



Geochemical Evolution of Groundwater in the Quaternary Aquifer in Beni Suef area, Egypt



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Abstract

Recent groundwater geochemical data from boreholes and surface recharge water in the Quaternary aquifer in the flood plain aquifer of the Beni Suef area have been utilized to try to assess the evolution of groundwater composition. The Nile flood sediment contains abundant sand and clay minerals. Evaporite minerals are common in the marl and marly carbonate deposits along the western and eastern flanks of the flood plain aquifer. The area characterized by high activities concerning agricultural, urbanization and reclamation and cultivation of the desert fringes along the western and eastern borders of the valley. The flood irrigation system and the lack of sewage network, in most of the area, deteriorate the groundwater aquifer. The least geochemically-evolved groundwater types groundwater type 1 (GWT1) and groundwater type 2 (GWT2) inevitably have salinity slightly higher than the surface waters (SW) which is the main recharge source of the aquifer. They have similar cation and anion ratios (approximately equal molar quantities of Cl, HCO₃, SO₄, Na, Ca and Mg) although they have a significantly lower pH than recharge waters due to a possible combination of soil gas CO₂ dissolution and dissociation. Sulphate reduction and de-nitrification of the oxidized forms of nitrogen reduced the NO₃ concentration of the groundwaters than the SW. The majority of the groundwater samples have higher salinity than recharge waters with salinity dominated by HCO₃ and Ca with subordinate SO₄ and Mg and they marginally saturated with calcite and dolomite. Careful analysis of the data reveals that water geochemical evolution is the result of congruent dolomite, gypsum dissolution and clay mineral-hosted cation exchange (increasing Na and Ca). A small region of the aquifer displays an extreme degree of aquifer-groundwater interaction. The groundwater here is saturated with respect to calcite and dolomite. Another region, beneath urban areas, has historically experienced pollution, evidenced by locally elevated nitrate concentrations, has commensurately higher SO₄, Cl, Ca and Na concentrations and is supersaturated with carbonate minerals. The main geochemical processes in the aquifer are congruent dolomite dissolution, gaining Na due to cation exchange, evaporite mineral dissolution reduction of SO₄ and NO₂ confirm the confined condition of the aquifer in most of the area.

Keywords: Flood plain, Quaternary; groundwater; geochemical evolution,

1. Introduction

Natural water-rock interaction processes in aquifers have a major impact on water geochemistry and water quality. Unconfined aquifers in urban and intensively farmed rural areas are especially vulnerable to

pollution and contamination. It is important to comprehend natural processes in a given aquifer before trying to address the impact and ultimate fate of any pollutants. It is important to understand how a groundwater-rock system evolves from the time

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surface water first enters the aquifer via outcrop or soil and a vadose zone; until the time when it either exists as surface waterlogging or recharging shallow water channels or is extracted from an abstraction wells.

The main objectives of this article directed to the identification of the primary controls on water geochemistry and the geographical changes in the groundwater composition in the area. This study was focussed on the controls on the composition and evolution of fresh groundwater. The Beni-Suef is a high population density area where the aquifer has a long history of industrial and urban land use. The specific objectives of the study include:

1. Evaluate the quality of ground and surface water through some of hydrological and environmental measurements (physiochemical characteristics of water [1]) from the study area.
2. Assess the progressive geochemical processes that control the variation and the extent of change in the composition of groundwater.
3. Investigate the environmental factors (either natural or artificial) that control the quality of the different water resources in the study area.
4. Evaluate the environmental impacts of water logging phenomenon in many rural areas and expect their mitigations.

The study area is located in Middle of Egypt between latitudes $28^{\circ} 45' 00''$, $29^{\circ} 24' 00''$ N and longitudes $30^{\circ} 47' 20''$, $31^{\circ} 14' 13''$ E, and encompasses many urban areas of surrounded countryside and extends east-west through the western bank of the Nile flood plain (Fig. 1). The western margin occurs where the Quaternary aquifer deposits unconformably overly the Eocene carbonate rocks. The climate in Beni Suef is called a desert climate; characterized by dry, hot weather condition and rainless in summer and rare rainfall in winter; dry winds with dust, (Khamassen windstorms), which are blown from southwest direction.

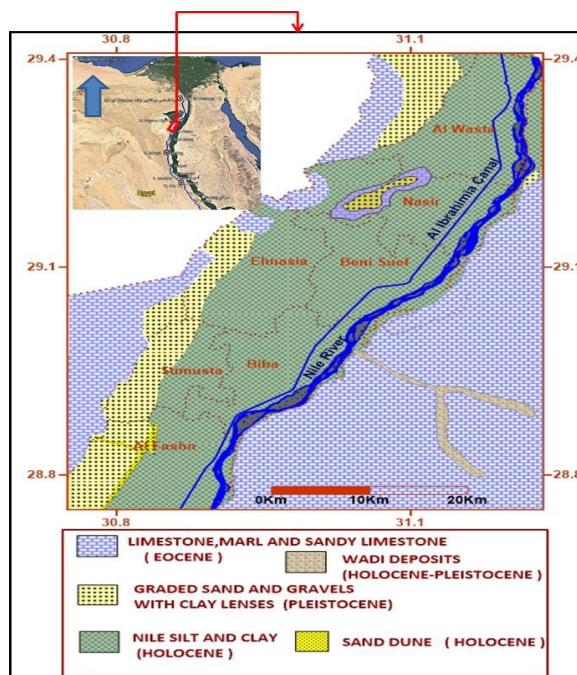


Fig. 1: The location and geologic map of the studied area.

Hydrogeological studies of the Quaternary aquifer in the Nile River flood plain date back to the 1974 when Attia [2], Idris and Nour [3] gave a general review of the parameters and characteristics of the groundwater reservoir in the Nile Valley and reported that the plans for groundwater development are usually based on the hydrogeological characteristics of the groundwater resources as well as on the environmental control of the discharge area. El Mahdy [4] inferred the hydrogeologic evaluation of the groundwater resources and stated that the groundwater potentialities of the Prenile aquifer possess high optimistic level in both quantity and quality in spite of high level of pollution. Based on the hydrochemical and environmental isotopes, El-Bakri et al., [5] concluded that the salinity of the Quaternary groundwater at Mallawi, to the south of the study area, ranges from 200-950 mg/l with a high degree of mixing. Based on the hydrochemical and hydrological characteristics, El-Sayed [6] studied the relationships between the different groundwater aquifers and the surface water and concluded that the groundwater of the middle Pleistocene aquifer is directly connected with the surface water in northern part of Upper Egypt. Abdel-Mageed [7] studied the quality of the Quaternary groundwater in Beni_Suef area and found that, about 33% of groundwater samples have total coliform exceeded the desirable limits. Korany and

Hussein [8] stated that the sources of groundwater recharge of Quaternary aquifer are the direct seepage from irrigation canals and branches, infiltration of return flow after irrigation and limited contribution by local rainfall. Hamdan [9] tackled the evaluation of the Nile valley aquifer using geophysical and hydrogeological methods indicated that the Sodium – Sulphate and Sodium Chloride facies are dominated in the groundwater of the Nile Valley aquifer. Awad [10] discussed the groundwater contamination in some districts in Egypt including El Fashn south Beni-Suef area. He found that the groundwater to the west of El Fashn has high salinity, nutrients, and some heavy metals such as Mn, Fe, Cd, Ba with concentrations exceed the permissible limits of drinking water. The National Water Research Center [11] mentioned that the River Nile from Aswan to El-Kanater Barrage receives wastewater discharge from 124-point sources, of which 67 are agricultural drains and the remaining are industrial sources. Abdel-Wahaab and Badway [12] studied the characteristics of the Nile water system and identify the major sources of pollution and its environmental and health effects. They found that the river receives a large quantity of wastewater, but it is still able to recover in virtually all the locations, with very little exception, due to the high dilution ratio. Gad [13] in his trial to mitigate the waterlogging problem in new reclaimed areas in the desert fringes of Beni-Suef and El-Minya governorates concluded that the reason of this phenomenon in the old cultivated land is the difference in topographic level, inadequate drainage system and the existence of shallow depth clay lenses beneath these sites. Faid and Mansour [14] investigated the reclamation impacts on the groundwater reservoir in the Maghagha aquifer system, to the south of the studied area, by using the modeling and remote sensing techniques. They inferred that the change in peizometric level and groundwater salinity has been associated with an increase in the cultivated land. Khalil [15] studied the major chemical components in the Quaternary aquifer in Beni-Suef area and found that they did not exceed the maximum permissible limits except at some sites where higher concentrations of Na, Fe, and Cl were recorded. Melegy et.al. [16] supported the suitability of surface and groundwater for drinking and irrigation purposes however high concentration of Al, Cd, Fe, Mn, Co in some places. They related them to anthropogenic activities, like fertilizers and pesticides, waste disposal and industrial wastes, seepage from

septic tanks, water pipes construction, and wastewater sewage from El-Moheet drainage and evaporation processes during flood irrigation. Using geoelectrical resistivity survey, Rabeh et al. [17] studied the aquifer potentiality in Beni-Suef area and detected a series of normal faults that act as sub vertical recharge conduits of the studied aquifer.

2. General geology and hydrogeology

In the study area, the rock successions consisted of sedimentary rocks range in age from Quaternary to Upper Eocene [18] and [19] (Fig. 1 and Table 1).

Eocene rock units have been represented by Middle and Upper Eocene rocks. The Middle Eocene rocks are subdivided into Qarara Formation (80 m thick), El-Fashn Formation (90 m thick), Beni-Suef Formation (100 m thick), and Shaibun Member, while the Upper Eocene is represented by Maadi Formation.

Pliocene rock units are expected subsurface and can be reached by borings. They are composed of dark green clays and shale of impermeable to semi-permeable characters. These units disappear at the east side and west side of the Nile Valley where the overlying quaternary section rests unconformity on the Middle Eocene limestone [20].

Plio-Pleistocene Rock units rest directly on the Pliocene clays and shale. They are intercalated layers of sand, clay with gravels in the eastern and western margins of the flood plain. They dominate the study area forming terraces of different elevations above the flood plain. They were formed of graded sands and gravels with clay lenses. The recorded maximum thickness reaches about 200 m, while the minimum thickness attains 100 m. They represent the main groundwater aquifer in the area under consideration

Holocene deposits consist of the unconsolidated to poorly consolidated sediments accumulated under different erosion condition. They include Nile silt, sand dunes, fanlomerates, and wadi deposits [21].

Table 1: Composite lithostratigraphic section of the exposed rock units, Beni Suef district [22] and [23].

