



# Assessment of the Groundwater at Ali Al-Garbi area, Iraq using Geochemical modeling and Environmental isotopes

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## ABSTRACT

Geochemical modeling and environmental isotopes (deuterium, oxygen-18, and tritium) were used to determine the hydrogeochemical evolution and the main factors controlling the groundwater chemistry in Misaan, South of Iraq. Groundwater samples were collected and analyzed for major ions at 20 sites for two periods in 2016. Moreover, 6 rainfall samples were collected to determine local meteoric water line. The main water types are Ca-SO<sub>4</sub>, which is the dominate type for two periods, while a few wells were (Na-SO<sub>4</sub>) or (Mg-SO<sub>4</sub>) dominate. All available δ<sup>18</sup>O and δD data for the study area are plotted to the global meteoric water line (GMWL) and Local meteoric water line (AMWL). They indicated to the meteoric origin of all waters. They are exposed to evaporation before entering the aquifer. Using PHREEQC, Geochemical modeling was conducted to calculate mineral saturation indices for all water samples. These results show that dissolution of dolomite, gypsum, halite and siderite and precipitation of calcite, Sylvie and hematite are the main chemical reactions in the first period, whereas there are no specific reactions can be shown in the second period. Hydrogeochemical evolution of groundwater as modeled with NETPATH-WIN, the inverse geochemical modeling results showed that the main reaction controlling the groundwater quality is Dedolomitization process (dolomite dissolution driven by anhydrite dissolution and calcite precipitation).

*Keywords:* Geochemical modeling, Environmental isotopes, Groundwater geochemical evolution, Iraq.

## 1. Introduction

WATEQ4F program mainly calculates the saturation indices (S.I), which developed by Ball and Nordstrom (1991). PHREEQC V.3 2016 can be used to calculate saturation indices, ionic strength and the distribution of aqueous species; it was issued by Parkhurst (1995). One of the most programs applied widely in geochemical modeling is NETPATH software, developed by Plummer et al., (1991). Later, those models were upgraded in according development of computer systems. The natural isotopes (stable & unstable) contributes in many applications of hydrological, hydrogeological and geochemical sciences, which give evidence about of water sources, quality, and ages of water, in addition to recharge and movement of groundwater (Verhagen et al, 1992). The first studies on isotopes techniques in water were involved of precipitation and seawater. The first study was about

survey on variations in concentration rate of <sup>18</sup>O, after that followed by a study about variation <sup>2</sup>H rate in natural waters, the variations of <sup>18</sup>O in global precipitation scale, involving a discussion in great detail on the meteorological patterns (Friedman, 1953; Dansgaard, 1960). Many hydrological studies use the stable isotopes (<sup>18</sup>O, <sup>2</sup>H) to determine the origin, recharge mechanisms and hydraulic connection of water molecules in groundwater. Isotopes can be divided into two types (Peters et al, 2005) This study is the first work in Ali Al-Gharbi district that comprises geochemical evolution of groundwater and environmental isotope in this area, there are many studied, which are related to geology, geomorphology, hydrogeology and hydrogeochemistry of the groundwater or neighboring area.

The purpose of this study has been to use environmental isotope techniques and a geochemical modeling to make better studies and clear image for groundwater type in

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quaternary aquifer. This includes calculate Saturation index and ionic strength to determine geochemical evolution in quaternary deposits of study area, also determine chemical reaction dominate on groundwater in study area. Draw of the Amarah Meteoric Water Line (A.M.W.L) using stable isotopic technique ( $^{18}\text{O}$  &  $^2\text{H}$ ) in rainwater samples and linking it with the Global Meteoric Water Line (G.M.W.L). Identify the variation of isotopic content in water then determine age of groundwater by tritium  $^3\text{H}$ . Locate the evaporation and origin of salinity in groundwater using stable isotopes  $^{18}\text{O}$ .

**2. Study area discretion**

The study area is district that is called Ali Al-Gharbi and located in the northeastern of Missan province, the area of study about (760 km<sup>2</sup>), (Fig. 1). The topography elevation ranges from (0–160 m). The surface is relatively flat in the central part of the area and bounded by Hemrin hills in the north-eastern near of the Iran. The surface elevations from north-east to south-west of the study area for district of Ali Al-Gharbi are decrease. The topographic elevation is derived from the Digital Elevation Model (DEM) produced by (USGS), (Fig. 2). The geological characteristics of study area are by the Rocks of uppermost Miocene and Pliocene are slope towards the Mesopotamian plain from the foothills along the Iraqi-Iranian border on the east. The rocks are buried under the Mesopotamian plain by thick layer deposits of Pleistocene and Holocene age (Buday and Jassim, 1987). The study area is covered with several sediments such as fluvatile, lacustrine, and Aeolian sediments of recent age (Barwary, 1993). The study area is Composed from different types of Quaternary deposits

mainly sand and alluvium deposits of recent and sediment of Pleistocene sequence. The sediments characterized of Quaternary are finer grained and unconsolidated than the underlying Mukdadiya and Bai Hassan Formations (Bellen et al., 1959; Naqib, 1967; Al-Siddiki, 1978). Many deposits such as Alluvial fan, depression fill, sheet runoff deposits, and Aeolian deposits are the major units in the study area (Al-Jaburi, 2005). The tectonic setting of study area was the largest part is within of eastern most units the stable shelf (Mesopotamian Zone). The study area bounded in the north -east by the high folded zone that represented in the Hemrin hills (Khalaf et al., 1985 in Jassim and Goff, 2006; Bashu, 2002).

