

Applications of Hydrogeochemical Modeling to Assessment Geochemical Evolution of the Pliocene Aquifer System in Wadi El Natrun Area, Western Desert, Egypt

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Abstract: Pliocene aquifer is the main source of water in the study area (Wadi El Natroun area), Western desert, Egypt. Area of the study was divided into three sectors (South, Centre and North). There is a deterioration of quality and increase salinity in water, salinity ranges between 300 and 6822 mg/l. The target of this study explaining and clarify the evolution mechanism of water in the Pliocene aquifer through three former sectors to understand the mechanism of the hydrochemical processes by applying hydrogeochemical – environmental program (Netpath Program) which performed for three groundwater paths (A-A'), (B-B') and (C-C') sector and it used to explain net geochemical mass-balance reactions which occurs between initial and final water point. The study showed that the process of dissolution of chlorides and sulphate salts (halite, gypsum and anhydrite) are the most common effected process, in contrast, deposition of carbonate salts and bicarbonate in the three sectors in area of the study, there is a significant effect of continuous cationic exchange between water and surrounding rocks leading to deterioration of water types and increasing salinity in the direction of water flow from East to West, also water quality change from bicarbonate water type in the east (initial points) to sulphate and chlorides water type in the west direction (final points) and these process represent late stage of mineralization.

Keywords: Geochemical Evolution, Netpath, Pliocene Aquifer, Wadi El Natrun

1. Introduction

Wadi El Natrun occupies a portion of the Western Nile Delta region (Fig. 1). It lies between longitude 30° 04' and 30° 30' E and latitudes, 30° 16' and 30° 30' N. The study area covers an area of about 67608 Feddans or 281 km². El- Abd, E. A. (2005).

The objective of this paper is to expound and examine the evolution mechanisms of a hydrogeochemical approach in the Pliocene aquifer. NETPATH model was used to explain net geochemical mass-balance reactions between initial and final water point which occurred within dissolution and precipitation, hypothetical salts, saturated index and to explain water-rock interaction of the local groundwater in the study area the Pliocene aquifer. Geochemical modeling was performed for three groundwater paths (South, Centre and North path 1 (A-A'), path 2 (B-B') and path 3 (C-C'))

2. Material and Methods

Complete chemical analysis of 15 groundwater points, table (1), the analyses occurred according to the methods adopted by ASTM (2002). The analyses conducted both in the field and laboratory include total dissolved solids (TDS), measurement of pH, electrical conductivity (EC), concentrations of Ca²⁺, Mg²⁺, Na⁺ and K⁺ as cations, CO₃²⁻, HCO₃⁻, SO₄²⁻ and Cl⁻ as anions. Also, (Plummer et al. (1994), discusses saturation indices were calculated with the help of NETPATH model computer program, A global positioning system (GPS) program. Garment 12 are using for determine the location and the elevation readings in this study. The NETPATH computer model program was used to simulate the major hydrogeochemical reactions contributing to explain the evolution of groundwater chemistry in Pliocene aquifer at area of the study (Wadi El Natrun.). Plummer et al. (1994),

described the model in detail;. (Lyon and Bird, 1995; and Soulsby et al., 1998.).

Table 1. Chemical analyses of the groundwater wells in the study area.

Sample No.	EC M.mohs/cm	TDS Mg/l	PH	Cations (ppm)				Anions (ppm)			
				K	Na	Mg	Ca	Cl	SO ₄	HCO ₃	CO ₃
1	1.64	1050	8.36	40	290	10.7	12.8	261	200	205	8
2	0.64	410	8.32	8	102	4.84	16	55	90	145	0
3	0.94	602	8.25	13	143	12.15	40	135	90	170	32
4	1.07	688	7.32	7	180	2.43	40	140	95	260	0
5	1.08	691	7.75	12	165	4.86	32	110	135	215	16
10	4.98	3187	8.03	44	1061	9.72	64	1230	670	160	0
11	2.41	1542	8.31	26	450	9.72	32	414	400	160	12
21	1.88	1206	7.48	13	380	9.72	16	296	380	100	16
33	0.97	621	7.48	27	130	16.52	16	90	90	249	0
34	0.14	930	7.55	17	250	19.44	32	300	200	111	0
30	0.47	302	7.5	6	51	4.86	32	50	61	100	0
36	0.12	800	7.5	12	195	3.4	62.4	250	128	150	0
37	2.00	1280	7.55	36	271	10.7	128	410	310	100	10
39	10.6	6822	7.48	32	2360	6.8	144	3000	1100	227	0
40	4.14	2650	7.55	7	617	11.66	96	831	360	110	0