Age	Formation		Symptom	Max. thickness	Lithologic description	Occurrence	
	Member	Member					
Quaternary	Holocene	Sand Dams		Variable	Sands	Cultivated land in the Nile Valley	
		Nile Silt		15m	Silt and clay		
Pleistocene		Abbasia Fm.		Variable	Gravel, sands and clays	Nile Valley area	
		Saifi Ghazib Fm.		25m	Sandstone		
		Kasr El-Basel Fm.		40 m	Conglomerates and Sandstone	G. (Umm Raqab, Labun, El-Naalam)	
Pliocene		Um Raqaba Fm.		30 m	Impure sand coquinaoid L.S, marl and clay topped with crystalline L.S	G.Homret Shaibun	
		Maadi Fm.		62 m	Nodular Limestone Nummulitic and marl with minor clay interbeds	Gebel Homret Shaibun north east of Beni-Suef	
Tertiary	Eocene	Upper Mokattam	Equivalent to Shaibun Member	100 m	Argillaceous Limestone top laminated clays, Argillaceous Limestone interbedded with clay and calcareous clay	Exposures lying south east of Beni-Suef and G. Shaibun	
							Beni-Suef Fm.
		Middle Eocene	Lower Mokattam Fm.	Observatory Member	90 m	Different facies north: limestone and marl complex south: chalky limestone and gypsiferous shales with chert	
							El-Fashn Fm.
Quarna Fm.		80 m	Karstified Nummulitic Limestone and (with caves)	East of Beni-Suef in G. Samur and G. Ghayda west of Beni-Suef G. Qarara			
Pre Middle Eocene not exposed							
					Total thickness = 442 m		

Hydrogeological setting: two main aquifers are encountered in the study area. The upper one is the Quaternary aquifer which is composed of sand and gravel interbedded with clay. It is recharged from River Nile through irrigation returned water or from the irrigation canals. This in addition to two more sources of recharge, the paleo River Nile water and Eocene aquifer [21]. The deeper one is the Eocene aquifer which is composed of the chalky limestone with chert bands or nodules of the lower part of El Fashn Formation and the sandstone and sandy limestone of the upper part of Qarara Formation. The Eocene aquifer is recharged from the Nile water through irrigation canals and occasionally from rainfall storms on the Eastern Desert. The transmissivity of Quaternary aquifer is $8 \times 10^3 \text{ m}^2/\text{day}$, hydraulic conductivity is 28.75 m/day , and the storativity is 4×10^{-4} [20]. Eocene aquifer has transmissivity values ranging from $782.5 \text{ m}^2/\text{day}$ in the western part to about $0.55 \text{ m}^2/\text{day}$ in the eastern part of the study area. The variation in transmissivity of the Eocene aquifer is mainly due to the dissimilarity of fractures density in the limestone [24].

The subsurface configuration of the groundwater aquifers related to depth, thickness, and type of layer as well as water-bearing formation was delineated by Ismail et al. [21] through geoelectrical cross sections C-C', D-D' and E-E' at the western bank (Figs. 2, 3).

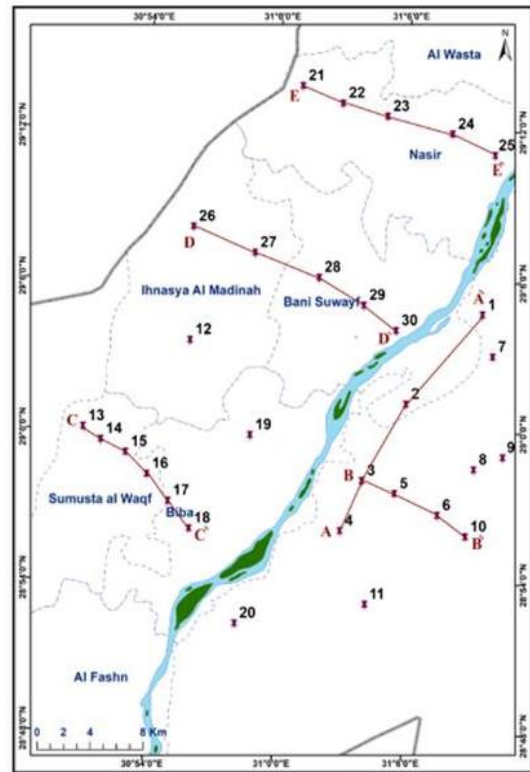


Fig. 2: Geoelectric cross sections trending NW-SE along the study area.

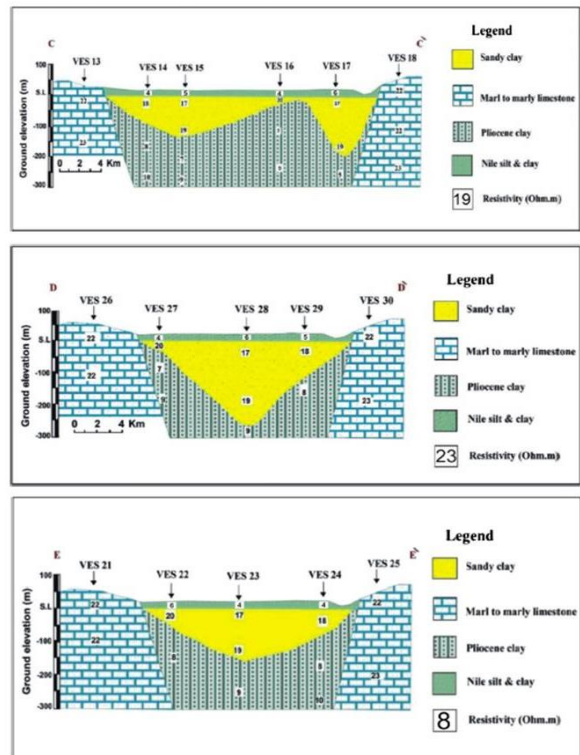


Fig. 3: The subsurface configuration of the groundwater aquifer based on geoelectrical cross sections. Compiled after [21].

Four hydrogeologic layers were recorded in the cross sections; the 1^{st.}, layer consisted of Nile silt and clay (Fig. 3). The 2^{nd.}, layer consists of sandy clay deposits and exhibits resistivity varies from 17 to 20 Ohm.m, and a thickness ranges from 10 to 250 m. The 3^{rd.}, layer in the cross section is made up of Pliocene clay deposits and has resistivity values that vary from 7 to 9 Ohm.m, and thickness varies from 40 to 250 m. The last layer represents the Eocene aquifer composed of marly limestone where its calculated thickness reaches more than 250m, and resistivity values vary from 22 to 23 Ohm.m.

3. Methodology

Forty-three groundwater samples were collected from the study area (Fig. 4). The groundwater samples were collected after the well pumped out water for 15 min. to purge the aquifer of stagnant water to acquire fresh aquifer samples for analysis. Thirty-four water samples from surface water (Nile River, Al Ibrahimia canal, Al Gizawia canal and Bahr Yusef) were collected between EL Fashn-Al Wasta area, Beni Suef district (Fig. 4). The location site is determined by GPS instrument (Trimble model Juno T41/5).

Water samples from each test site were collected in containers specialized to suit the nature of the parameter measured. Polyethylene containers of two-liter capacity were used for most chemical analysis.

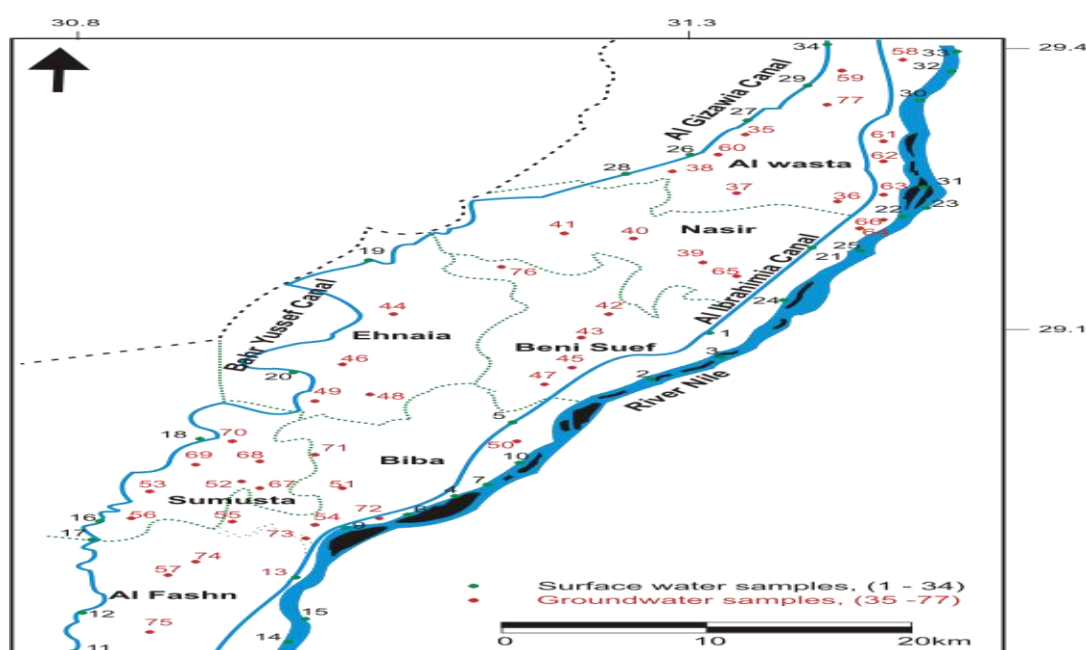


Fig. 4: location map of the collected water samples. The surface water samples are represented by green circles and black numbers from 1 to 34, while the groundwater samples are plotted in red circles and numbers from 35 – 77.

Water sampling, preservation, and physiochemical properties were determined according to Standard Methods for Examination of Water and Wastewater [1]. Field parameters including temperature, pH, electrical conductivity (EC), total dissolved solid (TDS) were measured in-situ by multi-probe system, model HYDROLAB multi-parameter sonde WTW 350i (the device was calibrated before using) and all results were verified in laboratory. Carbonate and bicarbonate were volumetrically determined by titration method (0.02 N H₂SO₄ with phenol phthalein and methyl orange as indicators). Total alkalinity for each sample was calculated from the

summation of carbonates and bicarbonates and recorded as mg/l. Major anions such as chloride (Cl⁻), sulfate (SO₄²⁻), and nitrate (NO₃⁻) were determined in water samples using ion chromatography (IC) Model ICS5000-DX, USA. Major cations (Na⁺, K⁺, Ca⁺⁺ & Mg⁺⁺) and heavy metals (Al, Ba, Cd, Cr, Cu, Fe, Mn and Zn) were determined using the Inductively Coupled Plasma-Emission spectrometry (ICP-MS) (model Perkin Elmer NexIon 300D, USA). The analyses were carried out in the Central Laboratory for Environmental Quality Monitoring, National Water Research Center in Cairo.