**3. Hydrogeologic settings**

Aquifer system in study area is subdivided into two aquifers: shallow aquifer (unconfined), deep aquifer (confined). These aquifers are separated by less permeable layers the hydraulic characteristics of which are unknown. The hydraulic connection between aquifer units is possible. Unconfined aquifer is shallow in nature. The sediments are sand (fine, medium) with little layer of silt and clay represents the main component of this unit and some of wells contain a gravel. Many dug wells in the study area penetrate this unit of aquifer and extract water; these Dug wells are with irregular diameters. Most of rainfall recharge goes to this part of aquifer; water quality is change depended on surface salt washing process. Confined aquifer is deep and found only in the eastern part of the area. This aquifer is limited extent in the study area and consists mainly of mixture of gravel and sand (sandy gravel), gravel and clay (clayey gravel) with significant amount of silt in some parts of the

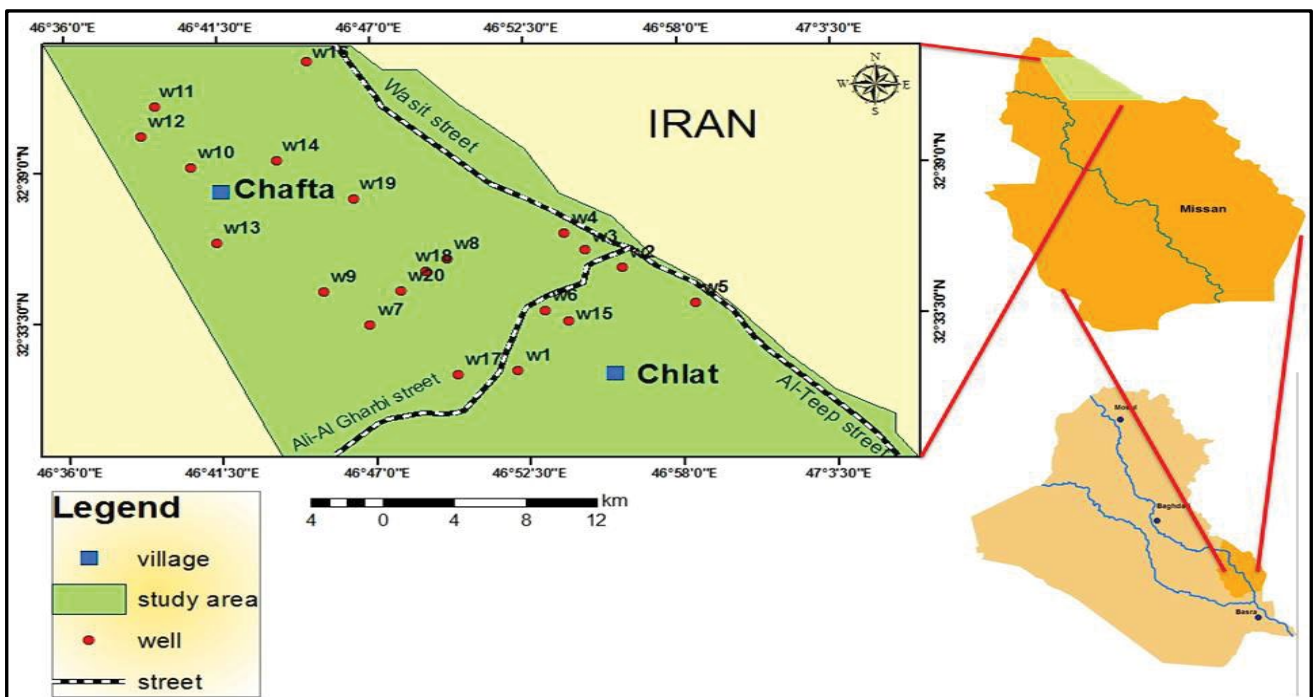


Fig. 1. Location Map of study area.

