GEOCHEMICAL MODELING OF GROUNDWATER IN THE DAMMAM FORMATION SOUTH OF RAZZAZA LAKE, MIDDLE OF IRAQ

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ABSTRACT

The study area is located at 25 Km west of Karbala city covering an area of about 640.57 Km². The Dammam, Euphrates, Nfayil, Fat'ha, Injana and Dibdibba formations are cropped out and coverd in some areas by recent Quaternary deposits. The study area is considered as a part of Western Desert (205000 Km²) and the hydrogeological unit produced in the area is Dammam ormation, which receives its recharge from its exposure at south western region. The general direction of groundwater flow is from west and south west towards east and north east. The groundwater is generally alkaline in nature with pH median ranging from 7.03 to 7.81. The TDS values range from 1693 to 1852 ppm and EC values range from 2410 to 2580 µmohs/cm. Five main groups of reaction path indicate five phases (gypsum, calcite, dolomite, exchange and halite). The first reaction path/1 located in the south part of the study area toward northeast, and the second reaction path/2 located in the southwest towards northeast, where path/1 is precipitated Gypsum, Dolomite and Exchange between Na/ Ca, while Calcite and Halite (NaCl) are dissolved along the flow path down gradient. The second path/2 is Calcite and Exchange between Na/ Ca, while Gypsum, Dolomite and Halite (NaCl) are dissolved along the flow path down gradient towards Razzaza Lake basin.

Keywords: Geochemical; Flow net; Hydrochemistry; Modeling; Saturation index

INTRODUCTION

Groundwater, which plays a vital role in regional water resource, is used for different purposes, such as industrial, agricultural, and domestic purposes (Al-Shamari, 2014). Management of this resource is very important to meet the increasing demand of water.

Nowadays, with increasing population and life standards, there is a growing need for the utilization of groundwater resources. However, due to some anthropogenic

causes such as unplanned urbanization and industrialization, the quantity of groundwater resources continues to decrease. Therefore, sustainable management strategies should be developed by decision makers to optimally utilize the groundwater resource, (Al-Shamari, 2014).

LOCATION OF THE STUDY AREA

The study area extends south of Razzaza lake bounded from the east by the Modern Village Project , from the west by Ayn Al-Tamur oasis, from the north by Razzaza lake, and from the south by Al-Najaf governorate, between the longitudes (43° 53' to 43° 29') East and latitudes (32° 23' to 32° 36') North (Fig. 1). The topography elevation ranges from (28 – 120 m) above sea level (Fig. 2) and the estimated total area of study is approximately (640.57) Km^2 (calculated by GIS program) which in turn is considered as a part of the drainage area of Razzaza lake.

AIMS OF THE STUDY

A- Determine the hydrochemical characteristics of groundwater in study area.
B- Using geochemical modeling to determine water rock interactions by processes of mineral dissolution and precipitation.

GENERAL GEOLOGICAL DESCRIPTION

Groundwater, which plays a vital role in regional water resource, is used for different purposes, such as industrial, agricultural, and domestic purposes (Al-Shamari, 2014). Management of this resource is very important to meet the increasing demand of water. Nowadays, with increasing population and life standards, there is a growing need for the utilization of groundwater resources. However, due to some anthropogenic causes such as unplanned urbanization and industrialization, the quantity of groundwater resources continues to decrease. Therefore, sustainable management strategies should be developed by decision makers to optimally utilize the groundwater resource, (Al-Shamari, 2014). The study area extends south of Razzaza lake bounded from the east by the Modern Village Project, from the west by Ayn Al-Tamur oasis, from the north by Razzaza lake, and from the south by Al-Najaf governorate, between the longitudes (43° 53' to 43° 29') East and latitudes (32° 23' to 32° 36') North (Fig. 1). The topography elevation ranges from (28 – 120 m.) above sea level (Fig. 2) and the estimated total area of study is approximately (640.57) Km^2 (calculated by GIS program) which in turn is considered as a part of the drainage area of Razzaza lake. This

study is aimed to determine the hydrochemical characteristics of groundwater in study area and using geochemical modeling to determine water rock interactions by processes of mineral dissolution and precipitation.