4. Results

Chadha [25] developed a useful genetic groundwater classification scheme to differentiate the types of water-rock interaction processes in aquifers. This classification plotted the difference in milliequivalent percentage between alkaline earth (calcium plus magnesium) and alkali metals (sodium plus potassium) plotted on the X axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong

acidic anions (chloride plus sulphate) plotted on the Y axis. The geochemical compositions of the surface and ground waters represent four discrete water types (Fig. 5a). Geochemical analyses of the river water samples have been added to the processed groundwater data to show how recharge must have evolved geochemically as it became groundwater and to help explain the relation between the surface water and groundwater. The geographical distributions of the different groundwater types in the area are shown in (Fig.5b).

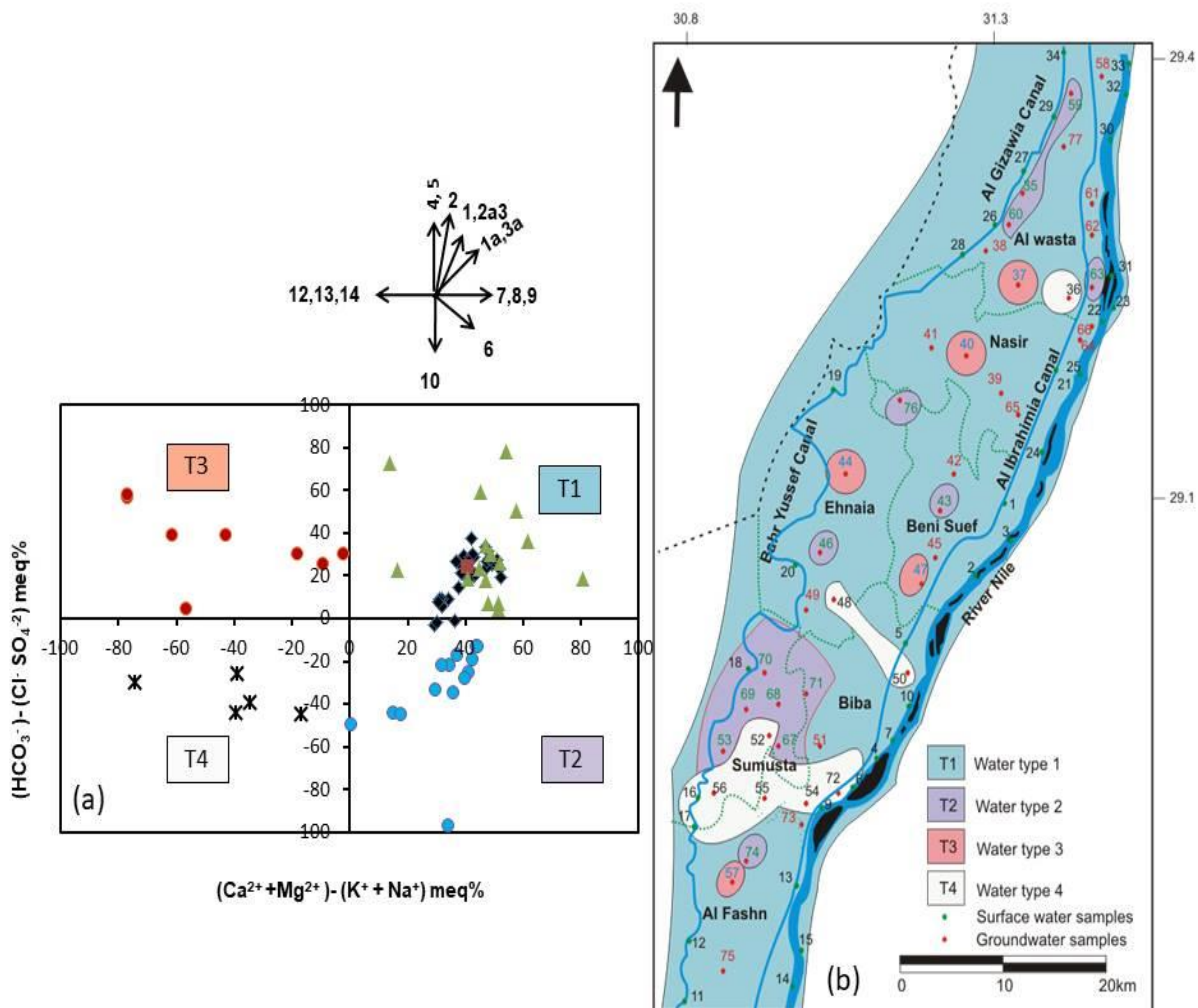


Fig. 5: Geochemical classification of groundwaters; (a) the groundwater types are T1: $[Mg^{2+} - Ca^{2+} - HCO_3^-]$, T2: $Mg^{2+} - Ca^{2+} - HCO_3^-$ with $MgSO_4$ and $MgCl_2$, T3: $K^+ - Na^+ - HCO_3^-$ and T4: $NaCl$ and Na_2SO_4 , and (b) the geographical distribution of the groundwater types in the aquifer. All data plotted on this figure are reported in Tables 2 and 3. The vectors, to be discussed later, represent potential geochemical reactions listed in Table that may have influenced the geochemical composition of groundwaters in the Quaternary aquifer of Beni Suef area.

4.1. Fresh groundwater type 1 T1 (Mg – Ca – HCO₃)

This water type represents all the surface water samples and the maximum number of groundwater samples. Regionally it can be considered the main water type in the whole aquifer as it represents the chemical composition of the majority of fresh groundwater samples in the whole area (Figs. 5a and 5b) lying in the upper right quadrant of the Chadha diagram. This water type is almost always alkaline (pH

> 7, Tables 2,3). Bicarbonate is the main anion in this water type, followed in concentration by SO₄ and Cl (Tables 2,3). Calcium with subordinate Mg and Na are the main cations (Tables 2,3). The variation in the total dissolved solids (TDS) of this water type reflects the variations in the sum of the concentrations of the dominant anion and cations: HCO₃, Ca and Mg (Tables 2,3). The waters are typically saturated with respect to calcite and dolomite except few samples.

Table 2: Chemical analyses of surface water samples.

No.	pH	TDS	K	Na	Mg	Ca	Cl	SO ₄	HCO ₃	NO ₃	Cal SI	Dol SI
1	8.23	205	5	27	12	31	24	31	130	0.5	0.3	1.0
2	8.38	252	7	28	12	33	26	30	121	0.31	0.5	1.3
3	8.00	206	5	26	11	28	23	26	122	0.24	0.0	0.4
4	8.58	220	6	27	11	30	21	22	111	0.1	0.6	1.6
5	8.14	213	5	28	11	29	23	24	134	1.2	0.2	0.8
6	8.2	201	7	28	9	27	22	15	131	0.1	0.2	0.8
7	8.15	205	5	27	8	26	21	21	114	0.1	0.1	0.5
8	8.45	186	6	28	10	30	23	25	117	0.23	0.4	1.3
9	8.43	198	7	27	11	29	25	25	130	0.27	0.5	1.4
10	7.5	317	6	45	14	35	41	37	157	0.21	-0.3	-0.2
11	8.12	229	7	28	10	32	25	22	134	0.36	0.2	0.8
12	7.89	344	8	52	15	38	47	45	166	0.41	0.1	0.7
13	8.31	219	5	27	10	28	21	20	128	0.33	0.3	1.1
14	8.7	203	5	28	6	26	20	21	112	0.24	0.6	1.5
15	8.35	239	5	28	11	32	24	23	131	0.24	0.4	1.2
16	7.95	279	7	36	12	34	31	34	144	0.47	0.1	0.6
17	8.03	262	6	35	11	33	30	33	142	0.36	0.2	0.7
18	7.99	259	7	35	11	32	31	34	140	0.1	0.1	0.6
19	7.62	337	7	51	13	36	45	42	157	0.77	-0.2	0.0
20	7.89	373	8	55	15	38	52	46	167	0.49	0.1	0.7
21	7.92	201	5	28	7	27	22	20	114	0.24	-0.1	0.0
22	8.39	197	5	26	9	24	20	21	114	0.35	0.3	1.0
23	8	236	6	31	10	26	28	24	122	0.38	0.0	0.4
24	8.41	225	6	29	11	27	30	20	119	0.34	0.4	1.2
25	8.55	221	5	30	10	26	28	21	120	0.23	0.5	1.5
26	7.82	358	7	50	12	35	44	41	153	0.48	0.0	0.4
27	7.93	305	6	48	11	33	43	37	142	0.64	0.1	0.5
28	8.16	423	7	62	18	47	71	53	185	0.38	0.5	1.5
29	7.84	346	7	54	11	37	51	49	142	0.54	0.0	0.3
30	8.23	335	6	52	12	35	50	48	143	0.61	0.4	1.1

31	8.39	222	5	29	9	26	24	22	120	0.46	0.4	1.1
32	8.47	262	5	36	11	29	32	27	137	0.56	0.5	1.5
33	8.47	250	6	34	10	28	30	21	133	0.42	0.5	1.4
34	7.65	278	6	39	11	31	32	26	153	0.43	-0.2	0.0