3. Geological and Hydrogeological Aspects

The Pliocene aquifer is located in the western side of the Nile River at Wadi El Natrun area. The Pliocene sediments act as a good aquifer in area of the study at Wadi El Natrun and northwest of it. The Pliocene sediments are mostly built up of clays underlying the Quaternary aquifer, and hence they represent the main aquiclude horizon in this area. The Pliocene sediments in Wadi El Natrun are mainly affected by several faults which facilitate the connection between The Pliocene and the Quaternary aquifers. These faults are trending NW-SE direction and bounding Wadi El Natrun from the east with downthrown side to the northeast. So the Quaternary aquifer lies in the front of the Pliocene one in the east. Also Wadi El Natrun is bounded from the south and west by clysmic NW-SE faults with downthrown side to the northeast. So the Miocene aquifer is located in the front of the Pliocene facilitating the hydraulic connection between them El- Abd, E. A. (2005).

3.1. Depth to Water and Groundwater Flow

The depth to water of the Pliocene aquifer ranges between 20 m to 30 m outside the wadi El Natrun and less than 10 m to flowing in the surface inside Wadi El Natrun. The Groundwater flows from northeast and southeast to southwest and northwest i.e. to Wadi El Natrun area. Also local cones of depressions spread in the western and southwestern side of Wadi El Natrun depression. Such local trends of groundwater movements are mainly attributed to the over exploitation of groundwater to irrigate the newly reclaimed lands. The aquifer in area of the study is mainly recharged from the Quaternary and Miocene aquifers through the hydraulic connection. The water of the latter aquifers are laterally flowing towards depression area (Wadi El Natrun), which acts as natural discharging area. The recharge to the Pliocene aquifer, which equals the permissible extraction rate

under any condition of future reclamation, was estimated by TRIWACO model to be 128040 m³/day (Diab et al, 2002). The Pliocene aquifer at wadi El Natrun receives other recharge from the southern portion of the Nile Delta through Wadi El Farigh (Abdel Baki, 1983).

3.2. General Hydrogeochemistry

The salinity contents ranging from 300 mg/l in well no. 30 at the south east to 6822 mg/l in well no.39 (Clay Quarries) at the midele part of wadi el Natrun, tables 1 and 2 the salinity increase from east to west in the same direction of water flow. The groundwater of the Pliocene aquifer is mainly belongs to brakish saline water(Fig. 2), Na⁺ is the major cation in the groundwater, followed by Ca²⁺ and Mg²⁺; major anions are Cl⁻ - SO₄²⁻, followed by HCO₃³⁻. Hydrochemical types are mostly Cl SO₄-Na-Ca - Mg type and the HCO₃-Cl -Na-Ca type.

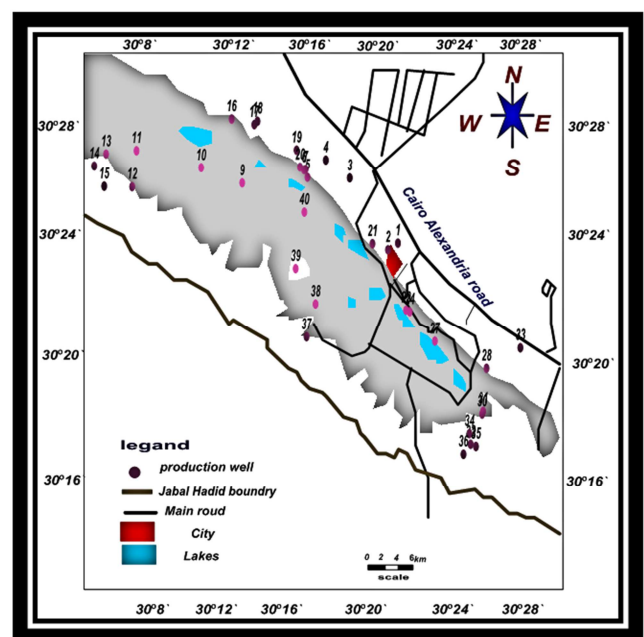


Figure 1. Wells location map.

