0.022 exhibits groundwater which is affected by continental condition (second class, 4 cluster).

The fourth cluster (IV) consists of four cases of water points (2, 11, 37), (13, 18), (15, 30) and (14, 17). This cluster is characterized by slightly brackish to brackish water salinity, (1549-2924 mg/l or 2660-4250 dSm^{-1}) and relatively low bromide and iodide (9-13 and 0.02-0.03mg/l). The independent cases involve the water points 3, 12 and 20 (with respect to the cases (2, 11, 37), (13, 18) and (four cases water points), respectively. The independent case 3 has water salinity less than that of case (2, 11, 37) while the independent case 12 has water salinity more than the case (13, 18). The independent case 20 has water salinity (6030 mg/l or 7980 dSm^{-1}), bromide and iodide (28 and 0.04 mg/l) more than the four cases water points.

The fifth cluster (V) involves one case water points (27, 28) and represents saline water zone D which is characterized by very salty to extremely salty water (9927-10525 mg/l or 11780-12520 dSm^{-1}) and high bromide and iodide (35-36 and 0.07mg/l). The independent case involves water point 19 which shows low value of iodide content (0.04 mg/l) with respect to cluster case (27, 28).

The sixth cluster (VI) contains one case water points (16, 34) which exhibit the low values of water salinity (1476-1861mg/l or 2460-2720 dSm^{-1}), fairly fresh to slightly brackish water and low bromide and iodide contents (7-9 and 0.02 mg/l). The independent case involves water point 36 which shows very low value of iodide content (0.01mg/l) with respect to cluster case (16, 34).

The seventh cluster (VII) is one case water points (10, Ain Fortaga) which exhibit the minimum values of water salinity (1205-2460mg/l or 1840-3030 dSm^{-1}), fairly fresh to brackish water, and very low bromide and iodide contents (2-6 and 0.01-0.02 mg/l). This cluster is characterized by less advanced stage of mineralization where the dominant anion is sulfate ($SO_4^{2-} > Cl^- > HCO_3^-$). This is rendered to the integrated recharge of subsurface infiltration of the runoff water from the hydrographic basin of wadi Watir.

Generally, the water points of cluster VII are affected by continental conditions more than the water points of clusters VI, V, IV, III, II and I in a descending order. On the other hand, the water points of clusters VII, VI, V, and IV are affected by continental conditions rather than marine conditions and vice versa in case of clusters III, II and I.

The independent case involves rain water with respect to all clusters which are considered as dependent cases when interpreted at a similarity level with a distance of 0.15 (Fig. 4), i.e. water samples of all clusters depend on the variation in chemical composition of rain water (independent case) which shows very low value of water salinity, bromide and iodide contents (30 mg/l or 50 dSm^{-1}, 0.08 and 0.01mg/l). This reveals that the groundwater samples have a meteoric origin affected, to an extent, by marine conditions.

The areal distribution of water points of clusters on basis of Q-mode dendrogram in delta wadi Watir is shown on fig. (5).