Table 3: Chemical analyses of groundwater samples

Type	No.	pH	(mg/l)									Cal SI	Dol SI
			TDS	K	Na	Mg	Ca	Cl	SO ₄	HCO ₃	NO ₃		
GWT1	38	8.2	539	4	55	39	34	39	14	329	0	0.7	2.2
	39	6.5	527	4	55	40	36	71	10	274	0	-1.1	-1.3
	41	8.1	817	8	76	26	96	36	5.3	555	0	1.2	2.7
	42	7.7	739	11	118	38	98	88	135	473	0	0.7	1.9
	45	7.9	301	0.1	14	15	44	36	34	153	0	0.2	0.7
	49	8.1	734	8	101	40	28	35	14	500	0.4	0.6	2.3
	51	7.9	589	4	51	32	60	71	0.05	372	0	0.7	1.9
	58	7.8	762	19	96	45	107.7	128	150	451	0.00	0.8	2.1
	61	7.92	551	7	49	33	69.7	46	53	313	1.70	0.7	1.8
	62	7.7	252	5	31	14.1	27.2	23	35	136	0.00	-0.3	0.0
	64	7.8	225	7	23	9.48	29.2	18	30	118	0.00	-0.2	0.0
	65	7.7	227	7	24	8.26	28.8	17	27	118	0.00	-0.3	-0.3
	66	7.3	262	7	30	11.7	32.4	23	49	118	0.00	-0.7	-0.9
	73	7.63	830	30	170	46.2	75.7	98	128	523	1.00	0.6	1.8
	75	7.4	266	7	29	10.5	36.4	25	49	122	0.00	-0.5	-0.7
77	7.49	677	8	107	42.5	100.1	97	109	442	0.00	0.5	1.5	
GWT2	43	7.5	301	7	50	15	39	48	75	125	2.4	-0.4	-0.3
	46	7.5	315	10	43	13	44	39	79	128	4.6	-0.3	-0.3
	53	7.8	425	8	46	40	22	142	0.05	165	0	-0.2	0.7
	59	7.58	371	9	51	21.1	33.2	50	84	123	0.00	-0.4	-0.1
	60	7.4	389	10	50	15.1	46.1	44	102	122	0.00	-0.4	-0.5
	63	7.57	1230	41	157	54	122.6	278	216	362	2.70	0.5	1.6
	67	7.61	795	9.8	147	45.9	84.5	238	108	272	0.00	0.3	1.2
	68	7.61	825	12	195	49.3	78.9	229	270	283	0.00	0.3	1.2
	69	7.5	787	10	112	49.8	91.7	130	170	339	0.00	0.3	1.3
	70	7.4	845	15	185	27	98.5	252	140	233	0.00	0.1	0.5
	71	7.89	968	13	151	43	98.5	208	124	330	0.00	0.7	2.0
	74	7.11	1475	14	329	44.2	111.7	390	420	402	0.00	0.0	0.5
76	7.41	391	8	48	15.1	40.9	43	108	118	0.00	-0.5	-0.6	
GWT3	36	7.7	1189	51	285	14.6	26	231	62	519	2.8	0.2	1.0
	48	8.3	1595	74	345	31	42	178	42	817	0	1.2	3.0
	50	8.2	1022	16	269	23	10	178	48	421	2	0.2	1.6
	52	8.2	625	12	115	34	16	106	0.05	305	0	0.3	1.8
	54	8.3	857	12	230	9	6	67	14	482	2.6	0.2	1.3

	55	8.2	504	8	99	26	10	82	0.05	262	1	0.1	1.3
	56	7.8	863	8	198	11	4	213	24	214	0	-0.9	-0.4
	72	7.33	644	6	159	19	52.5	39	124	420	0.00	0.1	0.5
GWT4	37	7.9	940	24	200	44	30	302	96	244	1.7	0.1	1.2
	40	7.4	1531	63	354	40	42	444	82	506	0.1	0.0	0.9
	44	7.3	851	24	214	15	36	314	7	238	3.2	-0.4	-0.3
	47	8.2	1263	63	304	23	46	355	125	299	2.2	0.7	1.9
	56	7.8	680	12	216	13	2	71	14	531	0	-0.8	0.1

There is a weak positive correlation between pH and HCO_3^- concentration in type 1 waters (Fig. 6a). With the continuous influx of atmospheric and biogenic CO_2 into the aquifer, the relationships between dissolved concentrations of Ca, Mg and HCO_3^- enables a distinction to be made between the principal carbonate minerals involving congruent (1 and 2) and incongruent (3) dissolution (e.g. [26]; Table 4). For example, congruent dissolution of calcite should give a ratio of Ca: HCO_3^- of $\sim 1:2$. Congruent dissolution of dolomite should give a ratio of Ca: HCO_3^- of $\sim 1:4$. In contrast incongruent (i.e. partial, that is calcite is left

behind as solid phase) dissolution of dolomite should give a ratio of Ca: HCO_3^- of 0:2 (i.e., no increase in Ca for increasing HCO_3^-).

Contributions to dissolved Ca due to the dissolution of anhydrite or gypsum can be subtracted from the total Ca to reveal how much calcium has been derived by carbonate mineral dissolution [26]. The molar plots of $(\text{Ca} - \text{SO}_4)$ and Mg versus HCO_3^- for this water type are shown in Fig. 6.a. $(\text{Ca} - \text{SO}_4)$ and Mg are positively correlated with HCO_3^- ($R^2 = 0.6$ and 0.7 , respectively) with Ca: HCO_3^- ratio of $\sim 1:1.3$ and Mg: HCO_3^- ratio of $\sim 1:4$ (Fig. 6a).

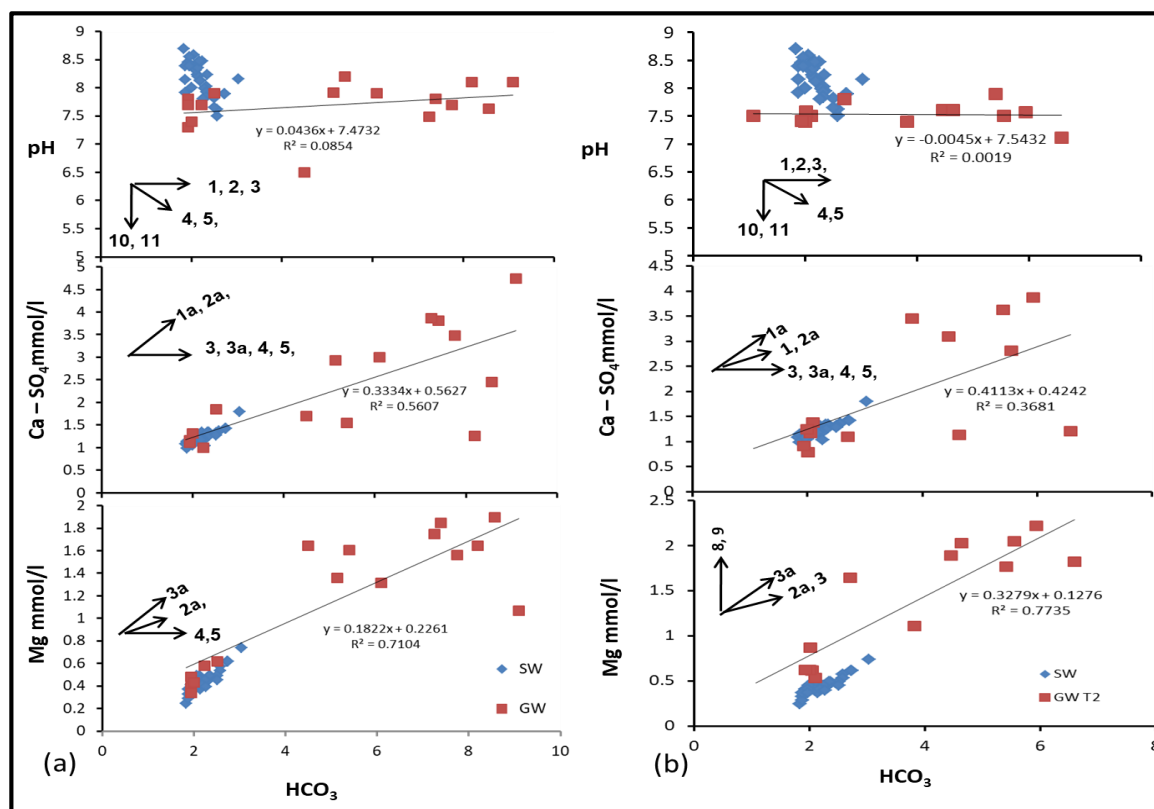


Fig. 6: Geochemical cross-plots of fresh groundwater types. (a) T1: direct correlation between HCO_3^- and pH, relationship between $(\text{Ca}^{2+} - \text{SO}_4^{2-})$ and HCO_3^- with a regression line equation: $\text{Ca}^{2+} = 0.33(\text{HCO}_3^-) + 0.56$, $r^2 = 0.6$, and relationship between Mg^{2+} and HCO_3^- with a regression equation: $\text{Mg}^{2+} = 0.18(\text{HCO}_3^-) + 0.7$, $r^2 = 0.7$. (b) T2: direct correlation between HCO_3^- and pH, relationship between $(\text{Ca}^{2+} - \text{SO}_4^{2-})$ and HCO_3^- with a regression line equation:

$\text{Ca}^{2+} = 0.41(\text{HCO}_3^-) + 0.42$, $r^2 = 0.37$, and relationship between Mg^{2+} and HCO_3^- with a regression equation: $\text{Mg}^{2+} = 0.33(\text{HCO}_3^-) + 0.13$, $r^2 = 0.77$. Reaction vectors, listed in Table 4, indicate the general evolutionary geochemical trajectories of water if the indicated reaction occurs in the water-rock system. Combination of reactions will lead to intermediate vectors. The vectors are not specific to any initial water type.

Kimblin [27] focussed on the contribution of sulphate mineral dissolution to the concentration of Ca in groundwater by studying the relationship between the non-carbonate mineral-derived Ca and Mg using the formula $[(\text{Ca} + \text{Mg}) - 0.5\text{HCO}_3]$ plotted against SO_4 . He also considered the possibility of cation exchange using the relationship between the molar excess of sodium over chloride ($\text{Na} - \text{Cl}$) and Mg with SO_4 .

Dissolution of sulphate minerals seems to have slightly affected nearly all the T1 groundwaters (correlation coefficient, R^2 , of 0.52, Fig. 7a). There is no significant correlation between the molar concentrations of ($\text{Na} - \text{Cl}$) and Mg with SO_4 in this water type where the R^2 value are 0.14 and 0.19, respectively, (Fig. 7b, c).

4.2. Fresh groundwater type 2 (T2); ($\text{Mg} - \text{Ca} - \text{SO}_4$ and $\text{Mg} - \text{Ca} - \text{Cl}$) with $\text{Mg} - \text{Ca} (\text{HCO}_3)_2$

This water type is characterized by higher concentrations of strong acidic anions ($\text{Cl} + \text{SO}_4$) than weak acidic anions mainly HCO_3 (Table 3). It is also characterized by higher concentrations of alkali earth elements ($\text{Ca} + \text{Mg}$) than alkali metals ($\text{K} + \text{Na}$) (Fig. 5a). The pH of T2 waters is uncorrelated with the molar concentration of HCO_3 (Fig. 6b). Regionally, this water type occurs in many places along the aquifer but in very narrow areas (Fig. 5b). This water type is always slightly alkaline ($7 < \text{pH} < 8$, Table 3). SO_4 and Cl are the main anions in this water type, followed in concentration by HCO_3 (Table 3). Calcium with subordinate Mg and Na are the main cations (Table 3). The variation in the total dissolved solids (TDS) of this water type reflects the variations in the sum of the concentrations of the dominant anion and cations: Cl , SO_4 , Ca and Mg (Table 3). The waters are almost saturated to under saturated with respect to calcite and dolomite.

The molar plots of ($\text{Ca} - \text{SO}_4$) and Mg versus HCO_3 for this water type (T2) are shown in Fig. 6b. ($\text{Ca} - \text{SO}_4$) and Mg are positively correlated with HCO_3 ($R^2 = 0.36$ and 0.8 , respectively) with $\text{Ca} : \text{HCO}_3$ ratio of $\sim 1:1.4$ and $\text{Mg} : \text{HCO}_3$ ratio of $\sim 1:2.7$ (Fig.6b).