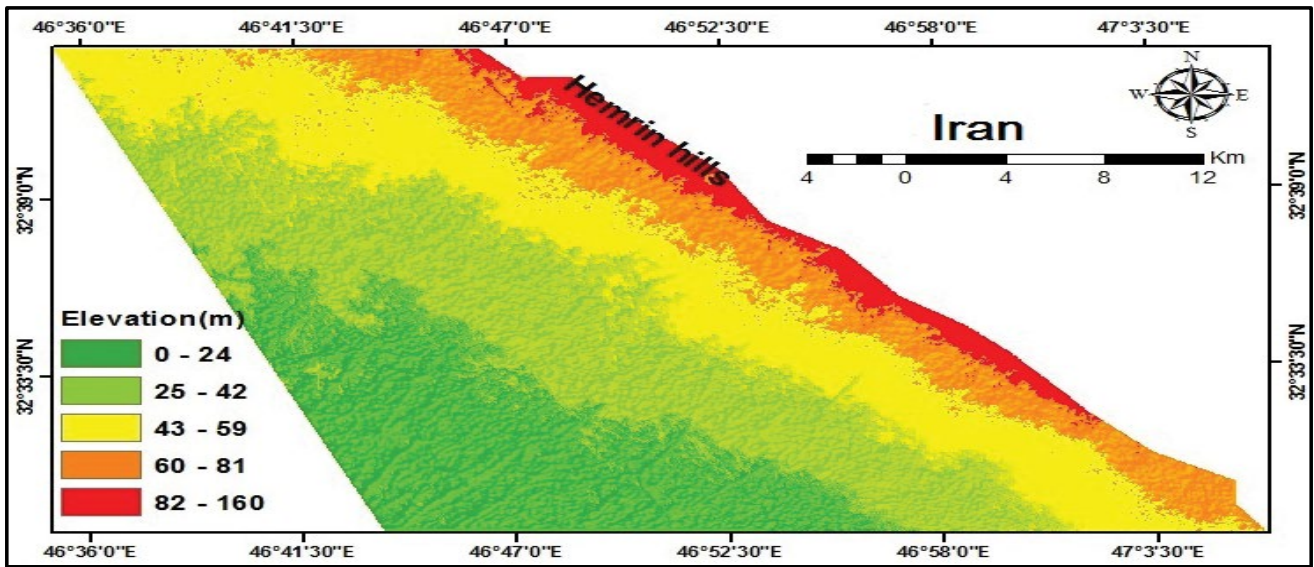


Fig. 2. Digital elevation's models of study area.

aquifer. Hydraulic conductivities values quaternary deposits in the study area are acquired from previous studies such as Al-Jaburi (2005). But no mention of the method used to get these values is given. The value of hydraulic conductivity for quaternary deposits between (0.5–5.3) m/day (Fig. 3). These values are less than other deposits, this may be because of.

**4. Methodology**

*4.1. Hydrogeochemical modeling*

Mass transfer along flow paths and geochemical reactions that control on water were modelled for (20) wells during two period of study area. The new software

computer code, NETPATH, these soft were estimate any change in mass transfer between any waters bodies when equipollent constraints are placed on reactive phases of initial water and product phases of final water chemistry. Saturation index (S.I) is index used in hydrogeochemical studies. It indicates the saturation status of minerals in the groundwater system and then determines the rock type which is in contact with groundwater. It has been defined through equation. So, the minerals in the aqueous phase are equilibrium status, supersaturation or undersaturation based. We can calculate the ionic activity from equation, and after that calculate the activity coefficient ( $\gamma$ ) by (Debye – Huckel) equation. The mineral saturation indices used to construct reaction models by PHREEQC V.3 (Parkhurst and Appelo, 2013). The Partial pressure of CO<sub>2</sub> is important