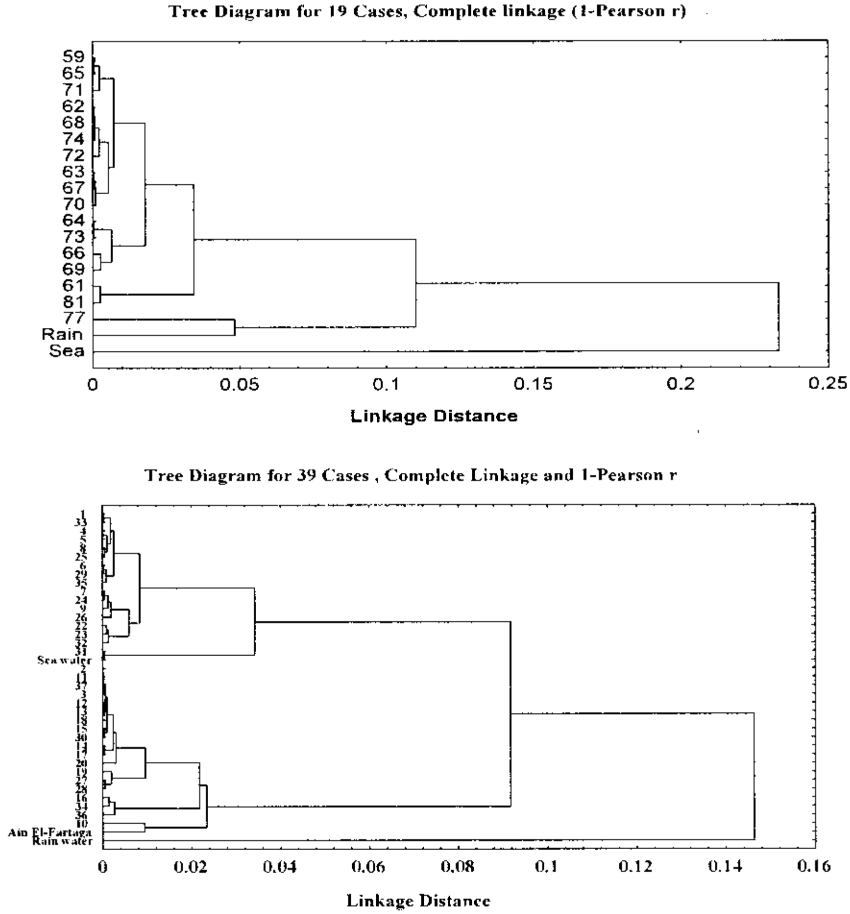
In the apex of the fan of wadi Umm Grafa, wadi Watir and wadi Saada, groundwater types are influenced by continental and marine conditions in the same time due to dissolution of the terrestrial and marine soluble salts from the catchment area of wadi Watir, which represents the carbonate rocks (marine environment), the basement rocks (rich in mafic minerals) and halite within alluvium aquifer matrices.

On the other hand, groundwater types are affected by meteoric conditions more than marine ones in the coastal area. This confirmed that the coastal part of the aquifer is more flushed than the apex of the fan of wadi Umm Grafa, wadi Watir and wadi Saada. From the R-mode dendrograms in both delta and wadi Watir (56 cases and 19 hydrochemical compositions, variables), table (5), it can be concluded that:

a- EC or TDS is highly significant, positively correlated with most major ions (Na^+, Cl^-, Br^-. K^+, Mg^{2+} I^-, SO_4^{2-}, Ca^{2+}), regardless of magnitude, indicating that these ions comprise a major bulk of the dissolved salts. On the other hand, EC or TDS is insignificantly correlated with (CO_3^{2-}

+HCO_3^-), F^- and SiO_2, indicating that these ions comprise a minor bulk of the dissolved salts (Table 1).

Furthermore, the low content of bicarbonate ions (mean115 and 183 mg/l at delta and wadi Watir, respectively) is mainly ascribed to the low solubility of solid carbonate in aquifers matrices and reversibility of bicarbonate to carbonate equilibrium as well as to other factors controlling P_{CO2} in the aquifers, where the bicarbonates were precipitated as carbonates along the recharge route from El Tih plateau to the basin of wadi Watir and its delta as clarified in most groundwaters, supersaturated with carbonate minerals (Table 6).



Tree Diagram for 19 Cases, Complete linkage (1-Pearson r)

Tree Diagram for 39 Cases , Complete Linkage and 1-Pearson r

Fig. (4). Vertical icicle plot of the studied water points of alluvium aquifer in wadi Watir basin and its delta (Q-mode).