The outcrop formations in the study area are configured from the oldest to the youngest by Injana and Dibdibba Formations in addition to the Quaternary deposits (Pleistocene – and Holocene) which appear south and southwest of Razzaza Lake represented by Gypcrete, Aeolian deposits, Sabkha sediments and valleys fill sediments in the region (Fig. 3).
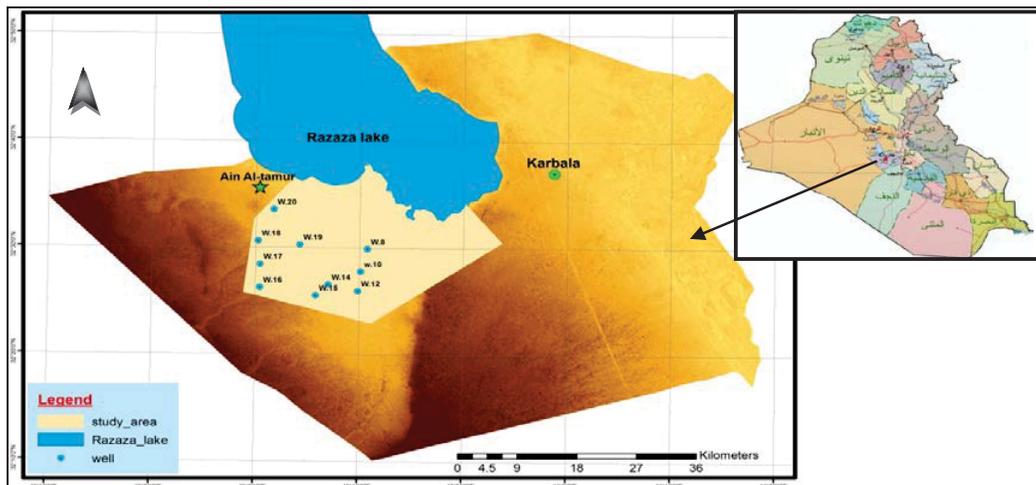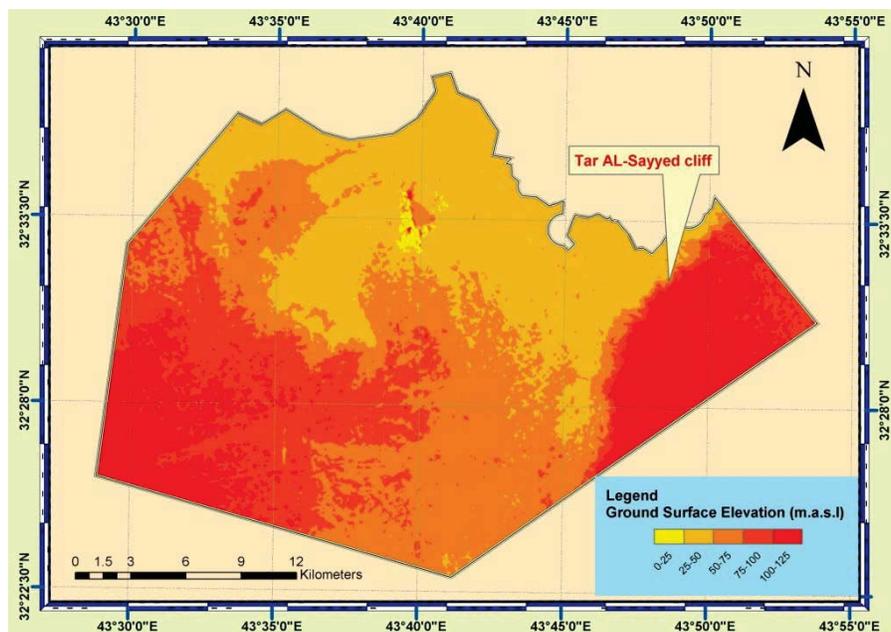

Fig. 1: Location map of the study area

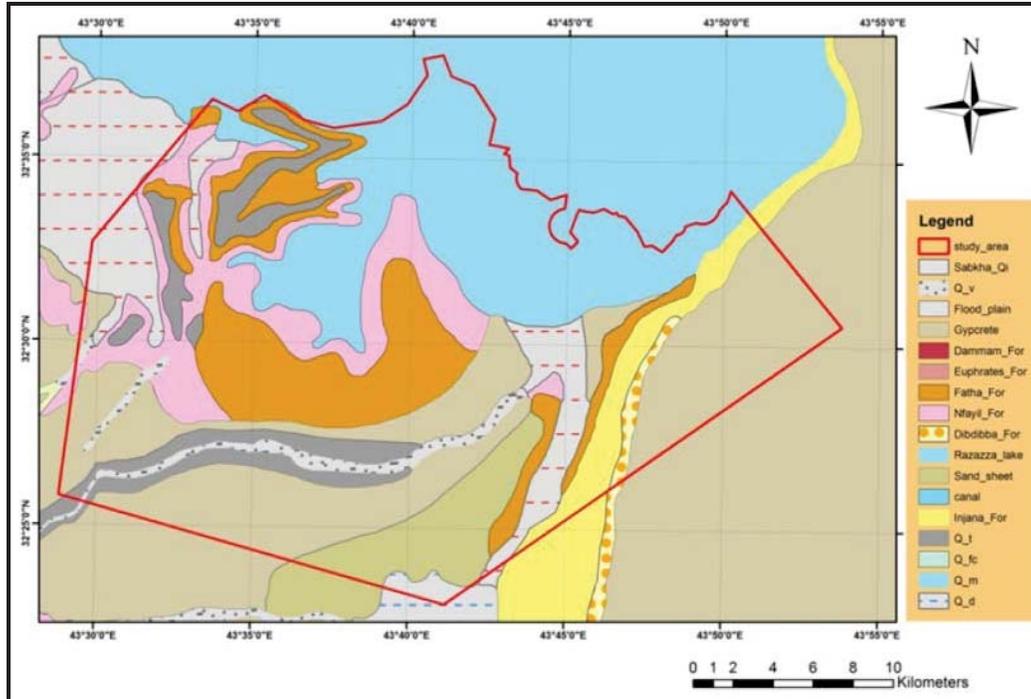**Fig. 2: Topography of the study area (after DEM-U.S.G.S.)**