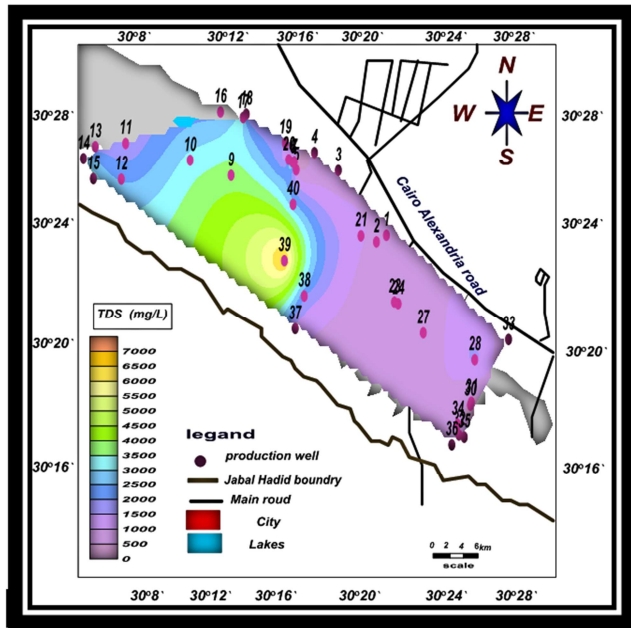


Figure 2. Salinity distribution contour map of the Pliocene aquifer at Wadi-El Natrun.

Table 2. Chemical analyses of selective wells (cations and anions by epm) in the study area.

Well No.	TDS	K ⁺ +Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻ +CO ₃ ²⁻
5	691	7.48	0.4	1.6	3.1	2.8	4.06
9	3712	60.51	0.6	1.2	45.07	13.42	3.72
12	2432	33.63	1.4	2.8	21.69	12.98	3.15
33	621	6.34	1.36	0.8	2.54	1.88	4.08
27	627	7.57	0.2	0.8	3.24	1.98	3.44
37	1280	12.6	0.88	6.40	11.55	6.46	1.97
2	410	4.64	0.4	0.8	1.55	1.88	2.38
21	1206	16.85	0.8	0.8	8.34	7.91	2.17
39	6822	103.43	0.56	7.2	84.5	22.92	3.72

4. Environmental Impacts on Hydrogeochemical Mass-Balance Reactions (Geochemical Modeling)

The NETPATH programs used to evaluate the subsurface geochemical processes and provides an indication of the reaction potential of the hydrogeochemical system, also it is used to perform a variety of aqueous geochemical calculations including the saturation indices (SI) of the major mineral phases, and water mixing models, Park, et al. 2005. NETPATH (Plummer, et al. 1988) was used to environmental simulate net geochemical mass-balance reactions which occurred between initial and final water point along flow path. NETPATH was used to perform a variety of aqueous geochemical calculations including; the saturation indices (SI) of the major mineral phases, testing of water corrosively, influencing of the River Nile on the groundwater and to apply water mixing models Bertolo, R., et al. 2006. Geochemical models are calculation tools to calculate chemical reactions in groundwater system, such as

dissolution and precipitation of solids, ion exchange and sorption by clay minerals. The two basic approaches to modeling aquifer geochemical interactions have been termed inverse and forward models Sun, Y. Q., et al. 2007. The program calculates the saturation indices of Calcite, Aragonite, Dolomite, halite, Siderite, Rhodochr, Gypsum, Anhydrite, Hematite, Goethite, Vivianit, H₂ Gas and Partial carbon dioxide P-CO₂. Geochemical modeling was performed for three groundwater paths.

5. Results and Discussion

5.1. Cation Exchange Process

The cation exchange playing an important roles in explain the process of evolution of hydrogeochemical composition, Whether the ion-exchange reaction can be expressed by the trend of the milligram equivalent(epm) concentration ratio of Ca²⁺ to Na⁺ {N(Ca²⁺)/N(Na⁺)}, from the start (initial) water sample to the end water sample. If N(Ca²⁺)/N(Na⁺) decreases, Ca²⁺ concentration in the water exchange with Na⁺ in the clay. If N(Ca²⁺)/N(Na⁺) increases, Na⁺ in the water exchange with Ca²⁺ in the clay (Sun, Y. Q et al. 2007; and Wang, P. M et al. 2010). From the N(Ca²⁺)/N(Na⁺) variation diagrams (Fig. 3) we can notes that N(Ca²⁺)/N(Na⁺) shows an upward trend through path 1 (AA\ where, N(Ca²⁺)/N(Na⁺) increases, there may be exchange between Na⁺ in the water and Ca²⁺ in the clay but a downward trend along path2 (BB\ and path 3 (CC\). Therefore, the cation exchange process may occur during groundwater flow along both pathes 1(AA\ path 2(BB\ and path 3 (CC\).