The contribution of sulphate mineral dissolution to the concentration of Ca in groundwater was studied through the relationship between the non-carbonate mineral-derived Ca and Mg, $[(\text{Ca} + \text{Mg}) - 0.5\text{HCO}_3]$ and SO_4 . The possibility of cation exchange was expected using the relationship between the molar excess of sodium over chloride ($\text{Na} - \text{Cl}$) and Mg with SO_4 . Dissolution of sulphate minerals seems to have weakly affected nearly all the T2 ground-waters (correlation coefficient, R^2 , of 0.4, Fig. 7a). There is a non-significant correlation between the molar concentrations of ($\text{Na} - \text{Cl}$) and Mg with SO_4 in this water type where the R^2 values are 0.5 and 0.3, respectively, (Fig. 7b, c).

Table 4: Different geochemical reactions that could be operating in the aquifer.

Process	Geochemical reaction	Reaction
Congruent dissolution of calcite	$\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^-$	1
	$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$	1a
Congruent dissolution of dolomite	$\text{CaMg}(\text{CO}_3)_2 + 2\text{H}_2\text{CO}_3 = \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-$	2
	$\text{CaMg}(\text{CO}_3)_2 + 2\text{H}^+ = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$	2a
Incongruent dissolution of dolomite	$\text{CaMg}(\text{CO}_3)_2 + 2\text{H}_2\text{CO}_3 = \text{CaCO}_3 + \text{Mg}^{2+} + 2\text{HCO}_3^-$	3
	$\text{CaMg}(\text{CO}_3)_2 + \text{H}^+ = \text{CaCO}_3 + \text{Mg}^{2+} + \text{HCO}_3^-$	3a
Biological processes and atmospheric gas	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	4
Sulphate Reduction	$\text{CH}_2\text{O} + \frac{1}{2}\text{SO}_4^{2-} = \frac{1}{2}\text{HS}^- + \text{HCO}_3^- + \frac{1}{2}\text{H}^+$	5
Dissolution of gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}_{(\text{aq})}^{2+} + \text{SO}_{4(\text{aq})}^{2-} + 2\text{H}_2\text{O}$	6
Na ⁺ & K ⁺ exchange by Ca ²⁺ & Mg ²⁺	$(\text{Ca}) - \text{Ex} + 2\text{Na}_{(\text{aq})}^+ = \text{Ca}_{(\text{aq})}^{2+} + (2\text{Na}) - \text{Ex}$	7a
	$(\text{Ca}) - \text{Ex} + 2\text{K}_{(\text{aq})}^+ = \text{Ca}_{(\text{aq})}^{2+} + (2\text{K}) - \text{Ex}$	7b
	$(\text{Mg}) - \text{Ex} + 2\text{K}_{(\text{aq})}^+ = \text{Mg}_{(\text{aq})}^{2+} + (2\text{K}) - \text{Ex}$	7c
Na ⁺ exchange by Mg ²⁺	$(\text{Mg}) - \text{Ex} + 2\text{Na}_{(\text{aq})}^+ = \text{Mg}_{(\text{aq})}^{2+} + (2\text{Na}) - \text{Ex}$	8
Mg ²⁺ exchange by Ca ²⁺	$\text{Mg} - \text{Ex} + \text{Ca}_{(\text{aq})}^{2+} = \text{Mg}_{(\text{aq})}^{2+} + \text{Ca} - \text{Ex}$	9
Iron sulphide oxidation	$\frac{15}{4}\text{O}_2 + \text{FeS}_2(\text{s}) + \frac{7}{2}\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + 2\text{SO}_4^{2-} + 4\text{H}^+$	10
Nitrification	$\text{O}_2 + \frac{1}{2}\text{NH}_4^+ = \frac{1}{2}\text{NO}_3^- + \text{H}^+ + \frac{1}{2}\text{H}_2\text{O}$	11
Halite dissolution	$\text{NaCl} = \text{Na} + \text{Cl}$	12
Dissolution of albite	$2\text{NaAlSi}_3\text{O}_8 + 2\text{H}^+ = 9\text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{H}_4\text{SiO}_4$	13
Muscovite dissolution	$2\text{K}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_{10}(\text{OH})_2 + 2\text{H}^+ + 3\text{H}_2\text{O} = 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+$	14
Cation exchange	$2(\text{Na}) - \text{X} + \text{Ca} = \text{Ca} - \text{X} + 2\text{Na}$	15a
	$2(\text{Na}) - \text{X} + \text{Mg} = \text{Mg} - \text{X} + 2\text{Na}$	15b
	$2(\text{K}) - \text{X} + \text{Ca} = \text{Ca} - \text{X} + 2\text{K}$	15c
	$2(\text{K}) - \text{X} + \text{Mg} = \text{Mg} - \text{X} + 2\text{K}$	15d
Carbonate precipitation	$\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O}$	16a
	$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaCO}_3 + \text{H}^+$	16b
	$\text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- = \text{CaMg}(\text{CO}_3)_2 + 2\text{H}_2\text{O}$	16c
	$\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^- = \text{CaMg}(\text{CO}_3)_2 + 2\text{H}^+$	16d

4.3. Fresh groundwater type 3 (T3); (Na – K – HCO₃) with Mg Ca (HCO₃)₂

Alkali metals Na and K exceed alkaline earths Ca and Mg while weak acidic anions HCO₃ exceed strong acidic anions Cl and SO₄ (Fig. 5a). Such water deposits residual sodium carbonate in irrigation use and causes foaming problems. The data points in the diagram represent Na–HCO₃- type [25].

The pH of T3 waters is uncorrelated with the molar concentration of HCO₃ (Fig. 8a). Regionally, this water type was expected in few numbers of samples

and very limited places (Fig. 5b). This type is always alkaline ($7 < \text{pH} < 8.5$ Table 3). HCO₃ is the main anion followed in concentration by Cl (Table 3). Na is the main cation. The variation in the total dissolved solids (TDS) of this water type reflects the high concentration of Na and Cl. The waters are almost saturated with respect to calcite and dolomite.

The molar plots of (Ca – SO₄) and Mg versus HCO₃ for this water type (T3) are shown in (Fig. 8a). (Ca–SO₄) and Mg are slightly correlated with HCO₃ ($R^2 = 0.4$ and 0.04 , respectively) with Ca: HCO₃ ratio of ~1: 9 and Mg: HCO₃ ratio of ~1: 12 (Fig.8a).

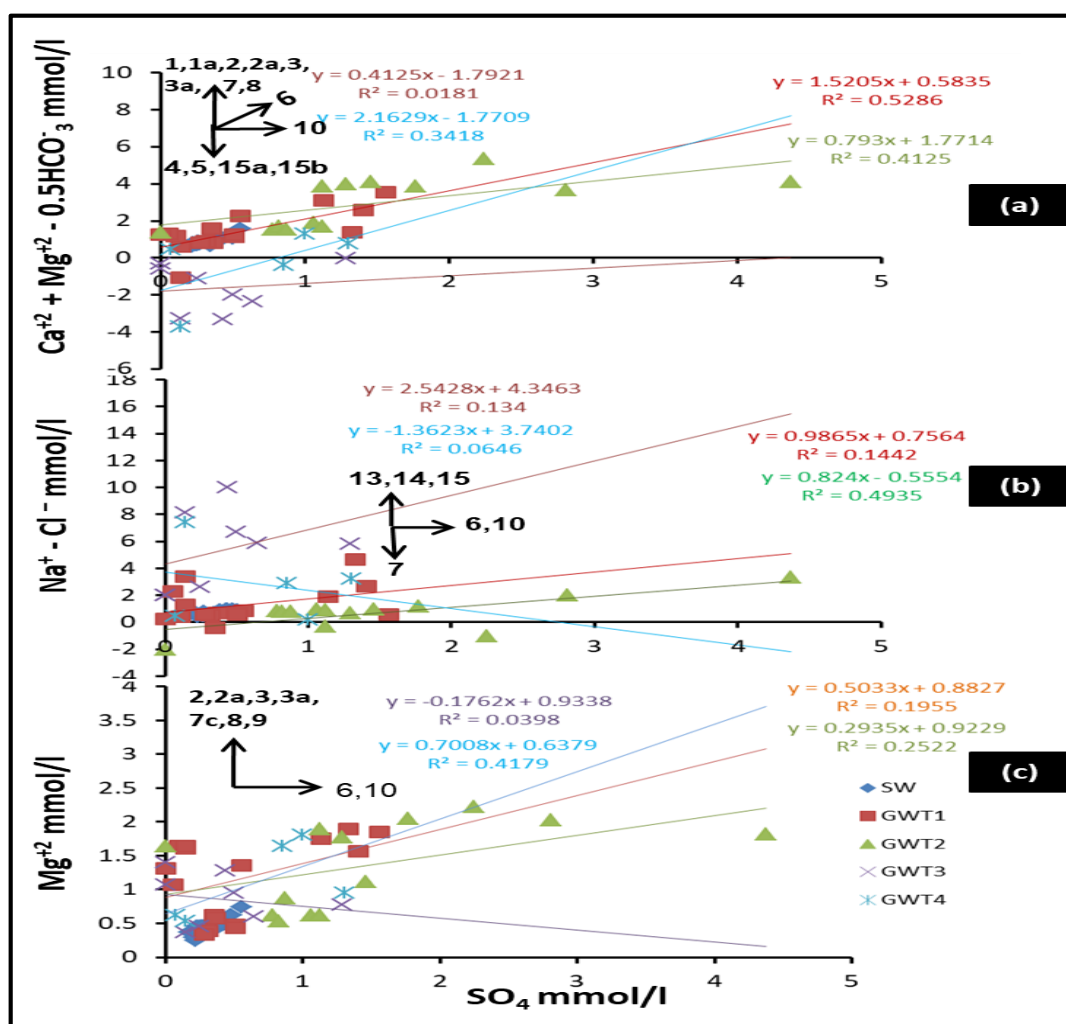


Fig. 7: Geochemical cross-plots surface water and groundwater types; (a) concentration of non-carbonate calcium and magnesium ($\text{Ca}^{2+} + \text{Mg}^{2+} - 0.5\text{HCO}_3^-$, vs. sulphate; (b) concentration of non-halite sodium of ($\text{Na}^+ - \text{Cl}^-$) vs. SO_4^{2-} and (c) Mg^{2+} vs. SO_4^{2-} in all samples. Reaction vectors, listed in Table 4, indicate the general evolutionary geochemical trajectories of water if the indicated reaction occurs in the water-rock system. Combination of reactions will lead to intermediate vectors. The vectors are not specific to any initial water type.