Fig. 3: Geological map of the study area (GEOSURV, 1995)

STRATIGRAPHY OF THE STUDY AREA

The stratigraphic units were obtained from many wells drilled by the General Commission for groundwater and the information obtained from coring well and from geophysical well logging that showed the formations (from older to younger): Dammam, Euphrates, Nfayil, Fatha, Injana, Dibdibba and Quaternary Deposits. Dammam formation is consider the aquifer of the study area, so it is necessary to be described:

Dammam Formation (Early – Middle Eocene)

The age of Dammam Formation in the eastern part of the western desert is early-middle Eocene (Al-Mubarak and Amin, 1983); the age of this formation (regionally) is middle-late Eocene. Drill cuttings, cores, and correlation of geophysical logs reveal that Dammam Formation in the studied area rich in cavities that are partially or completely filled with calcite or silica and the degree of karstification and thickness varies.

METHODOLOGY

Ten deep wells were chosen for chemical analyses including major and minor ions in addition to some trace elements covering all the study area and locating the wells by using GPS (Global Positional System) type (GPS map 78s, Garmin) was used to determine the accurate position (Longitude, Latitude and Elevation m (a.s.l.) for each well within the study area (Table 1) (Fig. 4). The water samples were collected immediately after purging the bottles; all information concerning the samples was noted and transported to analytical laboratory. Electrical conductivity and the degree of acidity (pH) were measured by using apparatus of HANNA/ pH/ EC/ TDS meter type, model (HI 9811). The measuring of (TDS) total dissolved salts was done also by the same device in addition to the measured water temperature.

After field work, office work was depended on the data obtained from the field tours, field measures, chemical analyses results, reviewing references and previous studies in addition to collecting geological information on the study area. Chemical speciation and saturation state of the groundwater with specific mineral phases were analyzed using geochemical modeling approach suggested by Plummer *et al*. (1994). Chemical reactions along selected flow paths at five main groups have been studied as well. All of the above processes were analyzed using geochemical codes, NETPATH developed by Plummer *et al*. (1994) and WATEQ4F program developed by Ball and Nordstrom, 1991. Many computer software and techniques were used to draw maps and diagrams.

Table 1: Geographic location of the selected wells

| Well No.	Wells depth (m)	Elevation (m)	Depth to water (m)	S.W.L (m) a.s.l.	Latitude	Longitude
W.8	100	50	15	35	32° 29' 54.08" N	43° 40' 45.99" E
W.10	140	60	0	60	32° 27' 48.27" N	43° 40' 8.38" E
W.12	90	49	1.45	47.55	32° 25' 58.47" N	43° 39' 51.88" E
W.14	100	52	3.64	48.36	32° 26' 34.88" N	43° 37' 1.09" E
W.15	90	67	14.5	52.5	32° 25' 32.42" N	43° 35' 48.22" E
W.16	100	78	17.8	60.2	32° 26' 16.67" N	43° 30' 26.09" E
W.17	110	76	5.6	70.4	32° 28' 26.08" N	43° 30' 27.05" E
W.18	120	62	6	56	32° 30' 38.58" N	43° 30' 14.67" E
W.19	90	58	5.2	52.8	32° 30' 18.15" N	43° 34' 14.60" E
W.20	97	56	4.52	51.48	32° 33' 34.54" N	43° 31' 43.01" E
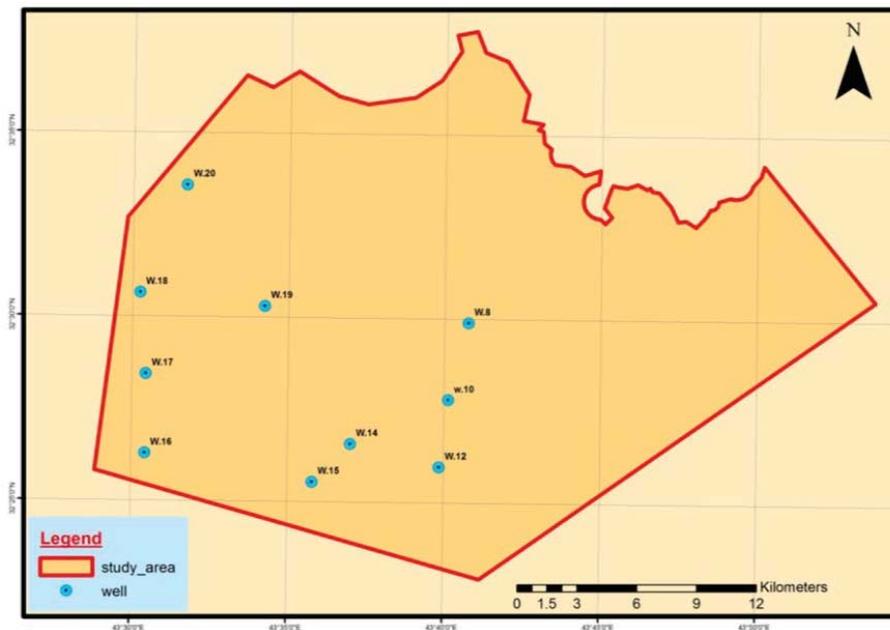
Fig. 4: Locations of the selected wells in the study area

HYDROCHEMISTRY

The hydrochemical study for groundwater in study area include the salinity (total dissolved solids, TDS), electrical conductivity (EC), acidity (pH) and temperature, (Table 2). Measurements of the Major concentrations Cations (Ca^{+2}, Mg^{+2}, Na^+, K^+) and Anions (Cl^-, HCO_3^-, SO_4^{-2}) (Table 3).