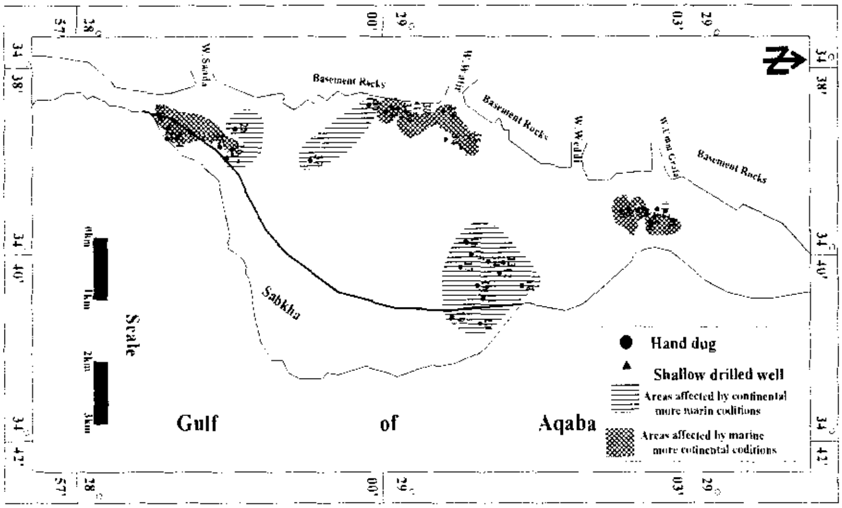


Fig. (5). Areal distribution of the groundwater samples of alluvium aquifer according to clusters in delta of wadi Watir (Q- mode dendrogram).

b- Concerning the high positive correlation between TDS and TH (Total hardness) in both wadi and delta, the concomitance of Ca^{2+} and Mg^{2-} ions in the forms of Cl^- and SO_4^{2-} leads to a corresponding increase in the total soluble salts.

c-Total hardness (TH) is positively correlated and highly significant with Ca^{2-}, Mg^{2-}, Na^-, K^-, SO_4^{2-}, Cl^-, Br^- and I^- (except HCO_3^-). This confirms the predominance of permanent hardness salts in both groundwater of wadi and delta (78 and 94% of TH, respectively). Nevertheless, the positive correlation of TH with Na^- and Cl^- is mainly attributed to the effect of leaching and dissolution of salts, especially NaCl concentration (effect of ionic strength) on increasing solubility of Ca^{2-} and Mg^{2+} in water (Freeze and Cherry, 1979; Hem, 1989). This does not exclude the contribution of CO_2 and longer residence time.

d-Nevertheless, major cations and anions are insignificantly correlated with pH, this is attributed to the neutrality of most, if not all soluble salts, i.e. the pH is principally affected by salt type rather than the salt content in the natural waters.

e-Soluble cations are highly significant, positively correlated with each other in both wadi and delta except for Fe^{2-} and Mn, respectively, which exhibit insignificant correlation with some other cations. This is due to weathering of basement and El Tih tableland (catchment area) beside leaching and dissolution of soluble cations found in the catchment area and aquifer matrices.

TABLE (5). Correlation coefficient matrices between different chemical variables of the groundwater of alluvium aquifer in wadi Watir basin and its delta.