The non-carbonate mineral-derived Ca and Mg, $[(Ca + Mg) - 0.5HCO_3]$, the molar excess of sodium over chloride (Na - Cl) and Mg with SO_4 are shown in Figure 7. Dissolution of sulphate minerals seems to have weakly affected nearly all the T3 groundwaters (correlation coefficient, R^2 , of 0.02, Fig. 7a). There is

a non-significant correlation between the molar concentrations of (Na - Cl) and Mg with SO_4 in this water type where the R^2 value are 0.1 and 0.03, respectively, (Fig. 7b, c).

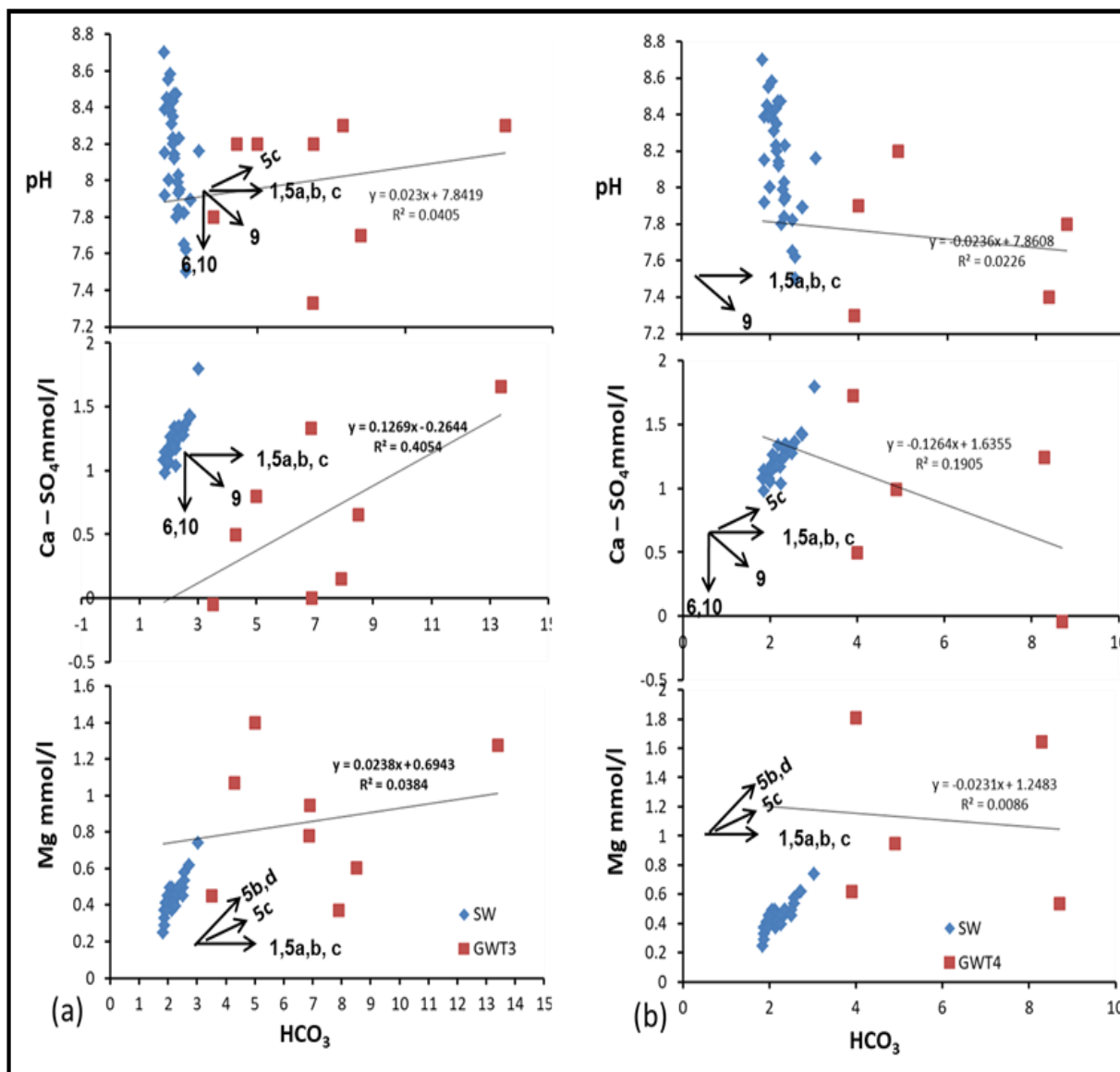


Fig. 8: Geochemical cross-plots of fresh groundwater types. (a) T3: direct correlation between HCO_3^- and pH, relationship between $(Ca^{2+} - SO_4^{2-})$ and HCO_3^- with a regression line equation: $Ca^{2+} = 0.13(HCO_3^-) + 0.26$, $r^2 = 0.4$, and relationship between Mg^{2+} and HCO_3^- with a regression equation: $Mg^{2+} = 0.02(HCO_3^-) + 0.7$, $r^2 = 0.04$. (b) T4: direct correlation between HCO_3^- and pH, relationship between $(Ca^{2+} - SO_4^{2-})$ and HCO_3^- with a regression line equation: $Ca^{2+} = -0.13(HCO_3^-) + 1.6$, $r^2 = 0.19$, and relationship between Mg^{2+} and HCO_3^- with a regression equation: $Mg^{2+} = -0.02(HCO_3^-) + 1.2$, $r^2 = 0.009$. Reaction vectors, listed in Table 4, indicate the general evolutionary geochemical trajectories of water if the indicated reaction occurs in the water-rock system. Combination of reactions will lead to intermediate vectors. The vectors are not specific to any initial water type.

4.4. Fresh groundwater type 4 (T4); (Na-K-Cl) and (Na-K-SO₄)

Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. Such water generally creates salinity problems both in irrigation and drinking uses. The positions of data points in the diagram represent Na–Cl-type, or Na₂SO₄ type [25].

The pH of T4 waters is uncorrelated with the molar concentration of HCO₃ (Fig. 8b). Regionally, this water type was expected in few numbers of samples and very limited places (Fig. 5b). T2 and T4 are more abundant in the southern part of the area (Fig. 5b). This type is always alkaline ($7 < \text{pH} < 8.5$ Table 3). Cl is the main anion followed in concentration by HCO₃ (Table 3). Na is the main cation with subordinate Ca and Mg. The variation in the total dissolved solids (TDS) of this water type reflects the high concentration of major components. The waters are almost saturated with respect to calcite and dolomite.

The molar plots of (Ca – SO₄) and Mg versus HCO₃ for this water type (T4) are shown in Fig. 8b. (Ca – SO₄) and Mg are slightly correlated with HCO₃ ($R^2 = 0.12$ and 0.009 , respectively) with Ca: HCO₃ ratio of ~1: 5 and Mg: HCO₃ ratio of ~1: 10 (Fig. 8a).

The non-carbonate mineral-derived Ca and Mg, [(Ca + Mg) – 0.5HCO₃], the molar excess of sodium over chloride (Na – Cl) and Mg with SO₄ are shown in Figure 7. Dissolution of sulphate minerals seems to have weakly affected nearly all the T4 groundwaters (correlation coefficient, R^2 , of 0.34, Fig. 7a). There is a non-significant correlation between the molar concentrations of (Na – Cl) with SO₄ and slightly correlation of Mg with SO₄ in this water type where the R^2 value are 0.06 and 0.4, respectively, (Fig. 7b, c).

The natural mechanisms controlling the world water chemistry can be assessed using Gibbs approach [28], [29]. According to Gibbs' work, three natural types of water are, in order of increasing salinity; (1) rain-dominated, (2) rock dominated and (3) evaporation dominated. At the join of the two arms, waters are dominated by weathering processes leading to increase calcium (leached out of rocks) with low degree of evaporation.

Application of the Gibbs diagrams to the water samples collected from the study area (Fig. 9) show that there is a distinctive chemical variation between the water samples collected from the area. Water rock interaction plays a significant role in the chemical

composition of surface water as well as the groundwater in the flood plan aquifer (Fig. 9).

Water rock interaction resulted in the increase of Ca and HCO₃ concentration in the water. The SW, GWT1 and GWT3 are closely related where the main controlling factor is water rock interaction. It is clear that there is a similarity in the composition between GWT2 and GWT4, and at the same time they are different from the other three types (Fig. 9). The increase of Na and Cl reflect the simple effect of evaporation process on the chemical composition of these two groundwater types. A great quantity of this surface water has been consumed in the area to irrigate the cultivated land. The cultivated land drains with a TDS concentration higher than the surface water associated with the increase in Cl and Na concentrations. Great quantity of these water recharges the groundwater.

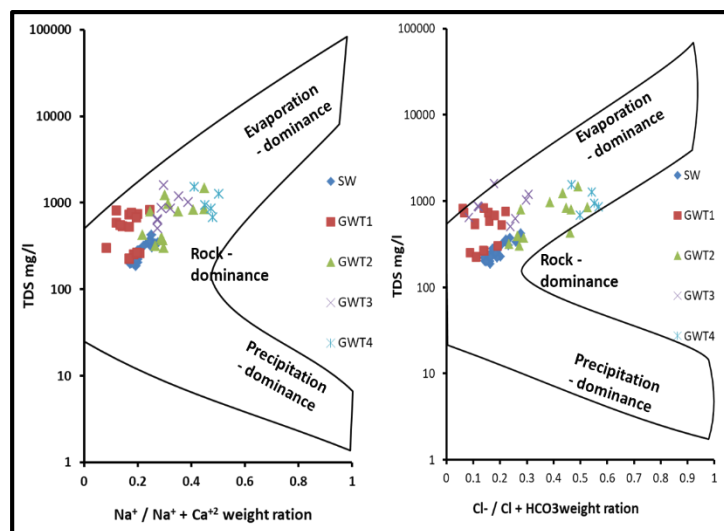


Fig. 9. Gibbs diagram for the studied water samples.

5. Discussion

To assist with the interpretation of the water-rock interaction processes that have controlled groundwater geochemistry in this aquifer, reaction-specific vectors (for reactions 1 to 15, Table 4) for the bivariate geochemical plots have been derived. All geochemical reactions that could possibly influence the X- or Y-axes have been plotted on each diagram. If a given reaction does not influence either the X or Y axis, then it cannot be plotted on the vector diagram. If a reaction only influences one or another axis, then the vector is

parallel to that axis. If a reaction influences both X- and Y-axis parameters, then the vector has a gradient specific to the particular reaction. Thus Figures 5 to 8 have summary vector diagrams to help reveal the dominant geochemical processes in the aquifer.

Reactions 1 to 3 represent the pH-neutral dissolution of carbonate minerals.