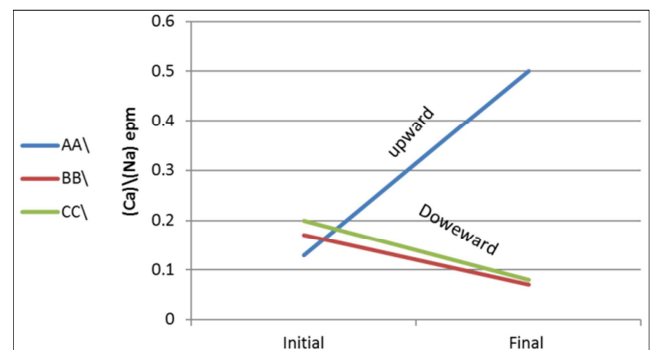


Figure 3. N(Ca)/N(Na) variation in simulated paths.

5.2. Calculation of Saturation Index for the Minerals

The saturation index method was used to explain the process of dissolution or precipitation trend. The saturation index Si is used indicator in hydrogeochemical study. It describes the saturation status of minerals in the groundwater. The positive signs of the saturation index (SI) mean that the solution is super saturated and consequently precipitation processes occurred. While the negative signs reflect that the solution is sub-saturated and dissolution processes occurred, zero value means that the solution is in equilibrium state (Luo et al. 2008; and Sharif, M. U., et al. 2008). The saturation index (SI) is expressed as: $SI = \log(IAP/K)$.

Where IAP is the relevant ion activity product in a mineral dissolution reaction, and K is the equilibrium constant of

mineral dissolution at a certain temperature (Plummer et al., 1994) and Xu, Z. H., (2009).

Table 3. Mineral equilibrium and saturation indices of minerals that present in groundwater of Pliocene aquifer.

Path number	Well No.	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	TDS	Ionic sequence
Path 1 A_A South	33	0.381	0.237	1.128	-2.304	-2.524	621	$\text{HCO}_3 > \text{Cl} > \text{SO}_4$) (Cl> $\text{SO}_4 > \text{HCO}_3$)
	37	0.341	0.197	-0.050	-1.072	-1.292	1280	
Path 2 B_B	2	0.184	0.4	0.197	-2.233	-2.453	410	$\text{HCO}_3 > \text{Cl} > \text{SO}_4$ (Cl> $\text{SO}_4 > \text{HCO}_3$)
	39	0.0587	0.0443	0.198	-0.892	-1.109	6822	
Path 3 C_C North	5	-0.126	-0.27	-0.725	-1.841	-2.061	691	$\text{HCO}_3 > \text{Cl} > \text{SO}_4$) (Cl> $\text{SO}_4 > \text{HCO}_3$)
	12	0.255	0.111	0.336	-1.264	-1.483	2432	

Positive sign (+): Supersaturation and precipitation process.

Negative sign (-): Undersaturation and dissolution process.

From table (3), the results obtained from WATEQF have established that groundwater samples collected from the Pliocene aquifer are seen to be supersaturated in Calcite, Aragonite as well as Dolomite with saturation indices range from 0.008 to 1.432 for calcite, 0.03 to 1.289 for Aragonite, 0.02 to 3.034 for Dolomite. On the other hand, all of the samples were subsaturated in Gypsum with saturation indices between -2.565 and -0.892, Anhydrite with saturation indices -2.785 and -1.109, H_2 gas with saturation indices between -19.92 to -14.64 and PCO_2 with saturation indices between -5.256 to -1.925 (Table 3). We can see that the minerals equilibrium along simulated path 1 have the same precipitation or dissolution trend as those along simulated paths 2 while simulated path 3 is different. Gypsum and anhydrite along the simulated paths showed unsaturated status with a dissolution trend, while the calcite, aragonite and dolomite (carbonate minerals) have supersaturated with a precipitation trend. According to water quality analysis results. On simulated path 1, the TDS of water samples at the initial point was 621 mg/L, and it increased to 1280 mg/L at the end point of the water sample. The hydrochemical water type varied from the $\text{HCO}_3 > \text{Cl} > \text{SO}_4$ type to the (Cl> $\text{SO}_4 > \text{HCO}_3$) type, which shows that from east to west, and from downward to upward.

Along simulated path 2, the TDS varied from 691 mg/L at the initial point to 2432 mg/L at the end point, and the hydrochemical type was the HCO_3 type at the initial point and changed to the SO_4 and chloride type at the end point, which also indicates that dissolution effects along simulated path 2 are strong and water quality gradually deteriorates. Along simulated path 3, the TDS varied from 410 mg/L at the initial point to 6822 mg/L at the end point, and the hydrochemical type varies from HCO_3 type at the initial point to the SO_4 and chloride type at the end point, which also indicates that dissolution effects along all simulated paths 1, 2 and 3 are strong and water quality gradually deteriorates and describes the occurrence of advanced stage of mineralization.