	EC	Ca	Mg	Na	K	HCO_3	SO_4	Cl	I	Br	TDS	Fe	Mn	F	pH	Na+Cl	$Ca+SO_4$	SiO_2	TH
EC	1.000	Wadi Watir basin																	
Ca	0.744	1.000																	
Mg	0.999	0.763	1.000																
Na	0.999	0.721	0.997	1.000															
K	0.999	0.724	0.998	1.000	1.000														
HCO_3	-0.04	0.331	-0.02	-0.07	-0.07	1.000													
SO_4	0.970	0.879	0.977	0.961	0.962	0.092	1.000												
Cl	0.999	0.721	0.997	1.000	1.000	-0.080	0.961	1.000											
I	0.995	0.690	0.993	0.997	0.997	-0.055	0.947	0.997	1.000										
Br	0.999	0.716	0.997	1.000	1.000	-0.083	0.959	1.000	0.997	1.000									
TDS	1.000	0.742	0.999	1.000	1.000	-0.057	0.969	0.999	0.995	0.999	1.000								
Fe	-0.37	-0.26	-0.38	-0.38	-0.37	0.072	-0.37	-0.38	-0.37	-0.38	-0.38	1.000							
Mn	0.996	0.700	0.994	0.998	0.998	-0.092	0.950	0.998	0.997	0.998	0.997	-0.33	1.000						
F	0.444	0.666	0.458	0.426	0.433	0.513	0.533	0.425	0.419	0.422	0.441	0.026	0.419	1.000					
PH	-0.27	-0.02	-0.26	-0.28	-0.27	0.31	-0.22	-0.28	-0.27	-0.28	-0.27	0.66	-0.25	0.512	1.000				
Na+Cl	0.999	0.721	0.997	1.000	1.000	-0.079	0.961	1.000	0.997	1.000	0.999	-0.38	0.998	0.425	-0.28	1.000			
$Ca+SO_4$	0.958	0.900	0.966	0.948	0.949	0.117	0.999	0.947	0.931	0.945	0.957	-0.37	0.936	0.552	-0.21	0.948	1.000		
SiO_2	-0.36	0.023	-0.35	-0.37	-0.37	0.355	-0.27	-0.37	-0.36	-0.37	-0.36	0.483	-0.36	0.105	0.583	-0.376	-0.247	1.000	
TH	0.994	0.811	0.997	0.990	0.990	0.020	0.990	0.990	0.982	0.988	0.994	-0.37	0.984	0.495	-0.24	0.990	0.983	-0.31	1.00
EC	1.000	Delta wadi Watir																	
Ca	0.512	1.000																	
Mg	0.960	0.572	1.000																
Na	0.990	0.406	0.936	1.000															
K	0.957	0.350	0.943	0.969	1.000														
HCO_3	-0.01	-0.25	-0.01	0.021	0.050	1.000													
SO_4	0.755	0.846	0.849	0.680	0.664	-0.135	1.000												
Cl	0.993	0.446	0.947	0.998	0.970	0.009	0.699	1.000											
I	0.849	0.349	0.825	0.852	0.867	0.032	0.586	0.857	1.000										
Br	0.994	0.521	0.952	0.981	0.949	-0.039	0.738	0.988	0.847	1.000									
TDS	0.995	0.525	0.970	0.989	0.962	-0.009	0.775	0.993	0.849	0.989	1.000								
Fe	0.366	0.481	0.351	0.285	0.206	-0.164	0.456	0.292	0.235	0.382	0.327	1.000							
Mn	0.079	0.116	0.024	0.029	-0.05	-0.101	0.087	0.017	-0.01	0.095	0.027	0.739	1.000						
F	-0.19	-0.10	-0.16	-0.20	-0.19	0.526	-0.08	-0.21	-0.15	-0.21	-0.19	-0.08	-0.19	1.000					
PH	-0.03	0.055	-0.09	-0.05	-0.07	0.040	-0.05	-0.05	-0.23	-0.04	-0.06	0.214	0.224	-0.03	1.000				
Na+Cl	0.992	0.432	0.944	0.999	0.970	0.013	0.693	1.000	0.856	0.986	0.992	0.290	0.021	-0.21	-0.05	1.000			
$Ca+SO_4$	0.722	0.903	0.811	0.638	0.612	-0.164	0.993	0.662	0.549	0.710	0.741	0.474	0.096	-0.09	-0.03	0.654	1.000		
SiO_2	-0.16	0.376	-0.04	-0.22	-0.19	0.219	0.181	-0.18	-0.13	-0.14	-0.13	0.130	-0.15	0.324	0.093	-0.198	0.229	1.00	
TH	0.901	0.794	0.953	0.844	0.828	-0.106	0.943	0.867	0.742	0.899	0.913	0.438	0.060	-0.15	-0.05	0.859	0.935	0.10	1.00