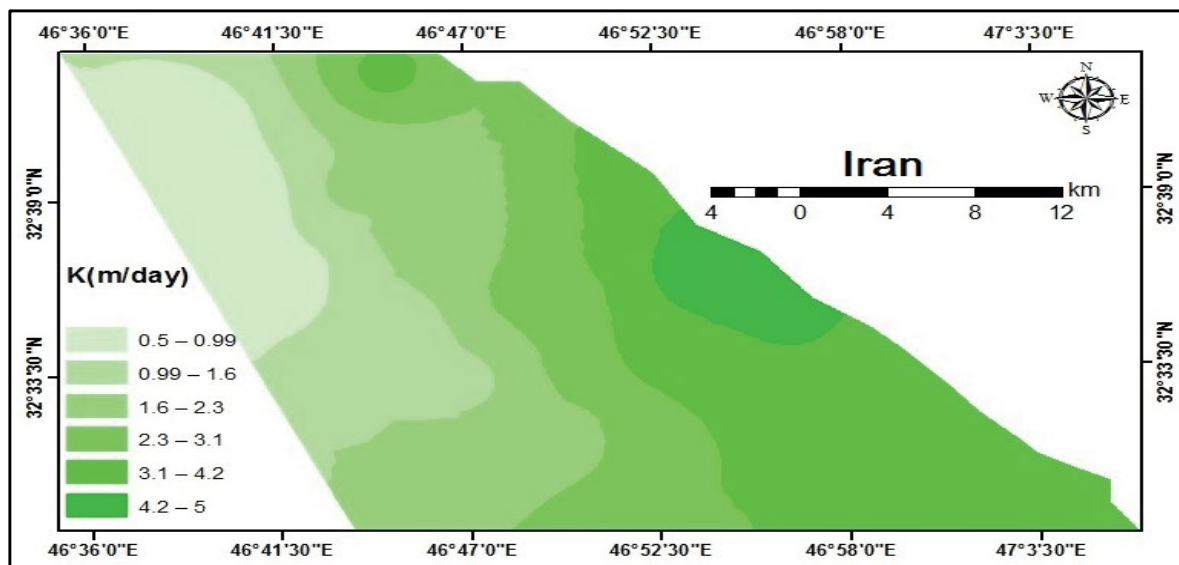


Fig. 3. Hydraulic conductivity of study area modify after Al-Jaburi (2005).

factor because it is control on chemistry system of natural water (carbonate – water). The reaction path models are based on the principle of mass balance transfer of chemical reactions needed for detailed calculations. One of the most important reaction flow paths for models is the evolutionary trend models along flow paths. These models provide important information on geochemical processes and (water-rock) interaction system. NETPATH uses chemical mass balance, (electron & isotope) mass balance equations with inverse geochemical modeling techniques (Plummer, 1984; Parkhurst and Plummer, 1993).

#### 4.2. Isotope

Stable isotopes are a powerful research tool in geology and environmental science (Andrews, 2006; Basak et al., 2009; Barros et al., 2010). The interest of stable isotopes in groundwater is that the two isotopes should display identical chemical behavior in the environment. Slight variations in isotopic abundance are caused by small differences in reactivity of the different isotopes.

For stable isotopes ( $^{18}\text{O}$ ,  $^2\text{H}$ ) of waters, the standard adopted is Vienna- Standard Mean Ocean Water (V-SMOW) (Clark and Fritz, 1997; Cook and Herczeg, 1999; IAEA, 2006).  $\delta$  (‰) is indicate to ratio of sample and a standard, when the sample is enriched in heavy isotopes, the values ( $\delta$ ) will be positives, while if the sample is depleted in heavy isotopes, the values ( $\delta$ ) will be negative.

In the present study, the isotopes ( $^2\text{H}$ ,  $^{18}\text{O}$  and T) content in water of studied area was evaluated by collected (10) groundwater samples and (6) samples for rainwater. All samples were analyzed at the laboratories of isotopes in Ministry of science and technology (Iraq).

## 5. Results and Discussion

### 5.1. Hydrogeochemical results

The reaction between groundwater and aquifer minerals plays a significant role in water quality, which is also useful

in understanding the genesis of groundwater (Ghalib, 2017). Chemical analysis of groundwater for two periods measuring the concentrations of major cation whose ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and the concentration of major anion ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ), and measurement of total dissolved salts (TDS) by evaporation inside the electric oven, also measurement electrical conductivity (EC) Table 1. The chemical data of groundwater (20) samples are used to calculate the saturation indices. Carbonate minerals and sulphate are taken in consideration based on the major ion's contents in groundwater. Later, the reaction path model (mass transfer) is activated through selected lines flow path. Table 2 shows us the log  $\text{PCO}_2$  for two periods. Log  $\text{PCO}_2$  has range from (-1.18) to (-1.86) in dry period, while in wet period range from (-1) to (-2.48), this range of log  $\text{PCO}_2$  is normal.

Ionic strength values give us important indicator to knowledge the behavior of solutions and solubility amount. The increase of values (Ionic strength) refers the total dissolved solid (TDS) increase; show us positive relationship between the ionic strength and the total dissolved solid. Also, it has positive relationship with the electrical conductivity (EC). The correlation coefficient between ionic strength and total dissolved solid (0.77) in the dry period and (0.85) in the wet period, this indicates a strong relationship between them (Fig. 4) as shown Table 2. Lower value appears in eastern part of study area for wells (w2, w3, w5) of confined aquifer, and increased value toward western part (discharge area).

The saturation indices of carbonate phases of groundwater in the study area are oversaturated during the wet period (w18, w20) for Calcite. It is found that the saturation S.I (Calcite) > S.I (Aragonite) > indices S.I (Dolomite) for two period. This is interpreted as due to dominant contents of  $\text{Ca}^{+2}$  in the lithological facies. Also, there is abundance of  $\text{Mg}^{+2}$  associated with  $\text{Ca}^{+2}$  to precipitate calcite in the groundwater phase. Gypsum values (S.I) are oversaturated found in all wells except (w2, w3, w5, w10, w14, w17, w20) for dry period, while found in wells (w1, w6, w7, w12, w13) for wet period, gypsum values (S.I) decrease because