5.3. Mass Balance Simulation (Model Results)

The results obtained from NETPATH have been

established table (4). The net geochemical mass-balance reactions between initial and final waters of three Profiles selected along the groundwater flow path of the Pliocene aquifer (Fig. 4.) was preceded. Sodium, Potassium, Calcium, magnesium, Chloride, Sulfur, Carbon, iron, Manganese, Nitrogen and Phosphorus were introduced into the model as constraints. Na-montmorillonite, K-montmorillonite, Ca-montmorillonite, Dolomite, Sodium Chloride, Gypsum, Aragonite, Goethite, Hematite and Exchange were selected as interactive phases of the aquifer. Table (5) equations of mineral and gas of the interactive phases. The results of mass – balance transfer along groundwater flow path are presented in table (6) and figures 5, 6, and 7.

Table 4. Shows the constraints and Phases used by DB and NETPATH in the Pliocene aquifer in the study area.

NO.	CONSTRAINTS	PHASES
1	Sodium	Na-Mont.
2	Potassium	K-Mont.
3	Calcium	Ca-Mont.
4	Magnesium	Dolomite
5	Chloride	Sodium Chloride
6	Sulfur	Gypsum
7	Carbon	Aragonite
8	Iron	Goethite
9	Manganese	Rhodochr
10	Nitrogen	NH_3 gas
11	Phosphorus	Vivianit

Table 5. Equations of mineral and (gas) dissolution.

Mineral	Equation of mineral (gas) dissolution
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O}$
Sodium montmorillonite	$3\text{Na}_{0.33}\text{Al}_{1.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 30\text{H}_2\text{O} + 6\text{OH}^- = \text{Na}^+ + 7\text{Al}(\text{OH})_4^- + 11\text{H}_4\text{SiO}_4$
Aragonite	$\text{CaCO}_3 = \text{Ca}^{2+} + 2\text{CO}_3^{2-}$
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + 2\text{CO}_3^{2-}$
Halite	$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$
Dolomite	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
CO_2	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$
Cation exchange	$2\text{NaX} + \text{Ca}^{2+} \leftrightarrow 2\text{Na}^+ + \text{CaX}_2$

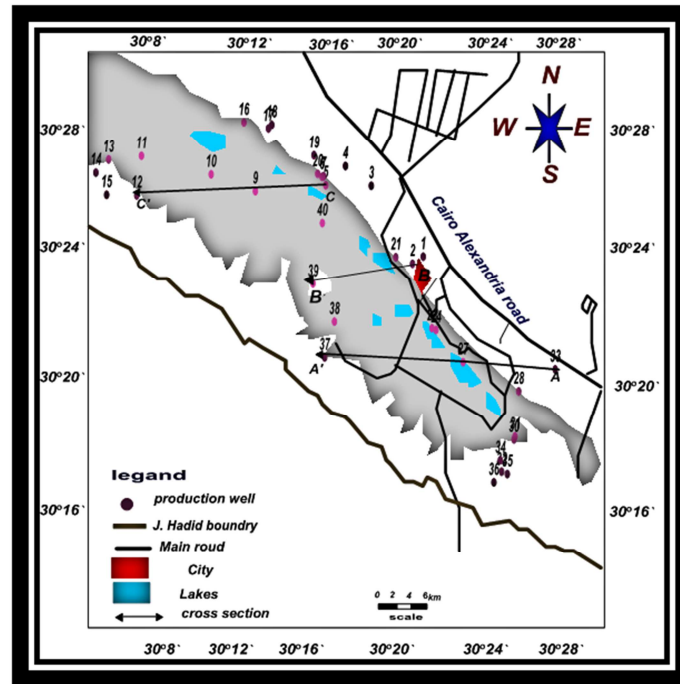


Figure 4. Profiles selected along the groundwater flow path in groundwater wells of the Pliocene aquifer in the study area.

Table 6. Minerals results of mass balance transfer (NETPATH MODEL) along a flow path in groundwater wells of the Pliocene aquifer in the study area.