The groundwater is generally alkaline in nature with pH median ranging from (7.03 to 7.81). The TDS values range from (1693 to 1852) ppm and EC values range from (2410 to 2580) µmohs/cm.

Table 2: Physical parameters for the water samples

Well No.	TDS (ppm)	EC. (µmos/cm)	T (°C)	pH
W.8	1852	2580	27.7	7.44
W.10	1730	2550	28.3	7.5
W.12	1693	2480	27.6	7.03
W.14	1752	2500	27.5	7.24
W.15	1720	2445	27.1	7.18
W.16	1800	2450	27.3	7.1
W.17	1700	2410	28.2	7.5
W.18	1750	2420	28.1	7.63
W.19	1785	2530	27.4	7.6
W.20	1831	2470	27.7	7.81
Max	1852	2580	28.3	7.81
Min	1693	2410	27.1	7.03

**Table 3: The concentrations of chemical properties of the
water samples by (ppm)**

Well No.	Ca^+	Mg^{+2}	Na^+	K^+	Cl^-	HCO_3^-	SO_4^{-2}
W.8	131	90	140	10	252	63	577
W.10	129	89	136	10	246	62	561
W.12	152	95	155	8.1	417	156	432
W.14	160	50	228	2.5	290	180	498
W.15	130.3	48.97	248.3	7.429	255.6	177.6	614.8
W.16	122	52	271	11.4	207	174	630
W.17	128	50	189	2.1	195	178	485
W.18	161	51	229	3.5	201	210	497
W.19	150.3	68.05	189.2	7.507	221.6	176.3	538.4
W.20	160	91	236	7	389	210	572

GEOCHEMICAL MODELING

Geochemical modeling is the practice of using chemical thermodynamics, chemical kinetics, or both, to analyze the chemical reactions that affect geologic systems, it used in a variety of fields, including environmental protection and remediation, the petroleum industry, and economic geology. Models can be constructed, for example, to understand the composition of natural waters; the transportation of contaminants in flowing groundwater or surface water; the formation and dissolution of rocks and minerals in geologic formations in response to injection of industrial wastes, steam, or carbon dioxide; and the generation of acidic waters and leaching of metals from mine wastes.

GEOCHEMICAL SPECIATION MODELING

Geochemical speciation is useful for calculating and modeling the distribution of dissolved solute and complex compound species in water, and also to compute saturation indices of minerals. Different parameters were calculated based on the chemical analysis of the water samples. These parameters are ionic strength, saturation indices, and PCO2, for calcite, aragonite, dolomite and gypsum. These parameters for each site were input into *NETPATH* software, a thermodynamic data-based computer program for calculating speciation of major elements in natural water. The program uses the Debye Huckel-coefficient approach for activity-coefficient corrections. The mass action law is one of the most useful relations in analyzing of the chemical processes in groundwater. It states that for a reaction:

$$aA + bB \longleftrightarrow cC + dD \quad \dots\dots\dots\dots\dots\dots\dots 1$$
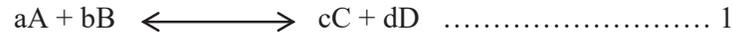
Where: a, b, c and d are the stochiometric fractions of the chemical constituents A, B, C and D respectively at equilibrium, the law can be stated as follows:

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots.. 2$$

Where: K_{eq}: is the equilibrium constant, which is a function of the temperature and pressure. Activity of the chemical species can be calculated using the following equation:

$$[i] = \gamma i \, (i) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots..\dots\dots\dots.. 3$$

Where: [i]: activity of the chemical species.

(i): is the molality of species i.

γi: is the activity coefficient.

We can calculate the activity coefficient for ions from one of several different activity models. The simplest is based on the Debye – Huckel equation.

$$\log \gamma i = \frac{-A z_i^2 \, (I)^0}{1 + B a_i \, (I)^{0.5}} \quad \dots\dots\dots\dots\dots\dots\dots.. 4$$

Where: A and B: are temperature-dependent constant.

a_i: is the radius of the hydrated ions in centimeters.

z_i: is the ion charge.

I: ionic strength.

Ionic strength, as sum parameter for strength, is calculated according to the following equation:

$$I = 0.5 \, \Sigma m_i . z_i^2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. 5$$

Where: I: ionic strength, m_i: molal concentration of the species, z_i: charge of the species. The primary purpose of the chemical speciation is to calculate mineral saturation indices, which are indicators of the saturation state of the solution with the specific mineral phases. The saturation index is defined as:

$$SI = \log (IAP / K_T) \quad \dots\dots\dots\dots\dots\dots.\dots\dots\dots. 6$$

Where: SI: saturation index.

IAP: is the ion activity product of the mineral-water reaction.