Table 1  
Statics chemical analysis for two periods of study area

Well NO.	Unit	Dry period				Well NO.	Wet period		
		Min.	Max.	Ave.	Stan. Dev.		Max.	Ave.	Sta. Dev.
EC	( $\mu\text{s}/\text{cm}$ )	619	7,660	4,302.3	1,812.64	EC	4,938	3,287.9	1,298.12
TDS	mg/L	400	5,800	3,048	1,334.57	TDS	3,900	2,479.7	1,039.87
pH		6.2	6.7	6.4	0.14	pH	6.99	6.79	0.25353
T	( $^{\circ}\text{C}$ )	27	30	28.6	0.80	T	26.3	23.71	1.588
$\text{Na}^+$	mg/L	25	1,135	482.6	306.15	$\text{Na}^+$	1,240	821.35	341.08
$\text{K}^+$	mg/L	3	52.5	16	13.08	$\text{K}^+$	29	9.92	7.98
$\text{Ca}^{+2}$	mg/L	104	1,100	738.8	279.40	$\text{Ca}^{+2}$	960	601.76	253.67
$\text{Mg}^{+2}$	mg/L	10	550	298.8	156.82	$\text{Mg}^{+2}$	450	219.59	125.11
$\text{Cl}^-$	mg/L	70	1,372	934.6	389.38	$\text{Cl}^-$	1,180	818.53	355.3
$\text{SO}_4^{2-}$	mg/L	300	3,050	2,070.1	793.10	$\text{SO}_4^{2-}$	2,850	1,647.6	680.29
$\text{NO}_3^-$	mg/L	1.9	30.59	11.2	9.45	$\text{NO}_3^-$	27	10.54	9.29
$\text{HCO}_3^-$	mg/L	40	204	126.4	55.09	$\text{HCO}_3^-$	200	115.44	49.48
$\text{Fe}^{+2}$	mg/L	0.23	0.86	0.5	0.19	$\text{Fe}^{+2}$	0.73	0.44	0.178

Table 2  
Ionic strength & Log PCO<sub>2</sub> for two periods

Well No.	Aquifer type	Dry period				Wet period			
		EC (μs/cm)	TDS (mg/L)	Ionic strength	Log PCO <sub>2</sub>	EC (μs/cm)	TDS (mg/L)	Ionic strength	Log PCO <sub>2</sub>
-	-	(μs/cm)	(mg/L)	-	-	(μs/cm)	(mg/L)	-	-
w1	unconfined	7,660	4,000	0.107	-1.233	4,240	3,800	0.085	-1.557
w2	confined	792	510	0.013	-1.542	787	400	0.013	-2.133
w3	confined	808	600	0.022	-1.48	1,020	700	0.02	-2.033
w4	confined	3,383	2,600	0.097	-1.588	2,870	2,400	0.086	-1.92
w5	confined	619	400	0.016	-1.586	610	500	0.015	-2.477
w6	unconfined	3,200	2,500	0.111	-1.512	2,730	2,100	0.091	-1.002
w7	unconfined	6,340	5,800	0.131	-1.18	4,450	3,900	0.12	-1.499
w8	unconfined	5,270	4,800	0.122	-1.644	3,800	3,100	0.097	-1.692
w9	unconfined	5,140	3,850	0.104	-1.197	-	-	-	-
w10	unconfined	4,340	3,100	0.118	-1.3	-	-	-	-
w11	unconfined	4,900	3,800	0.093	-1.339	-	-	-	-
w12	unconfined	4,467	3,900	0.11	-1.523	3,900	3,100	0.098	-1.873
w13	unconfined	5,790	3,700	0.118	-1.367	4,450	3,600	0.103	-1.764
w14	unconfined	5,130	4,120	0.097	-1.453	4,160	3,100	0.088	-1.852
w15	unconfined	4,443	2,466	0.088	-1.861	3,900	2,140	0.076	-2.351
w16	confined	3,383	2,600	0.103	-1.387	2,600	2,200	0.084	-2.076
w17	unconfined	5,620	3,242	0.091	-1.55	4,938	2,930	0.084	-2.317
w18	unconfined	4,170	3,000	0.098	-1.207	3,550	2,646	0.086	-1.703
w19	unconfined	4,740	2,871	0.094	-1.304	3,740	2,600	0.077	-1.726
w20	unconfined	5,850	3,100	0.093	-1.266	4,150	2,940	0.084	-1.694