Path number	Well No.	K-Mon	Calcite	Dolomite	Gypsum	Sodium Chloride	Aragonite	Ca-Mon	Hematite	Exchange
Path 1 A_A South	33 & 37	0.69976	-1.773	-0.218	2.29381	9.0395	-1.77352	-0.0009	-0.0004	-2.49
Path 2 B_B Middle	2 & 39	1.876	1.39	0.08248	10.5933	83.65	1.396	-7.28	0.0053	7.637
Path 3 C_C North	5 & 12	1.2446	-1.9	0.5009	5.095	18.667	-1.919	-0.0107	-0.00529	3.5795

Positive sign (+): dissolution of mineral (m. mole/Kg)

Negative sign (-): Precipitation of mineral (m. mole /Kg)

Initial water (Well No.33) Na-K-Ca-Mg-Cl-SO ₄ -HCO ₃ -NO ₃ -PO ₄		
Rock formation Dissolution	Groundwater	Rock formation Precipitation
6.3550 mmole/kg Na-Mon	-0.0217 mmole/kg Dolomite	
0.6997 mmole/kg K-Mon	-2.4958 mmole/kg Exchange	
2.2938 mmole/kg Gypsum	-1.77 mmole/kg Aragonite	
9.0395 mmole/kg Sodium Chloride	-0.0008 mmole/kg Goethite	
	-0.00044 mmole/kg Hematite	
	-1.773 mmole/kg Calcite	
Final water (Well No.37) Na-K-Ca-Mg-Cl-SO ₄ -HCO ₃ -NO ₃ -PO ₄		

Figure 5. Mass balance transfers of profile AA\ along a flow path in groundwater wells of the Pliocene aquifer in the study area.

Rock formation Dissolution	Groundwater	Rock formation Precipitation
1.876 mmole/kg K-Mon		
0.0824 mmole/kg Dolomite		
83.65 mmole/kg Sodium Chloride		
10.593 mmole/kg Gypsum		
1.39 mmole/kg Aragonite		
0.0106 mmole/kg Goethite		
1.39 mmole/kg Calcite		
0.0053 mmole/kg Hematite		
7.637 mmole/kg Exchange		
Final water (Well No.39) Na-K-Ca-Mg-Cl-SO ₄ -HCO ₃ -NO ₃ -PO ₄		

Figure 6. Mass balance transfers of profile BB\ along a flow path in groundwater wells of the Pliocene aquifer in the study area.

Initial water (Well No.5) Na-K-Ca-Mg-Cl-SO ₄ -HCO ₃ -NO ₃ -PO ₄		
Rock formation Dissolution	Groundwater	Rock formation Precipitation
1.2446mmole/kg K-Mont		
0.5009 mmole/kg	-1.919 mmole/kg	
Dolomite	Aragonite	
5.09507 mmole/kg	-0.0107 mmole/kg	
Gypsum	Goethite	
18.6675mmole/kg	-1.9 mmole/kg	
Sodium Chloride	Calcite	
3.5795 mmole/kg	-0,00529 mmole/kg	
Exchange	Hematite	
Final water (Well No.12) Na-K-Ca-Mg-Cl-SO ₄ -HCO ₃ -NO ₃ -PO ₄		

Figure 7. Mass balance transfers of profile CC\ along a flow path in groundwater wells of the Pliocene aquifer in the study area.

The following can be concluded:

a) Profile (AA): The results of mass-balance transfer along this profile fig. (5), reflect precipitation of -1.7735 mmole Aragonite, -0.00089 mmole Goethite, -1.773 Calcite, -0.2178 Dolomite, -2.49588 Exchange and -0.00044 Hematite. while dissolution of 6.3550 mmole Na-Mont, 0.6997 mmole K- mon, 2.2938 mmole Gypsum, 9.0395 mmole Sodium Chloride. (all expressed mmole per kg of groundwater). At the same time, cation exchange between Na^+ and Ca^{2+} occurred. During this process, Na^+ from the halite and sodium montmorillonite, dissolved into the water then underwent exchange with Ca^{2+} absorbed on the rock surface. Ca^{2+} from the rock surface dissolved into the water, and Na^+ was absorbed into the rock surface. Na^+ adsorption reaction played the leading role in the dissolution and the precipitation process and its precipitation amount reach to 2.49mmol/L, followed by, calcite, and aragonite, with amounts of 1.773mmol/L, and 1.77mmol/L, respectively.