K_T: is the thermodynamic equilibrium constant.

SI value of zero indicates that the water is in equilibrium or saturated with respect to the mineral phase, a value less than zero, indicates undersaturated (mineral dissolution is possible) and value greater than zero, indicates oversaturated (mineral precipitation is possible) (Plummer *et al*., 1983).

SPECIES ACTIVITY AND MINERALS SATURATION

The main species activity for water sample are shown in (Table 4) and Figures (5 and 6), the magnitude of activity among different species. Minerals saturation indices for wells shown in Figures (7 and 8). More samples are under saturated with respect to P_{co_2} Figures (9 and 10). SI value of zero indicates that the water is in equilibrium or saturated with respect to the mineral phase, a value less than zero, indicates under saturated (mineral dissolution is possible) and value greater than zero, indicates oversaturated (mineral precipitation is possible) (Plummer *et al*., 1983). Partial pressure of carbon dioxide (PCO2) is an important factor controlling the precipitation and dissolute ion of carbonates. P_{co_2} can be calculated by the following equation (Plummer *et al*., 1994):

$$\log P_{co_2} = \log k + \log \alpha HCO_3^- + \log \alpha H^+ - \log \alpha H_2O \ldots\ldots\ldots\ldots\ldots\ldots 7$$

Where: K: is the equilibrium constant.

α: is the species activity.