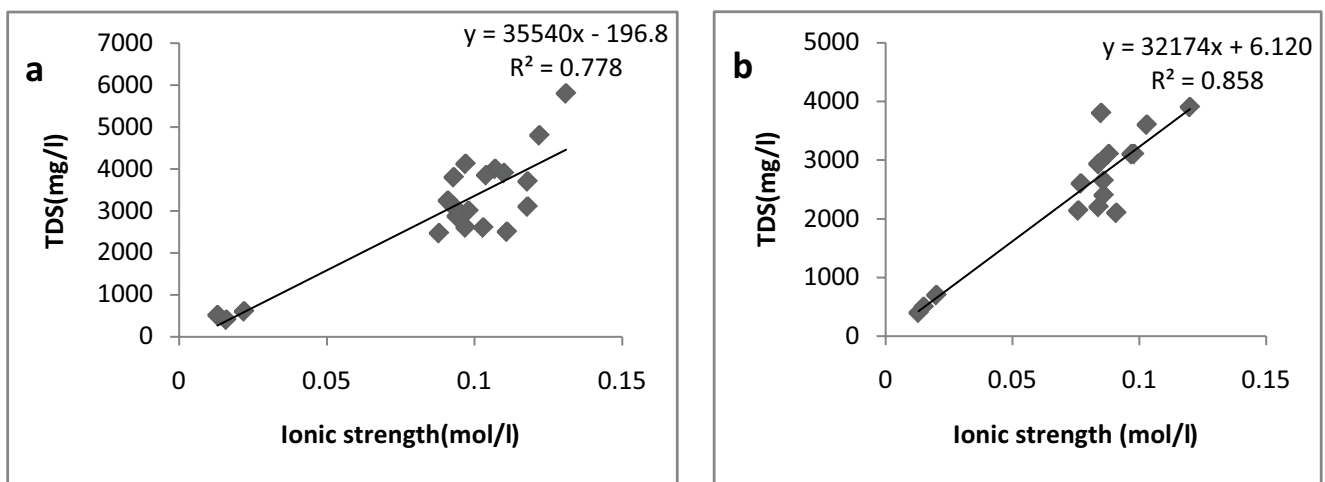


Fig. 4. TDS and ionic strength relationship for in the study area, (a) dry period and (b) wet period.

of amount of water recharge. Anhydrite values (S.I) are undersaturated in groundwater within dry and wet periods. Saturation indices of them are SI (Gypsum) >SI (Anhydrite), gypsum is dissolved more than anhydrite. Iron minerals are found in clay minerals. The deposition of these minerals in the study area is very high. The results of S.I. for hematite and goethite are high value which shows that the solutions are over saturation for both periods (dry and wet) in study area except (w8) in wet period because of amount of water

recharge. Halite (NaCl) is found in many current evaporative deposits. The deposition of this minerals in the study area are very low, Table 3. The results of S.I for halite are low value which shows that the solutions are under saturation for both periods (dry and wet).

Carbonate minerals show us transient variations. That is, for dolomite, calcite and Aragonite there is an overall upward trend in PCO<sub>2</sub> values during the two periods, which indicates the deposition carbonate minerals with decrease

Table 3  
Saturation index (S.I) for two period

Well No.	Dry period								
	Calcite	Aragonite	Dolomite	Siderite	Gypsum	Anhydrite	Hematite	Goethite	Halite
w1	-0.44	-0.58	-1.08	-1.29	0.14	-0.07	5.29	1.42	-5.07
w2	-1.68	-1.83	-4.02	-2.08	-1.08	-1.29	4.03	0.87	-6.80
w3	-1.29	-1.43	-3.00	-1.61	-0.73	-0.93	5.07	1.24	-6.97
w4	-0.50	-0.64	-0.93	-1.50	0.04	-0.16	6.09	1.75	-5.32
w5	-1.72	-1.86	-3.34	-2.09	-1.07	-1.28	4.31	0.86	-6.92
w6	-0.42	-0.56	-0.90	-1.71	0.16	-0.04	5.53	1.40	-5.14
w7	-0.56	-0.70	-0.96	-1.47	0.07	-0.13	4.93	1.17	-4.61
w8	-0.41	-0.55	-0.99	-1.62	0.12	-0.09	6.06	1.81	-4.58
w9	-0.35	-0.49	-0.65	-1.32	0.05	-0.15	5.36	1.46	-5.02
w10	-0.31	-0.45	-0.38	-1.28	0.00	-0.21	5.85	1.70	-4.82
w11	-0.19	-0.33	-0.68	-1.34	0.20	0.00	5.81	1.68	-5.52
w12	-0.01	-0.15	0.06	-0.90	0.02	-0.18	7.45	2.50	-5.09
w13	-0.28	-0.42	-0.61	-1.10	0.08	-0.13	6.34	1.95	-4.69
w14	-0.38	-0.52	-0.56	-1.35	-0.14	-0.34	6.21	1.88	-4.86
w15	-1.00	-1.14	-2.33	-1.79	0.02	-0.18	5.85	1.63	-4.94
w16	-0.69	-0.83	-1.25	-1.69	0.02	-0.17	5.01	1.14	-5.19
w17	-0.98	-1.12	-2.29	-1.66	-0.06	-0.26	5.40	1.33	-4.76
w18	-0.29	-0.43	-0.74	-1.60	0.02	-0.18	4.92	1.17	-4.94
w19	-0.19	-0.33	-0.55	-1.40	0.02	-0.19	5.62	1.59	-5.07
w20	-0.20	-0.35	-0.29	-1.14	-0.12	-0.33	6.06	1.81	-5.25
Wet period									
w1	-0.24	-0.38	-0.99	-1.33	0.01	-0.21	6.24	2.02	-5.08
w2	-1.02	-1.16	-2.70	-1.82	-1.07	-1.29	6.88	2.36	-6.93
w3	-0.52	-0.66	-1.42	-1.53	-0.88	-1.11	7.08	2.68	-6.97
w4	-0.11	-0.25	-0.14	-1.15	-0.05	-0.27	7.94	2.89	-5.39
w5	-1.20	-1.34	-2.37	-1.34	-1.11	-1.33	8.51	3.32	-6.98
w6	-1.10	-1.25	-2.66	-2.33	0.08	-0.15	1.14	-0.10	-5.14
w7	-0.37	-0.51	-0.64	-1.35	0.06	-0.16	5.90	1.98	-4.73
w8	-0.36	-0.51	-0.94	-1.20	-0.04	-0.27	6.62	2.51	-4.73
w12	0.19	0.04	0.21	-0.76	0.03	-0.20	8.35	3.39	-5.13
w13	-0.03	-0.18	-0.16	-0.84	0.00	-0.23	7.78	3.09	-4.80
w14	-0.18	-0.33	-0.16	-0.78	-0.22	-0.45	8.40	3.27	-4.90
w15	-0.73	-0.87	-1.77	-1.42	-0.06	-0.29	7.81	3.05	-5.11
w16	-0.21	-0.36	-0.47	-1.06	-0.03	-0.26	8.05	3.24	-5.41
w17	-0.41	-0.55	-1.19	-1.06	-0.09	-0.32	8.88	3.51	-4.83
w18	0.04	-0.11	-0.05	-1.18	-0.10	-0.32	7.25	2.62	-5.00
w19	-0.23	-0.37	-0.47	-1.14	-0.16	-0.39	7.04	2.66	-5.17
w20	0.10	-0.04	0.29	-0.77	-0.16	-0.38	8.13	3.06	-5.29