f- With regard to anions in wadi Watir and its delta, the highly significant positive correlation are between (Cl^-, Br^-), (Cl^-, I^-) and (Br^-, I^-). This can be explained on the premise of halogen group but Cl^- is much more abundant. Furthermore, the groundwater acquires its quality from leaching and dissolution of marine salts which is supported by the highly significant positive correlation of Br- and I^- with Cl^- or EC (Table 5). The insignificant correlation of Cl^- with F^-, is expected due to the fact that the chemical behavior is different from that of other halogens as F^- is the most electronegative among all halogens. On the other hand, the significant positive correlation between Cl^- and SO_4^{2-} can be explained on the basis of the ionic strength effect of the four ionic species Na^+, Ca^{2+}, Cl^- and SO_4^{2-}. In other words, when the salinity ($Na^+ + Cl^-$) increases the solubilities ($Ca^{2+} + SO_4^{2-}$) increase is caused by decreases in activity coefficients of δ Ca^{2+} and δ SO_4^{2-} as a result of increased ionic strength (Freeze and Cherry, 1979; Hem, 1989). Also, the highly significant positive correlation between both Br^- and I^- with SO_4^{-2} is anticipated due to marine deposits in aquifer matrices and catchment area.

Table (6). Mean saturation indices (SI) of the groundwater due to chemical equilibrium with Quaternary aquifer in wadi Watir basin and its delta.

Locality	Aragonite	Calcite	Dolomite	Magnesite	Chalk
Wadi Watir	**Fresh water (TDS up to 1500 mg/l, μ up to 0.03)**				
Basin	+0.52	+0.66	+1.43	**+0.40**	**+0.08**
	Brackish water(1500 <TDS up to 5000 mg/l, 0.03 <μ up to 0.1)				
	+.65	+0.80	+1.71	**+0.53**	**+0.07**
Aquifer	+0.54	+0.68	+1.48	**+0.42**	**+0.08**
Delta wadi	**Brackish water(1500 <TDS up to 5000 mg/l, 0.03 <μ up to 0.1)**				
Watir	+0.31	+0.45	+0.97	**+0.15**	**+0.03**
	Saline to Extremely saline water (5000 <TDS >10000 mg/l, 0.1<μ> 0.2)				
	+0.34	+0.48	+1.16	**+0.27**	**+0.06**
Aquifer	+ 0.46	+ 0.54	+ 1.18	**+0.30**	**+0.17**

1-Aragonite ($CaCO_3$) 2-Calcite ($CaCO_3$)
3-Dolomite $\{CaMg(CO_3)\}_2$ 4-Magnesite ($MgCO_3$).5-Chalk ($CaCO_3$).

g- Soluble cations and anions of both wadi and delta Watir display highly significant correlation with each other except for HCO_3^-, Fe^{2+} and SiO_2 which exhibit insignificant correlation with other cations and anions (Table 5). In this accord, the magnitude of correlation coefficients is strikingly strong between Na^+ and Cl^-, K^- and Cl^-, $Mg^{2+}$and Cl^-, $Mg^{2+}$and Br^-, $Mg^{2+}$and SO_4^{2+}, $Ca^{2+}$and SO_4^{2+}, $Mg^{2+}$and I^-. Na^+ and SO_4^{2+} as well as Ca^{2+} and Cl^-, depending on whether water is saline, brackish or fresh and nature of recharge as well as the aquifer type (Table 5). The high significant positive correlation of Na^+- Cl^- follows Mg^{2+}- Cl^-, Ca^{2+} - Cl^- and Na^+- SO_4^{2-} correlations in a descending order in wadi Watir, indicating dissolution of the terrestrial and marine salts found in the catchment area and aquifer matrix. These correlations are in harmony, to a great extent, with the following hypothetical salts of the groundwater in the alluvium aquifer of wadi Watir:

Assemblage I: $NaCl$, Na_2SO_4, $MgSO_4$, $CaSO_4$ and $Ca\ (HCO_3)$ (18 % of the total samples).

Assemblage II: $NaCl$, $MgCl_2$, $MgSO_4$, $CaSO_4$ and $Ca\ (HCO_3)$ (82 % of the total samples).

On the other hand, the highly significant positive correlation of Na^+-Cl^- follows Mg^{2+}- Cl^- and Ca^{2+} - Cl^- correlations in a descending order in delta wadi Watir, indicating dissolution of the marine salts in the catchment area and aquifer matrix. These correlations agree, to a great extent, with the following hypothetical salts of the groundwater in the delta:

Assemblage II: $NaCl$, $MgCl_2$, $MgSO_4$, $CaSO_4$ and $Ca\ (HCO_3)$ (78 % of the total samples).