Reactions 1 and 2 are the complete dissolution of the common carbonate mineral cements, calcite and dolomite. Reaction 3 is the partial, or incongruent, dissolution of dolomite resulting in remnant calcite (also known as dedolomitisation). Reactions 1a to 3a are also carbonate dissolution reactions but differ from 1 to 3 in that they require acidity and lead to different cation to anion ratios. Reaction 4 is the dissolution and dissociation of CO₂ from any source (atmospheric and biogenic, primarily). Reaction 5 is the bacterially-mediated reduction of SO₄ resulting in increased acidity and bicarbonate concentrations. Note that reaction 5 produced acidity not consumed acidity ($H^+ + 2CH_2O + SO_4^{2-} = H_2S + CO_2 + HCO_3^-$) because of the pH of the groundwater which is generally above 7. The consumed acidity sulphate reduction required much lower pH <7. Reaction 6 is the dissolution of sandstone sulphate mineral cement resulting in elevated Ca and SO₄. Reactions 7 to 9 and 15 involve clay-mediated cation exchange processes and only affect cation ratios. Reaction 10 is the process that leads to acid-mine drainage; iron sulphide mineral oxidation. This results in elevated acidity and increased SO₄ concentration. Reaction 11 is the oxidation of reduced nitrogen species such as ammonia and also results in elevated acidity. Reactions 13 and 14 represent the dissolution of common silicate minerals that increase the concentration of sodium dissolved silica (reaction 12) and potassium (reaction 13) in the water.

5.1. Carbonate; congruent and incongruent dissolution of dolomite

The Quaternary aquifer is an unconfined aquifer in most of the study area that is open to atmospheric and biogenic inputs. During the infiltration of surface water, through overlying soil and the unsaturated part of the aquifer, a continuous influx of CO₂ has been maintained as a result of biochemical oxidation of organic matter and respiration of the plant roots [30],[31],[32]. The influx of CO₂ might enhance dissolution processes of any carbonate minerals present in the aquifer. A reaction sequence between groundwater and carbonate mineral phases can be characterized by variations in pH and the concentrations of dissolved Ca, Mg and HCO₃ (Table 3).

Dissolution of carbonate minerals seems to affect the geochemical composition of surface and groundwater type T1 since both HCO₃ and alkaline earth element concentrations increase (Fig. 5a). Non-sulphate sourced calcium (Ca-SO₄) and HCO₃ in this water type are slightly correlated ($R^2 = 0.56$) with the ratio of Ca to HCO₃ being approximately 1: 1.3 (Fig. 6a). This suggests that reaction 1a and to some extent 2a the congruent dissolution of calcite and dolomite dominates the geochemical evolution of T1 water type (see vector 1a, 2a Fig. 6a). This is further supported by a higher level of correlation ($R^2 = 0.7$) between Mg and HCO₃ also with a slope of 1:4 (Fig. 6a). There is some scatter on the plot of Mg versus HCO₃ (Fig. 6a) which could be due to localised dissolution of calcite (samples close to SW) or even the incongruent dissolution of dolomite (the remaining samples with high Mg and HCO₃, vectors 2a and 3a, Fig. 6a).

The dominant recharge of this aquifer is either directly from percolated agricultural drainage or, more probably, via surface waters (i.e. Ibrahimia, Bar Youssef and Gizawia canals as well as Nile River water). The surface waters in this area tend to be alkaline (AVE pH about 8.15, Fig. 6a) and lower TDS (AVE 259 mg/l). The lower TDS T1 groundwaters have a mean pH of about 7.7 and AVE TDS of about 518.7 mg/l. The reduction in surface water pH at the preliminary stage of groundwater infiltration could be due to dissolution and dissociation of biogenic CO₂ (reaction 4); the oxidation of sulphide minerals (reaction 10); or nitrification of natural or anthropogenic ammonia (reaction 11). These reactions supply acidity to the system (vectors 4, 10 and 11, Fig. 6a). There is a hint in the spread of the data at lower bicarbonate concentrations that pH increases with increasing bicarbonate suggesting that pH-neutralising carbonate dissolution reactions (e.g. reactions 1a-3a) may have been effective to one degree or another, especially at the early stages of water-rock interaction (Table 4, Fig. 6a). This is besides the dissolution of silicate that may enhance the pH level.

T2 groundwater has low concentrations of HCO₃ typical of percolating meteoric water suggesting that in addition to water – rock interaction, there has been another geochemical process plying a significant role in the geochemical formation of this water type. These processes resulting in the higher TDS (AVE 710 mg/l) compared to SW and GWT1 water types without drastic change in pH. However, T2 groundwaters are slightly more acidic than surface waters suggesting that one or more of reactions 4, 10 or 11 has occurred. The lack of increase in HCO₃ for some of the high TDS samples suggests that at least some acidification of the

surface water must have occurred via sulphide or ammonia oxidation (vectors 10 and 11, Fig. 6b). In fresh groundwater type GWT2; the dissolution of carbonate has led to an increase in the concentration of HCO_3^- without great change in pH values (Fig. 6b) which shows that GWT2 may have evolved from the SW due to typical carbonate minerals dissolution (vector 1, 2 or 3, Fig. 6b). Non-sulphate sourced calcium (Ca-SO_4) and HCO_3^- in this water type are marginally correlated ($R^2 = 0.36$) with the ratio of Ca to HCO_3^- being approximately 1: 1.4 (Fig. 6b). This suggests that reaction 1a and to some extent 2a the congruent dissolution of calcite and dolomite dominates the geochemical evolution of GWT2 water type (see vector 1a, 2a Fig. 6b). This is further supported by a higher level of correlation ($R^2 = 0.77$) between Mg and HCO_3^- also with a slope of 1: 2.7 (Fig. 6a). There is some scatter on the plot of Mg versus HCO_3^- (Fig. 6b) which could be due to localised dissolution of calcite (samples close to SW) or even the incongruent dissolution of dolomite (the remaining samples with high Mg and HCO_3^- , vectors 2a and 3a, Fig. 6b).

GWT3 have higher pH and increased HCO_3^- that suggest that pH-neutral carbonate dissolution processes (reactions 1-3) may have become predominant as the degree of water-rock interaction, and so TDS, increased (Fig. 8a) in the later stages of water evolution. Both (Ca-SO_4) and Mg are weakly correlated with HCO_3^- ($R^2 = 0.4$, and 0.04 , respectively, Figs. 8a) with the slopes of the best-fit correlations for groundwaters most closely resembling the effect of biological processes and atmospheric gas with SO_4 reduction in addition to congruent dissolution of dolomite (reactions 2, 4,5; Figs. 8a). These values suggest that congruent dissolution of carbonate minerals dominate the hydrogeochemical evolution of this water type (GWT3) which is further supported by the saturation with respect to calcite and dolomite of this sub-type groundwater samples (Table 3).

Like GWT3 water type, the carbonate mineral-water reactions evolved to incongruent dissolution of dolomite with biological processes and atmospheric gas to increase the HCO_3^- concentration that dominate the geochemical evolution of GWT4 (Reaction 2, Table 4, and Fig. 8b). This is supported by the saturation with respect to calcite and dolomite in these water types.

In summary, for both T1 and T2 groundwaters congruent dissolution of carbonate minerals (calcite and dolomite) were dominant processes leading to increasing Ca, Mg and HCO_3^- associated with the biological process and sulphate reduction to slightly

reduce the alkalinity of the waters. The continuous effect of biological process and atmospheric gas develop the groundwaters GTW2, GWT3, and GWT4 in localized areas.

5.2. Dissolution of sulphate minerals

Groundwaters with lower SO_4 concentrations of about 10-50 mg/l are likely to have acquired their SO_4 from rainwater (surface waters), possibly concentrated by evaporation during recharge (e.g. Fig. 8; [27]).

Sulphate concentrations >50 mg/l are dominant in both SW and GWT1 types although a few samples have concentrations <50 mg/l (Tables 2, 3). To acquire aqueous SO_4 the waters must either induce sulphate mineral (e.g. gypsum or anhydrite) dissolution or undergo sulphide mineral oxidation (reactions 6 and 10; Table 4). The bulk of the data of all groundwater types conform to the vector for reaction 6 (i.e. non-carbonate sourced Ca increases commensurately with SO_4) which suggests that dissolution of calcium sulphate is the main source of the increased aqueous SO_4 during the development of the groundwater types after surface water (Figs. 8a). The anhydrite-rich deposits are absent over the study area although note that anhydrite and gypsum are common as mineral cements and intercalated layers in the Eocene and overlying deposits along the Western Desert fringes. This area has intensive agricultural reclamation activities recently, which led to discharge of agricultural wastewater directly to the low land aquifer in the Nile flood plan. In addition to the anthropogenic source of sulphate, the evaporate minerals in these sediments are one of the natural sources of sulphate in the groundwater.

In GWT1 and GWT2 waters, the molar concentration of non-carbonate Ca plus Mg and SO_4 are slightly correlated, while they are weakly correlated in GWT3 and GWT4 ($R^2 = 0.52$, 0.4 , 0.02 , and 0.34 respectively, Fig. 8a). The stoichiometric dissolution of gypsum (reaction 6, Table 4) should give a slope of 1 to figure 8a. The best fit line on Figure 8a is slightly >1 in GWT1, GWT2, and GWT4 revealing that the concentrations of Ca and Mg in these water types are greater than would be expected from the dissolution of carbonate and sulphate minerals alone. While in GWY3 the slope is less than 1 which means that other reactions reducing the concentrations of Ca and Mg in this type lower than would be expected from the dissolution of carbonate and sulphate minerals alone. It is likely that some degree of clay-mineral hosted cation exchange of Na by Ca (and possibly Mg; reactions 7 and 8 Table 4 and

vectors 7 and 8, Fig. 8a) could have led to a slope >1 in GWT1, GWT2 and GWT4. On the other hand, reactions 15a, 15b could be responsible for the reduction of Ca and Mg in GWT3 (Fig. 8a). This process is the reverse of the reaction normally expected where Ca displaces Na. This implies a high sodium source should be expected in the aquifer (see section 3.5.4). So the evaporite minerals in the western Desert new cultivated lands on the desert fringe of the study area, and anthropogenic influences such as fertilizer applications, agricultural and urban waste seepage, and agricultural and urban soil disturbance might be the main sources of SO_4 in this area.

5.3. Chloride; multiple minor possible sources

The Cl concentration in most the SW is well correlated with SO_4 and NO_3 which is greater than expected from atmospheric inputs alone (Tables 4). This excess Cl could be acquired from the anthropogenic pollution. In addition to the anthropogenic source of Cl, the dissolution of evaporite minerals from the desert fringes deposits could control the Cl concentration in the groundwater types as the Cl is well correlated with the SO_4 in all these groundwater types (Table 4). However, the elevated Cl concentration relative to atmospheric and surface water input in almost all groundwaters must be from a widespread regional source.