of  $\text{PCO}_2$ . Sulphates minerals show us overall upward trend in  $\text{PCO}_2$  values during the two periods.

The mass transfer of selected mineral phases (mmol/kg  $\text{H}_2\text{O}$ ) for the existing flow paths is given in Table 4. Depending on chemical analyzes entered, mineral phases to determine chemical reaction along flow path of study area for two periods, has been getting two models for each flow path and chosen one model suitable with the chemical

results and mineral phases. Flow path 1 shows different time evolution between dry and wet period, and the reaction products are calcite and dolomite. In wet period they are transformed from dolomite to calcite, and other minerals are soluble minerals. Calcite mineral sedimentation occurs three flow path, flow path 2 has similar to flow path 1 and, for two period calcite and sylvite precipitate along flow path. Flow paths 3 Show difference than other flow path,

Table 4  
Mineral phases for each flow path

Mineral phases	Calcite	Dolomite	Halite	Sylvite	Gypsum	Hematite
Flow path No						
F1(dry)	5.13	-2.44	10.05	0.10	2.66	0.00
F1(wet)	-22.33	12.20	51.80	0.50	31.01	0.01
F2(dry)	-20.91	10.11	8.17	-0.26	9.31	0.00
F2(wet)	-17.97	8.69	5.33	-0.16	11.87	0.00
F3(dry)	-1.34	0.54	3.53	-0.01	1.13	0.00
F3(wet)	-2.70	1.30	8.63	0.14	4.12	0.00
F4(dry)	3.16	-1.90	-1.63	-0.07	-3.04	0.00
F4(wet)	3.05	-1.80	-1.26	-0.06	-2.79	0.00

calcite, sylvite and hematite precipitate in dry period while wet period dissolution all minerals just calcite precipitate. Flow path4 show only calcite precipitate and dissolution the remaining minerals. Generally, there is change in the calculated mass transfers of selected minerals, and we can be seen as a “characteristic reaction” that dominates the field.

### 5.2. Isotope results

Six rain water samples are collected during three month, December, 2015 and January, February 2016. The results for all isotopes are expressed in  $\delta$  record as per mil deviation from internationally accepted standard V-SMOW (Vienna standard mean ocean water). The changes of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in rainwater throughout Iraq are due to rainfall intensity (amount effect) and are attributed to passage of air mass from the Mediterranean Sea. (Kattan, 1997). The results are reported in negative numbers because they are showing how much less  $^{18}\text{O}$  isotopes are present compared to the ocean water. The low negative numbers indicate heavier water with a higher concentration of  $^{18}\text{O}$ , whereas the high negative numbers signify lighter water where more of the  $^{18}\text{O}$  has been precipitated out.