Assemblage III: $NaCl$, $MgCl_2$, $CaCl_2$, $CaSO_4$, and $Ca\ (HCO_3)_2$ (22 % of the total samples).

Finally, these results of significant correlations indicate that the groundwater acquires its quality from leaching and dissolution of salts.

5- Geochemical evolution of groundwater.

The main changes in groundwater chemistry of alluvium aquifers in wadi Watir basin and its delta during its movement from recharge area to discharge area are discussed through Back and Hanshaw's (1979) system.

Applying Back and Hanshaw's (1979) groundwater evolution system, the changes in groundwater chemistry of the alluvium aquifers in the study area are discussed as follow (Fig.2):

a- In most groundwater samples (94%) of wadi Watir, there is one reaction pathway for evolution, R----->D, indicating that runoff recharge source(R) directly moves down- gradient to the saturated zone (R----->D, beside dissolution of dolomite and gypsum). On the other hand, few groundwater samples (6%) display less mineralization (pure meteoric water, less advanced mineralized water) and did not undergo any evolution processes, where the metasomatic sequence did not reach the final sequence of more advanced stage ($Cl > SO_4 > HCO_3$).

b- In the delta two reactions pathways for evolution are as follows:

Dissolution
i-R(recharge area) ------------> D(down-gradient movement of groundwater)
Process

Marine salts
ii- D (down-gradient movement of groundwater) ------------------->
M(marine water type) Encroachment

During this process, some of the most profound mineralogical reaction paths are shown in fig. (2). In recharge area (R), groundwater is typically of the Ca-HCO_3 type (fresh water). During its movement down-gradient R→D,

Mg^{2+} increases owing to dissolved dolomite, while Ca^{2+} remains relatively constant, also SO_4^{2-} increases as gypsum is sparingly dissolved and HCO_3^- remains relatively constant. Another reaction pathway is also possible from D→M; this involves marine salts encroachment into deeper parts of the aquifer; leading to leaching and dissolution as well as dolomitization (Back and Hanshaw,1979).

In brief, the changes in groundwater chemistry in wadi have a reaction pathway R→D while in delta they displayed two pathways R→D and D→M. Consequently, the reaction pathway D→M in delta Watir is shown to be more influenced by marine sediments than that wadi Watir basin. This leads to abrupt increase in water salinity of delta Watir more than that of wadi Watir.

CONCLUSION

This study reveals that two water salinity zones in wadi Watir basin, one is the fresh water (82%.) which occupies most subbasins and, the second is the brackish water in the subbasin El-Sheikh Attia. On the contrary, the most dominant zone in delta Watir is the brackish water (75%, zone C) which occupies the western parts and the rest is saline to extremely saline water (25%, zone D), dominating the coastal plain and southeastern part. Therefore, the dominance of fresh water is in wadi Watir and brackish water in its delta.

Based on ion relationships, the chemical composition of most groundwater from the wadi Watir shows a great resemblance to that of the inland rain water while most groundwater samples of delta Watir show a great resemblance to sea water.

The genetic diagrams, show that most groundwater of wadi Watir is dominated by alkaline earth's and strong acid (secondary salinity) while most groundwater of its delta is dominated by alkalis and strong acid (primary salinity). On the other hand, most groundwater of wadi Watir is plotted on the sub-square sulfate-magnesium water while most groundwater of its delta is located near the end of the trend of major metasomatic changes of water quality (halite and bischofite subquadrants). This may confirm that the general flow of groundwater is from west to east, i.e. from the wadi to the delta and it is of meteoric origin.

The multivariate statistics, cluster and correlation analyses were conducted using computer program "Statisical for Windows"(Statistics Multivariate Exploratory Techniques, 1984-2003) indicates:

1- Examination of Q-mode dendrogram reveals one groundwater facies in wadi Watir basin, which is affected by continental condition (three clusters) while two groundwater facies are found in delta wadi Watir, one affected by marine condition (three clusters) and the other is affected by continental condition (four clusters).