Along the flow path line, the concentrations of Na^+ , Cl^- , Ca SO_4 and gradually increased because of the increasing dissolution effects of halite, Na Mont., and gypsum, respectively, while the reduction of CaCO_3 and Ca-Mg CO_3 could respectively be attributed to the precipitation of calcite, aragonite and dolomite. Dissolution of a large amount of halite and gypsum leads to increase the concentration of Na_2SO_4^- and Na Cl^- , together with the reduction of Ca^{2+} , caused the groundwater hydrochemical types to change from the HCO_3^- -Ca-Mg-Na type to the SO_4^- , Cl^- Na-Mg- Ca type.

When CO_3 dissolved in water causes decrease the water PH, leading to dissolution of gypsum. In addition, cation exchange process occurred between Na^+ and Ca^{2+} , during this process, dissolving high amount of Na^+ from the halite (83.56 mmol/L) into the water then exchange with Ca^{2+} absorbed on the clay surface. Ca^{2+} from the clay surface dissolved into the water causing formation of carbonate minerals (calcite, aragonite and dolomite), and Na^+ was absorbed into the rock surface. Na^+ adsorption reaction played the leading roles in

the dissolution and the precipitation process, where 7.637mmol/L exchange

$2\text{NaX} + \text{Ca}^{2+} \leftrightarrow 2\text{Na}^+ + \text{CaX}_2$ and its precipitation amount was up to -7.3 mmol/L calcium montmorillonite.

Dissolution of a large amount of halite and gypsum leads to increase in the concentration of Na_2SO_4^- and Na Cl^- , together with the reduction of Ca^{2+} , caused the groundwater hydrochemical types to change from the HCO_3^- -Ca-Mg-Na type to the SO_4^- , Cl^- Na-Mg- Ca type. According to the groundwater analysis results and simulation results, we notes that the cation exchange is playing an important roles along path AA\ (path 1). From $N(\text{Ca}^{2+})/N(\text{Na}^+)$ relationship showed a clear upward trend, we conclude that the dissolution effects of chlorides and sulphate salts (halite and gypsum) were more significant than the precipitation of calcium carbonate minerals.

b) Profile (BB): The mass-balance transfer along the simulated path2 BB\ in the middle part, fig. (6), halite accounted for the largest amount of dissolution, reaching 83.6 mmol/L, followed by the dissolution of gypsum, which was 10.59 mmol/L. At the same time, 1.876mmole K- Mont, 0.0824mmole Dolomite, 0.01066 mmole Goethite, 1.39 mmole Calcite, 0.00533 Hematite also dissolved on different levels. The cation exchange process between Na^+ and Ca^{2+} also occurred along simulated path BB\ (path 2). Where Calcium montmorillonite accounted for the largest amount of precipitation, 7.28 mmol/L. along the water flow path, CO_2 dissolved in large volume as a result of dissolving of carbonate minerals; (calcite, aragonite and dolomite), caused the reduction of the pH, and also the dissolution of gypsum.

A large amounts of gypsum and dolomite dissolution in the water solution leads to increase in Ca^{2+} also, K- Mont dissolved, which theoretically should have left HCO_3^- - $\text{Al}(\text{OH})_4^-$ and SiO_2 in the groundwater. However, they were quickly converted into calcium montmorillonite, which meant that dissolution of K- Mont., gypsum, dolomite, calcite and aragonite led to the precipitation of calcium montmorillonite.

In addition, cation exchange process occurred between Na^+ and Ca^{2+} , during this process. Dissolution of a large amount of Na^+ from the halite (83.56mmol/L) dissolved into the water then exchange with Ca^{2+} absorbed on the clay surface, also dissolution of Ca^{2+} from the rock surface into the water causing formation of carbonate salts (calcite, aragonite and dolomite) and Na^+ was absorbed on the clay surface. Na^+ adsorption reaction played the leading roles in the dissolution and the precipitation process, where 7.637mmol/L exchange

$2\text{NaX} + \text{Ca}^{2+} \leftrightarrow 2\text{Na}^+ + \text{CaX}_2$ and its precipitation amount was up to -7.3 mmol/L calcium montmorillonite.

Dissolution of a large amount of halite and gypsum leads to increase in the concentration of Na_2SO_4^- and Na Cl^- , together with the reduction of Ca^{2+} , caused the groundwater hydrochemical types to change from the HCO_3^- -Ca-Mg-Na type to the SO_4^- , Cl^- Na-Mg- Ca type. According to the groundwater analysis results and simulation results, we determined that the cation exchange had more effects along path BB\ 2 and $N(\text{Ca}^{2+})/N(\text{Na}^+)$ relationship showed a clear

downward trend, which helped us to conclusion that the dissolution effects of halite and gypsum are more significant than the precipitation of calcium montmorillonite.

c) Profile (C): The mass–balance transfer along this profile fig. (7), precipitation -1.919 mmole of Aragonite, -0.0107 mmole of Goethite, -1.9 Calcite and -0.00529 mmole of Hematite. and dissolution of 1.2446 mmole K-Mon., 50092 mmole Dolomite, 5.095 mmole Gypsum, 18.66mmole Sodium Chloride, and 3.579mmolecation exchange reactions between Na^+ and Ca^{2+} also occurred along simulated path 3CC¹.