Table 4: The main species of groundwater samples

| species	W8	W10	W12	W14	W15	W16	W17	W18	W19	W20
HCO_3^-	9.8394E-04	8.3663E-04	2.0370E-03	2.4595E-03	2.3311E-03	2.3994E-03	2.4315E-03	3.0066E-03	2.4210E-03	3.1649E-03
H_2CO_3	6.6664E-05	5.7314E-05	4.1496E-04	3.0927E-04	3.3803E-04	4.1739E-04	1.6675E-04	1.5302E-04	1.3302E-04	9.0191E-05
HSO_4^-	1.0386E-08	7.6849E-09	1.5582E-08	1.2591E-08	1.7297E-08	2.2715E-08	7.1495E-09	5.5833E-09	5.9753E-09	4.1260E-09
$CaOH^+$	7.5254E-09	7.2920E-09	3.0956E-09	4.9206E-09	3.5105E-09	2.5611E-09	7.3465E-09	1.1340E-08	1.0298E-08	2.1206E-08
$CaCO_3$	2.8713E-06	3.3116E-06	3.3272E-06	6.3597E-06	4.2310E-06	3.2030E-06	9.6571E-06	1.8358E-05	1.3047E-05	2.5313E-05
$CaHCO_3^+$	1.8385E-05	1.5550E-05	4.6995E-05	5.5537E-05	4.2879E-05	3.8819E-05	4.5470E-05	6.4253E-05	4.9869E-05	7.0134E-05
$CaSO_4$	6.7906E-04	6.6443E-04	5.7728E-04	7.4243E-04	7.3147E-04	6.9895E-04	6.2359E-04	7.5274E-04	7.3830E-04	7.3880E-04
$CaHSO_4$	1.6581E-10	1.1946E-10	3.0827E-10	2.4468E-10	2.7780E-10	3.1856E-10	1.1222E-10	1.0051E-10	1.0631E-10	7.8126E-11
$MgOH^+$	2.2816E-07	2.3336E-07	8.6038E-08	6.7180E-08	5.5377E-08	4.6426E-08	1.3253E-07	1.6468E-07	2.0145E-07	5.3818E-07
$MgCO_3$	1.7578E-06	2.0235E-06	1.8848E-06	1.7862E-06	1.4252E-06	1.2170E-06	3.3576E-06	5.1864E-06	5.3001E-06	1.2972E-05
$MgHCO_3^+$	1.8099E-05	1.5160E-05	4.2525E-05	2.4923E-05	2.3102E-05	2.3577E-05	2.5227E-05	2.8970E-05	3.2375E-05	5.7844E-05
$MgSO_4$	9.1226E-04	9.0319E-04	7.1598E-04	4.5553E-04	5.3344E-04	5.7752E-04	4.8122E-04	4.7093E-04	6.5369E-04	8.3082E-04
$NaOH$	9.3006E-10	1.0407E-09	4.1164E-10	9.4986E-10	9.3932E-10	8.1351E-10	1.4535E-09	2.2204E-09	1.7806E-09	3.6621E-09
$NaCO_3^-$	1.4787E-07	1.4467E-07	1.3285E-07	3.6760E-07	3.3521E-07	3.0295E-07	5.8322E-07	1.0943E-06	6.7365E-07	1.8775E-06
$NaHCO_3$	2.4338E-06	2.3404E-06	6.6577E-06	1.1438E-05	1.2313E-05	1.3195E-05	9.5008E-06	1.3307E-05	9.2137E-06	1.2984E-05
$NaSO_4^-$	7.2698E-05	5.9250E-05	4.8062E-05	8.9756E-05	1.2272E-04	1.3913E-04	7.7108E-05	9.2147E-05	7.9976E-05	1.1391E-04
KOH	2.0253E-11	2.3333E-11	6.5678E-12	3.1786E-12	8.5680E-12	1.0428E-11	4.9322E-12	1.0359E-11	2.1558E-11	3.3111E-11
KSO_4^-	4.3566E-06	3.6795E-06	2.1080E-06	8.2477E-07	3.0604E-06	4.8865E-06	7.2401E-07	1.1882E-06	2.6559E-06	2.8343E-06
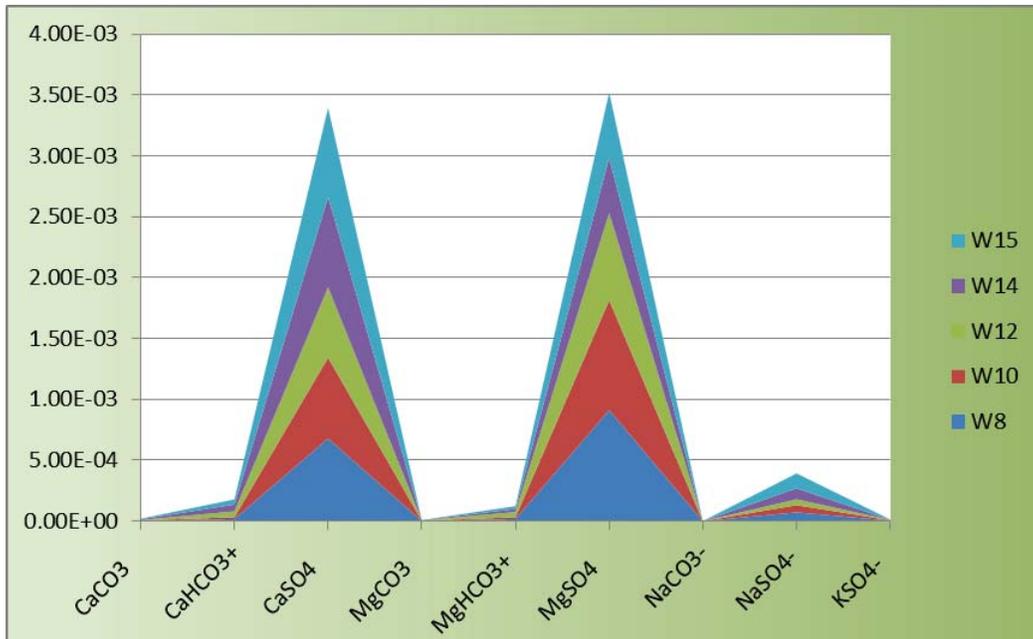
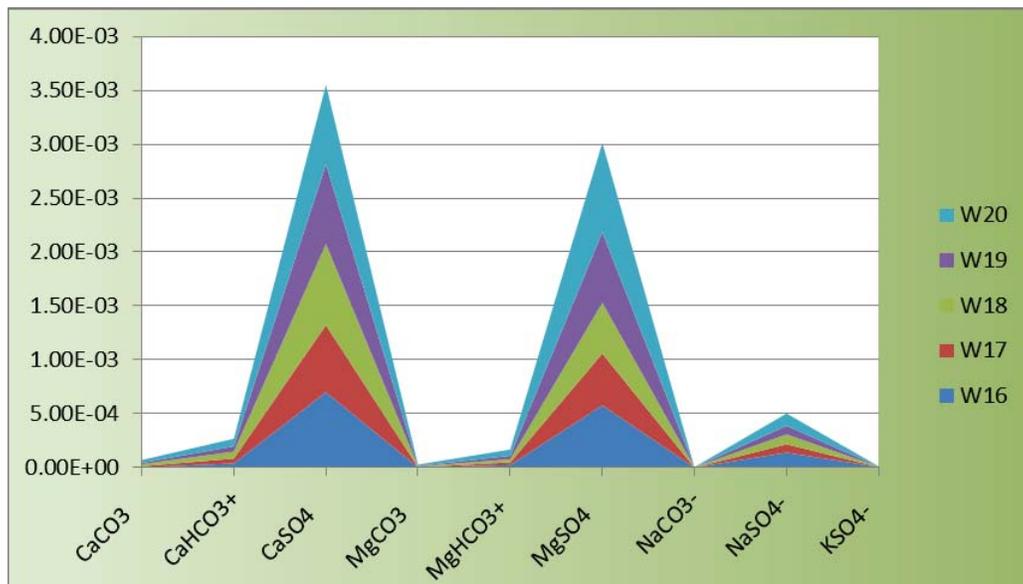**Fig.5: The magnitude of activity among different species**
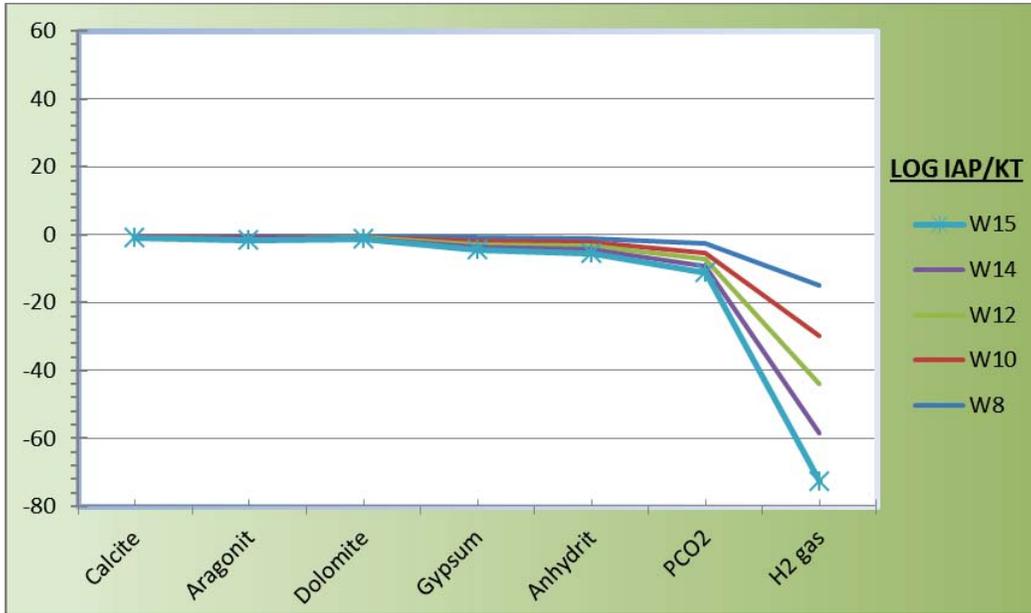