2- From the R-mode dendrograms in both delta and wadi, it can be concluded that:

i- EC or TDS is highly significant, positively correlated with most major ions while being insignificantly correlated with most soluble minor elements in both wadi and delta.

ii- Total hardness is highly significant positively correlated with Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, Br^{-} and I^{-} (except HCO_3^{-}) in both wadi and delta.

iii- Major cations and anions are insignificantly correlated with pH in both wadi and delta.

iv- Soluble cations are highly significant, positively correlated with each other in both wadi and delta except for Fe^{2+} and Mn^{2+}.

v- With regard to anions in wadi Watir and its delta, the highly significant positive correlations are between (Cl^{-}, Br^{-}), (Cl^{-}, I^{-}) and (Br^{-}, I^{-}).

vi- Soluble cations and anions of both wadi and delta Watir display highly significant correlation with each other except for HCO_3^{-}, Fe^{2+} and SiO_2.

Finally, these results of significant correlations indicate that the groundwater acquires its quality from leaching and dissolution of salts.

The main changes in groundwater chemistry in wadi Watir according to Back and Hanshaw's (1979) are only of one reaction pathway R (recharge area) →D (down-gradient movement of groundwater) while in the delta, it is characterized by two pathways R→D and D→M (marine water type), the latter pathway (D→M) showed more influence by marine sediments in the delta than in the wadi.

RECOMMENDATIONS

In order to develop the groundwater in wadi Watir and its delta, the following guidelines are recommended:

1- Exploration of drilled wells can be performed in the areas of decreasing water salinity and increasing water level or limited fluctuation (withdrawal, less than or equal to recharge), west of wadi Watir delta and wadi Watir basin.

2- Establishment of new communities in the area of El-Sheikh Attia and the peneplained area of the northern part of the wadi Watir basin where the good water supplies are mainly extracted from the Quaternary wadi fill aquifer.

3- The activities in the alluvial fan should be limited to agriculture, trading and tourism while the inhabitants and employees should be transported out of the fan to El Sheikh Attia and the area of the northern part of wadi Watir basin where water quality is more suitable.

4- Desalination of brackish groundwater using reverse osmosis membrane technique for drinking purposes of delta (which occupies the western parts, water zone C) is much cheaper than saline and Gulf water.
5- Full utilization of Ain Fortaga spring in Nuweiba town can partially solve the water crisis in this area.

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دراسة مقارنة لنوعية المياه بخزانات العصر الرباعي في حوض وادي وتير ودلتاه، جنوب شرق سيناء- مصر

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يهدف البحث إلى تقييم البيانات الهيدروكيميائية للمياه الجوفية في خزان الغرين بحوض وادي وتير و دلتاه.وتقييم العمليات الهيدروكيميائية المؤثرة على نوعية المياه بالإضافة إلى مصادر تمعدن المياه الجوفية و التطور الجيوكيميائى لها. وقد توصل الباحث إلى ما يلي:

١-وجود نطاقين للمياه الجوفية بحوض وادي وتير الأول نطاق المياه العذبة السائد (٨٢ % من عدد عينات المياه) , و الثاني نطاق المياه متوسطة الملوحة(الأسنة) و يمثل ١٨% من عدد عينات المياه ، ويتواجد في منطقة الشيخ عطية بالحوض حيث تتشابه كيميائية المياه الجوفية للنطاقين مع كيميائية مياه الأمطار .أما في دلتا وادي وتير يوجد أيضا نطاقين للمياه الجوفية وهما نطاق المياه متوسطة الملوحة (الأسنة) السائدة(٧٥%) في المنطقة الغربية من الدلتا و نطاق المياه المالحة و تشغل ٢٥% ويتواجد في المناطق الساحلية و الجنوبية الشرقية حيث تتشابه كيميائية هذه المياه الجوفية بالنطاقين مع كيميائية مياه البحر وهذا لا يعكس وجود تداخل لمياه البحر وإنما يعكس تأثرها بالرواسب البحرية.