5.4. Sodium; cation exchange influences

The molar concentration of (Na-Cl), a measure of the deviation from a 1:1 ratio as a result of non-conservative behaviour of Na, is not significantly correlated with SO_4 (Figs 9b). Assuming conservative behaviour for Cl, (e.g. [33]) these figures indicate that Na has been added to the groundwater. This increase of sodium is probably due to cation exchange with calcium and magnesium (reactions 15a, b, Table 4, Figs 9b) and/or dissolution of silicate minerals (albite) reaction 13. The addition of Na due to cation exchange by clay is expected during the evolution of all groundwater types since these samples lie on the gypsum dissolution trend (reaction 6, Fig. 9a). This lack of cation exchange signals that GWT4 waters represent the earliest stages of water-rock interaction.

Magnesium is slightly correlated with the molar concentration of SO_4 (Fig. 9c). The combination of reactions of local importance, demonstrated earlier, has resulted in the overall increase in Mg with increasing SO_4 . Thus reaction 2 (congruent dolomite dissolution) and reaction 8 (cation exchange) (Figs. 7

and 8) probably led to elevated Mg while reaction 6 (sulphate mineral dissolution; Figs 7 and 7) led to elevated SO_4 . The local relative importance of cation exchange and dolomite dissolution has led to the local variation of concentrations Mg with SO_4 . It has been suggested that cation exchange contributes to the geochemical evolution of Quaternary groundwater at various places in Ben-Suef flood plain aquifer.

5.5. Activity relations in groundwater

The activity diagrams in Figures 10a, b are expressed in terms of the log ratio of the activities of Mg to H versus the log of the activity of Na, and Ca to H. The rate of change of concentration of cations depends upon their molar charge. Thus to maintain charge balance the slope of $a\text{Na}/a\text{H}$ relative to $a\text{Mg}/(a\text{H})^2$ should be approximately 2 while the slope of $a\text{Ca}/(a\text{H})^2$ relative to $a\text{Mg}/(a\text{H})^2$ should be approximately 1 [32]:

$$\log [a\text{Ca}/(a\text{H})^2] = \log C + 1 \log [a\text{Mg}/(a\text{H})^2] \quad \text{E1}$$

$$\log [a\text{Mg}/(a\text{H})^2] = \log C + 2 \log [a\text{Na}/a\text{H}] \quad \text{E2}$$

Figure 10a has slopes of nearly 2 for both SW and GWT4 and decrease than 2 in GWT1, GWT3 and GWT2. This means that, SW confirming the importance of cation exchange processes.

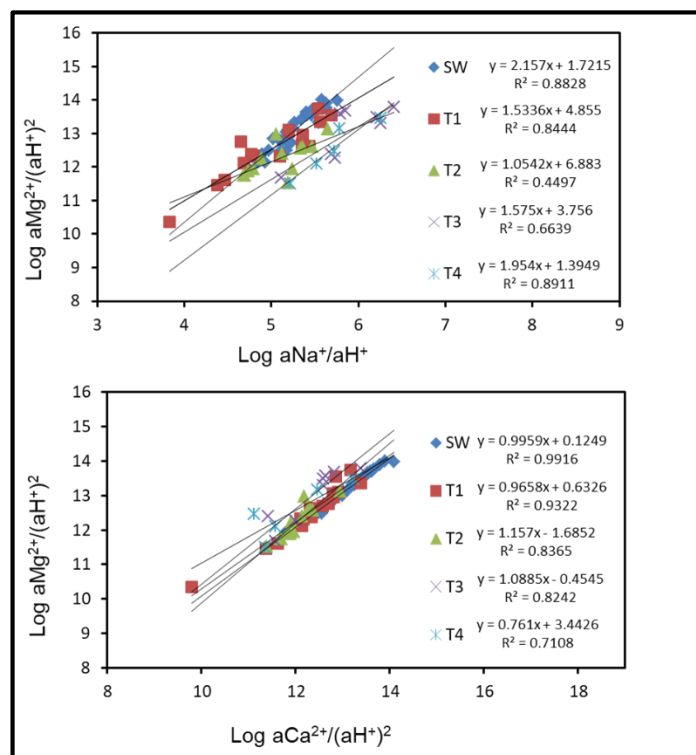


Fig. 10: The activity diagrams; (a) $\text{Log } a\text{Mg}^{2+}/(a\text{H}^+)^2$ vs. $a\text{Na}^+/a\text{H}^+$ displaying a slope of ~ 2 only in SW and < 2 with different degrees in the all the groundwater types. (b) $\text{Log } a\text{Mg}^{2+}/(a\text{H}^+)^2$ vs. $a\text{Ca}^{2+}/(a\text{H}^+)^2$

$aMg^{2+}/(aH^+)^2$ vs. $aCa^{2+}/(aH^+)^2$ displaying a slope of ~ 1 in SW as well as all groundwater types.

Furthermore, Figure 10b has a slope of 1 for SW water seeming to confirm that (1) cation exchange may operate for the alkaline earth elements and (2) that congruent dissolution of dolomite is much more important than incongruent dissolution of dolomite since the latter would result in increasing Mg for no increase in Ca. As for other types of groundwater that develop from surface water. The continuous recharge of the groundwater aquifer with different wastewater, especially agricultural drainage increases the calcium and magnesium concentrations in the aquifer. This leads to an aggravation of the ion exchange process that increases the proportion of sodium in the groundwaters. Therefore, the deviation of this ratio less than 2 is due to the high concentration of Na on the expense of Ca and especially Mg in all groundwaters (Fig. 10a). As for the concentration of calcium and magnesium, the slope is close to 1 (Fig. 10b), which indicate that the ion exchange process between them leads to ionic equilibrium and the congruent dissolution of carbonate minerals is dominated in the geochemical evolution of SW to result in different types of groundwaters in Quaternary aquifer in the study area.

5.6. Geochemical evolution of water in the Quaternary aquifer in Beni-Suef Area

Based on the previous discussion of the hydrogeochemical processes, that effectively control the geochemical composition of the groundwater in the aquifer, the geochemical evolution of the groundwater has been summarised in a schematic diagram (Fig. 11).

It seems that SW is the main source of the groundwater. GWT1 is the most "primitive" groundwater having close affinity to the SW. The TDS is higher than SW, high concentrations of HCO_3 , Mg and Ca, relatively alkaline and being saturated with carbonate minerals. This water is most like surface water and may have developed in the soil or vadose zone by carbonate mineral dissolution associated with proton-generating reactions such as biogenic CO_2 dissolution and dissociation, sulphide mineral oxidation or ammonia oxidation and cation exchange processes that raising the Na concentration. (Table 4; Fig. 11). The recently recharged groundwater (GWT2) developed directly from SW or after GWT1 by a small degree of aquifer mineral dissolution (gypsum and congruent dolomite dissolution). The intensive cation exchange processes increasing Na on the expense of

Mg and Ca leads to develop GWT3 and GWT4 in localized areas in addition to all the geochemical processes that control the other groundwater types (Fig. 5, 11). The groundwaters evolved from surface water directly or via GWT1 groundwater through progressive congruent dissolution of dolomite, cation exchange processes (loss of aqueous Mg, Ca gain of Na) and sulphate dissolution, influencing the dominant cations and anions (Fig. 11).

With increased contact time in the aquifer and more extensive water-rock interaction, the TDS increased and saturation indices approached calcite and dolomite saturation.

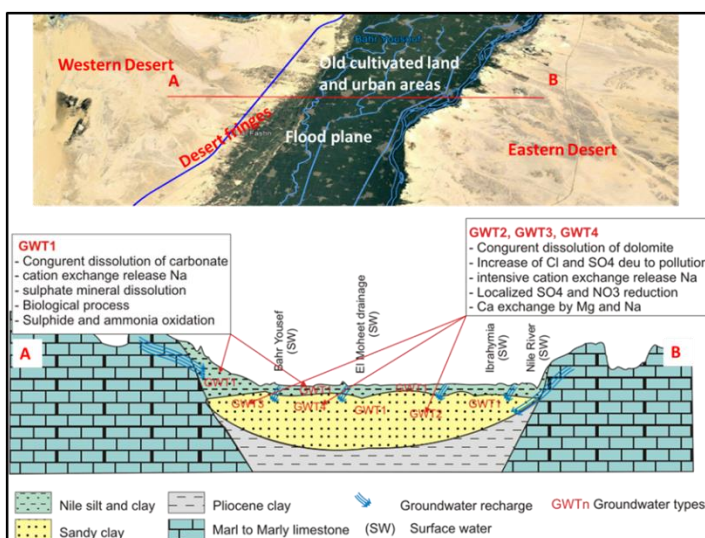


Fig. 11. Schematic cross section showing the suggested evolution paths of the groundwater types in the study area.

6. Conclusions

- 1) There are four geochemically distinct types of water in the Quaternary aquifer in the Beni-Suef area. The principal types (GWT1 and GWT2) have anions dominated by the weak acidic anions (HCO_3) with alkali metals (Na, K) dominated. The other two types (GWT3 and GWT4) are dominated by strong acidic anions (SO_4 and Cl) with dominated alkaline earth elements (Mg and Ca).
- 2) The aquifer has undergone regional recharge from surface waters (originally River Nile water, irrigation return wastewater as well as sewer wastewater). The groundwater have developed from the recharged surface waters where GWT1 spatially distributed in the whole areas and broadly resemble surface

waters except they have slightly higher salinity, possibly due to anthropogenic pollution and water – rock interaction.

- 3) GWT1 groundwater presumably represents the earliest stages of groundwater evolution. These immature groundwaters evolved into the regionally dominant GWT1 groundwaters through a combination of congruent dolomite dissolution, cation exchange and sulphate mineral dissolution. These processes resulted in increasing Ca, Mg, HCO₃ and SO₄. The extents of water-rock interaction processes are reflected in the increase of Na due to cation exchange. Biogenic and atmospheric CO₂ dissolution and dissociation enhance the HCO₃ concentration.
- 4) The agricultural and sewage wastewaters recharged indirectly to the aquifer are responsible for the increase of Cl, SO₄, and Na in the groundwaters. This leads to the development of GWT2 and GWT3 in very localised areas.
- 5) The continuation of the previous geochemical reactions, in addition to some limited ones, led to the formation of other types of groundwaters. Nitrification or sulphide oxidation surges the NO₃ and SO₄ concentration in the surface water. The confined condition of the aquifer in most of the area prevent the atmospheric O₂ to fluxes into the aquifer, so reduction of SO₄ and NO₃ are significantly affect the chemistry of the groundwater in much localized areas. This leads to the development of GWT4 in very restricted areas. This is noticed through the reduction of SO₄ and NO in almost all the groundwater samples.

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