Along the water flow path, CO_2 dissolved in large volume, coupled with the dissolution of dolomite, which together caused the reduction of the pH, and in leads to the dissolution of gypsum. Similar to the case of simulated path 2, Gypsum and dolomite dissolution in the aqueous solution should have caused increase in Ca^{2+} and CO_3^{2-} in addition to cation exchange, a large amount of calcite precipitation occurred. Thus, we came to the assumption that Ca^{2+} and CO_3^{2-} together responsible for formation of calcite and aragonite; that is to say, gypsum and dolomite caused calcite precipitation, also amounts of Mg^{2+} were left in the water. Dissolution of a large amount of halite and gypsum leads to increase in the concentration of Na_2SO_4^- and Na Cl^- , together with the reduction of CaCO_3 , caused the hydrochemical groundwater types to change from the HCO_3^- , Ca·Mg·Na type to the SO_4^- , Cl·Na·Mg- Ca type.

We notes determined that the cation exchange had significant effects along path CC\ (path 3) and $N(\text{Ca}^{2+})/N(\text{Na}^+)$ relationships showed a clear downward trend, which helped us to conclude that the dissolution effects of halite and gypsum were greater than the precipitation effects of carbonate salts (calcite and aragonite).

Conclusionnaly that, the predominant reactions for all profiles appear to be dissolution of Sodium Chloride, Gypsum, Dolomite, Rhodochr and Vivianit. and precipitation of Ca-mon, Aragonite, Goethite with different values. So there is increase in salinity in all profiles in the same direction of groundwater flow, and change in hydrochemical groundwater types from the HCO_3^- -Ca·Mg·Na type to the SO_4^- , Cl·Na·Mg- Ca type.

Even through primary silicate minerals (clay minerals) predominate in the mineralogy of the Pliocene aquifer in Wadi El Natrunarea, the mass balance modeling indicates that reactions with these minerals are secondary to those of the more reaction carbonate, sulfate and chlorides. The concentration ofsodium and chloride in the Pliocene aquifer shows that, Na^+ ion exceeded Cl^- in all samples. So, ion exchange and dissolution are the main processes along the flow path respect to the Na-Clwater type in this aquifer. This reaction agreement with the sequence of cations ($\text{Na}^+ > \text{Ca}^{++} > \text{Mg}^{++}$), ($\text{Na}^+ > \text{Mg}^{++} > \text{Ca}^{++}$) and anions ($\text{Cl}^- > \text{SO}_4^- > \text{HCO}_3^-$). From these profiles we notes that the groundwater types change from less advanced stage of mineralization ($\text{HCO}_3^- > \text{SO}_4^- > \text{Cl}^-$) to more advanced stage of mineralization ($\text{Cl}^- > \text{SO}_4^- > \text{HCO}_3^-$)

6. Conclusions

The aim of this paper is to evaluate the geo-chemical processes controlling the composition of ground waters, using hydrogeochemical models and considering the final composition as the result of the interaction between groundwater and rocks. water-rock interactions in Wadi El Natrun area were simulated and examined during hydrogeochemical modeling (NETPATH program),, and the following conclusions were drawn:

1. Geochemical modeling (Netpath) shows that the special type of composition responsible for the waters mineralization can be explained by dissolution of large amounts of halite and gypsum leads to increase in the concentration of Na_2SO_4^- and Na Cl^- , together with the precipitation of carbonate minerals leads to reduction of CaCO_3 .
2. The changes in groundwater types and chemical composition from the HCO_3^- , Ca·Mg·Na type to the SO_4^- , Cl^- Na·Mg- Ca type result from the combined actions of aforementioned dissolutions and precipitations process, as well as cation exchange reactions.
3. The reaction of cation exchange had significant effects along pathes 1, 2 and 3.
4. The relationships between $N(\text{Ca}^{2+})/N(\text{Na}^+)$ showed a clear downward trend in both simulated path 2 and 3 while upward trend in the simulated path 1 in the south sector, which helped us to conclude that the dissolution effects of halite and gypsum are more significant than the precipitation of calcium carbonate minerals.

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