٢-أظهرت الأيونات السائدة ومخططات بيبر و دروف و التحاليل الإحصائية أن مصدر تمعدن المياه الجوفية في حوض وادي وتير و دلتاه هي مياه الأمطار المحلية التي تأثرت بالرواسب البحرية و القارية المتواجدة في مناطق التغذية ورواسب الخزان. كما أظهر مخطط دروف أن المياه الجوفية متطورة كيميائيا جهة الشرق (مناطق التفريغ ،الدلتا) بينما كانت غير متطورة كيميائيا جهة الغرب(مناطق الشحن ،حوض، وادي وتير) مما يؤكد أن حركة المياه الجوفية من الغرب إلى الشرق.

٣-أوضح تحليل المجاميع من النوع Q-mode لمياه حوض وادي وتير وجود نوع واحد من المياه الجوفية (ثلاثة مجاميع) المتأثرة بالأمطار المحلية بينما يوجد في دلتا وادي وتير نوعين من المياه الجوفية الأولى متأثرة بالظروف البحرية(ثلاثة مجاميع) والثانية متأثرة بالظروف القارية(أربعة مجاميع).كما أوضح تحاليل معامل الارتباط من النوع R-mode أن ارتباط التوصيل الكهربي أو الملوحة الكلية في المياه الجوفية لكلا من حوض وادي وتير ودلتاه بالأيونات الأساسية المختلفة ارتباطا عاليا موجبا بينما أظهرت بعض الأيونات الثانوية في المياه الجوفية عدم ارتباط التوصيل الكهربي أو الملوحة الكلية بهذه الأيونات. وارتبط العسر الكلى ارتباطا عاليا موجبا مع أيونات الكالسيوم ، الماغنسيوم ، الصوديوم ، البوتاسيوم ، الكبريتات ، الكلوريد واليوديد (ماعدا البيكربونات) في كلا من حوض وادي وتير و دلتاه، وكذلك عدم ارتباط الأس الهيدروجيني (رقم الحموضة) للمياه الجوفية مع معظم الكاتيونات و الأيونات. وبتطبيق مخطط باك وهانشو لدراسة التطور الكيميائي للمياه الجوفية بالخزان الغرينى يخضع لنوع واحد من التفاعلات الكيميائية ، في كلا من حوض وادي وتير ودلتاه وهو:

(منطقة التغذية R) $\xleftarrow{\text{عمليات الغسيل والإذابة}}$ (D حركة المياه إلي أسفل) بينما تخضع مياه الدلتا لنوع آخر من التفاعلات الكيميائية بالإضافة إلي النوع الأول ، وهو

(D حركة المياه إلي أسفل) $\xleftarrow{\text{غزو الأملاح البحرية}}$(M مياد بحرية) ، وهذا النوع الآخر يفسر زيادة ملوحة مياد الدلتا عن مياد الوادي في الخزانات الغرينية.

بناءً على نتائج هذا البحث يوصى بحفر الآبار في المناطق الأقل ملوحة وهي حوض وادي وتير والمناطق الغربية من دلتاه. كما يمكن إقامة مجتمعات جديدة في منطقة الشيخ عطية

والمناطق الشمالية بوادي وتير وذلك لجودة نوعية المياه بالخزان الجوفي الغرينى بها. كما يراعى تقليل النشاط الزراعي بمنطقة الدلتا لارتفاع ملوحة المياه بها و تركيزها في منطقة الشيخ عطية والمناطق الشمالية بحوض وادي وتير. أما تحلية المياه متوسطة الملوحة بدلتا وادي وتير باستخدام تقنية أغشية الضغط الأسموزي المضاد لغرض الشرب يعتبر ارخص اقتصاديا من تحلية مياه البحر. وأخيراً يوصى بالاستفادة الكاملة من مياه عين فرتاجة في التغلب علي النقص الحاد للمياه في منطقة الدلتا.