Fig.6: The magnitude of activity among different species
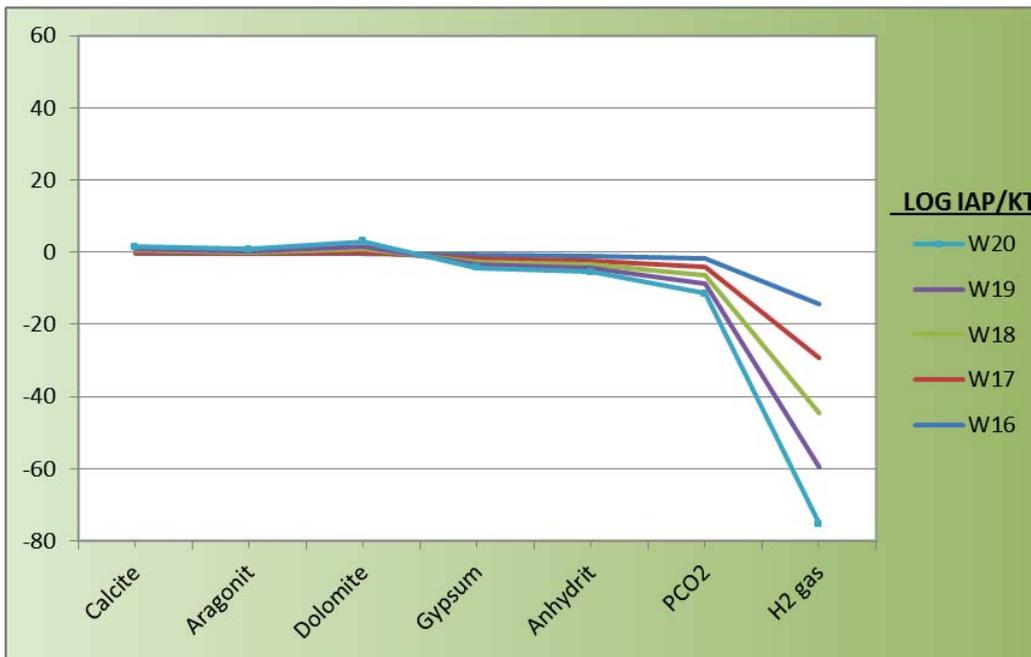
Fig.7: Minerals saturation indices for wells

Fig.8: Minerals saturation indices for wells

Fig.9: Samples are under saturated with respect to Pco$_2$

Fig.10: Samples are under saturated with respect to Pco$_2$

INVERSE MASS BALANCE

Computer Code NETPATH is frequently used to construct quantitative models of the chemical evolution of the groundwater along real or hypothetical flow paths in the aquifers or other hydrologic systems using hydrochemical data. These models provide important information about the geochemical processes and water-rock interactions that can be used to place constraints on numerical models of groundwater flow. NETPATH uses an inverse geochemical modeling techniques and equations of chemical mass balance, electron balance and isotope mass balance to quantify all possible net geochemical reactions between the analyzed initial and final water composition evolutionary path in the aquifers. Inverse geochemical modeling based upon the principle of mass balance between the reactant and product phases in which mass transfer of certain mineral phases can be calculated according to the following equation:

Initial water + reactant phases → Final water + product phases
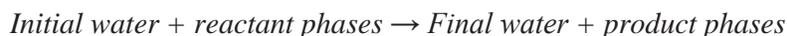
The main goal of the mass balance modeling is to define the net mass of minerals dissolved or precipitated along the flow path down gradient.

Tables (5 and 6), describes the magnitude of mass transport for choosing mineral phases. It was chosen two reaction path in the study area for five different phases, Gypsum, Calcite, Dolomite, Exchange and NaCl Fig. (11).

Table 5: Flow Path/1 W15 ⟶ W14

PHASE	Model 1	condition
Gypsum	-0.94971	precipitation
Dolomite	-0.04953	precipitation
Calcite	0.23642	dissolution
Exchange	-1.34755	precipitation
NaCl	1.33250	dissolution

Table 6: Flow Path /2 W17 ⟶ W19

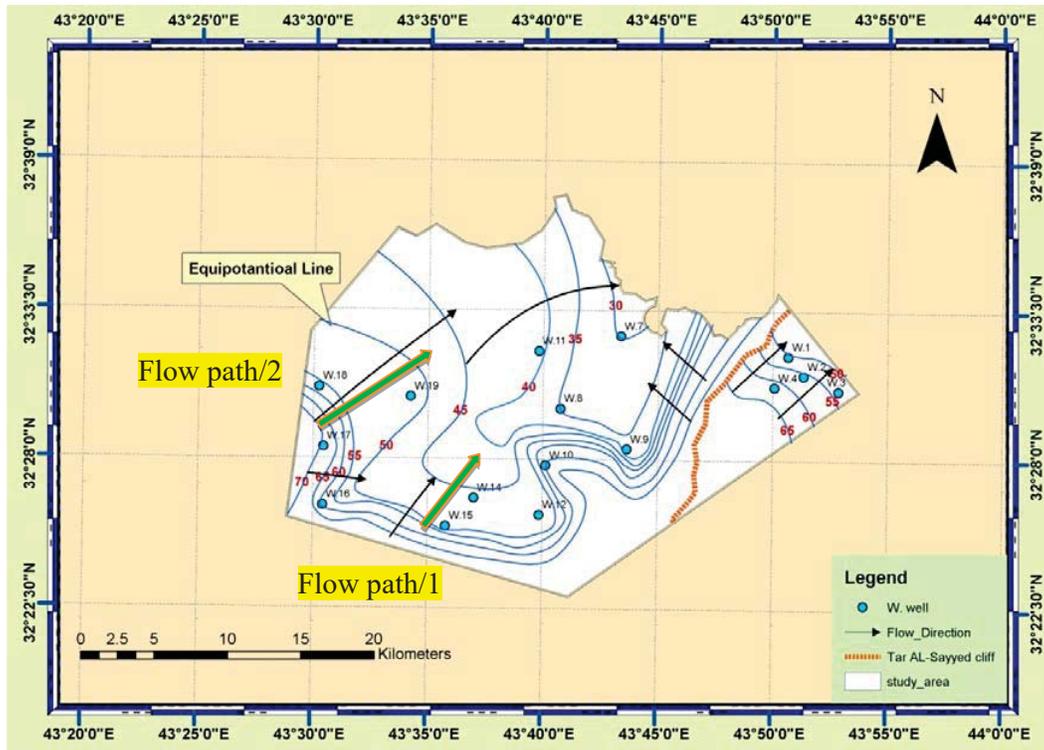| PHASE	Model 1	condition
Gypsum	0.68105	dissolution
Dolomite	0.68071	dissolution
Calcite	-1.36838	precipitation
Exchange	-0.48283	precipitation
NaCl	0.80535	dissolution

Fig. 11: Groundwater flow direction map of the study area

CONCLUSIONS

The main species activity for water sample can be arranged in order, which reflects, the possibility to form precipitant from the reaction between two ions. There are five main groups of reaction path indicate system state for five different phases, Gypsum, Calcite, Dolomite, Exchange and halite. The first reaction path/1 located in the south part of the study area toward northeast, and the second reaction path/2 located in the southwest towards northeast, where path/1 is precipitated Gypsum, Dolomite and Exchange between Na/Ca, while Calcite and Halite (NaCl) are dissolved along the flow path down gradient. The second path/2 is Calcite and Exchange between Na/Ca, while Gypsum, Dolomite and Halite (NaCl) are dissolved along the flow path down gradient towards Razzaza Lake basin. This could be due to the inflow of runoff rain water with its dissolved calcium salts from the surrounding surface soils, especially Gypsum and Anhydrite outcrop beds from Nyfil Formation in the south and southwest part of Razzaza Lake basin, in addition to the inflow of runoff by valleys and cracks within western desert. The high concentration of sulfate ions in all water samples are solutions

of sulfate minerals exist in sedimentary rocks like Gypsum and Anhydrite, and from oxidation of barite mineral (Todd, 2007).

This high concentration of sulfate ions increases common ion effect, which making Calcium is supersaturated with respect to Calcite. In the case of Dolomite, it is evident that the concentrations of Mg^{2+} are lower than Ca^{2+} and Na^+ ions, because the Mg^{2+} ion are smaller than Na^+ and Ca^{2+} ions, which could be accommodated in the structure of most clays in addition to its adsorption on them. So Mg^{2+} is under saturated with respect to Dolomite, in turns decreases in common ion effect, lead to further dissolution of Dolomite.

In general, in the case of carbonate dissolution that means dissolution in aquifer material, in turn, increases porosity and permeability in geological formation, and vice versa. By comparing between tow flow paths, we will note that is a decreasing in dissolution of phases NaCl and Calcite, the latter will precipitated as mentioned in Tables (5 and 6), so we can conclude that the saturation index increases with distance of flow but remains under saturated along all flow paths.

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