In Missan for district of Ali al Gharbi,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  relationship for all the samples data during the observation periods of December, 2015 and January, February 2016, may

define initial Amarah meteoric water line (AMWL) which fits with the relation below a regression line coefficient  $R^2 = 0.94$  as shown in Fig. 5.

$$\delta\text{D} = 7.51 \delta^{18}\text{O} + 10.82 \quad (1)$$

The equation defines the Local (Missan) Meteoric Water Line (LMWL). The slope of the line (7.51) is slightly different from the slope of GMWL (8) and interception (10.82), because of the varying climate conditions. The Slope (7.51) shows that no evaporation occurred during precipitation (Scholl, 2011). The slope of the regression line for the relationship between ( $\delta^{18}\text{O}$ – $\delta^2\text{H}$ ) in rainwater is <8, Fig. 5, which is the climate characteristic is a semi-arid (Geyh et al., 1998). The slope of the linear regression is less than the GMWL and ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) relationship provides a good characterization of air mass origin (Al-Charideh, 2011).

Many factors such as evaporation, condensation, and melting, freezing, chemical and biological process affect in heavy isotopes (Craig, 1961; Povinec et al, 2008; Al-Paruany, 2013). Generally, fresh water wells supply in study area is limited due to scarce precipitation, high evaporation and salinity. For evaluation of the groundwater resource in the study area requires determination of origin of groundwater, water age, salinity, and interaction between the surface and groundwater, if found surface water in study area. Stable isotopes composition in groundwater samples in study area,

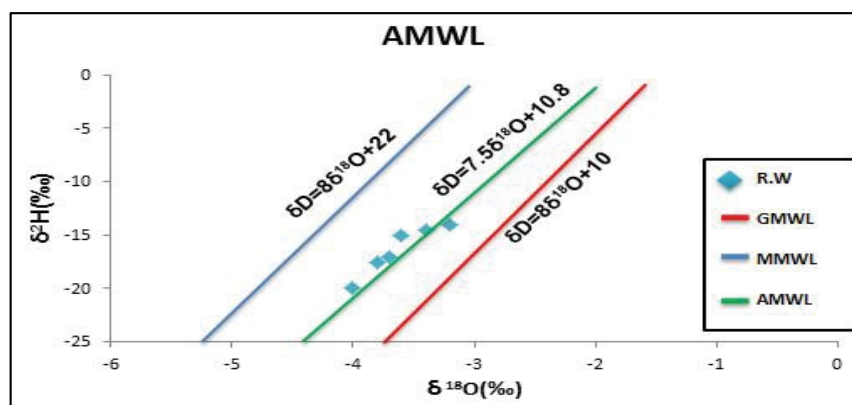


Fig. 5. LMWL for Missan (Ali Al-Gharbi) during the observation periods December 2015 and January, February 2016.

ranges from (-3.55 ‰) to (-2.19 ‰)  $\delta^{18}\text{O}$  with the average (-3.01) in the dry period, and (-4.7 ‰) to (-2.22 ‰)  $\delta^{18}\text{O}$  with the average (-3.35) in the wet period and from (-16.2 ‰) to (-8.23 ‰)  $\delta^2\text{H}$  with the average (-12.54) in the dry period, while the ranges from (-19 ‰) to (-11.3 ‰)  $\delta^2\text{H}$  with the average (-14.18) in the wet period.

The results of stable isotope in groundwater ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), that have proved the isotopes content in the groundwater samples have no remarkable trend of seasonal isotopes change. Also, the average values of ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) in groundwater of the study area are relatively low compared with rainwater samples. The variation in stable isotopes signature of water in study area is caused mainly by natural evaporation, change of stable isotopes content in rain water and mixing. Depended on distribution for all sample in two periods on  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  diagram, we have two groups in study area, Fig. 6. the first group (A) includes the wells (W2, W3), this well located in east part of study area (confined part). The stable isotopes composition in this group ranges from (-3.98) to (-4.7) for  $\delta^{18}\text{O}$  with the average (-4.31) and from (-14.7) to (-21.2) for  $\delta^2\text{H}$  with the average (-17.4). The second group (B) is represented mainly by the remaining wells, the isotopic concentration in this group ranges from (-3.23) to (-2.18) for  $\delta^{18}\text{O}$  with the average (-2.74) and from (-12.9) to (-10.2) for  $\delta^2\text{H}$  with the average (-11.81), this value are relatively low compared with that of the first group. According all above, we have two wells in group (A) belong in confined part and other wells in group (B), this indicates presence hydraulic connection and mixing processes between confined and unconfined part.

The relationship between ( $\delta^{18}\text{O}$  /  $\delta^2\text{H}$ ) in groundwater is plotted as seen in Fig. 11. the distribution of the samples of groundwater in the study area is located between the

GMWL and MMWL, which that the evaporation is not an influential factor this indicates that groundwater in this study, where recharge water comes from the precipitation. This suggested that stormwater rapidly infiltrates processes throughout quaternary sediment and the highly permeable deposits in the recharge areas. The variation in the isotopic composition in all points indicates that groundwater is affected by different degree of evaporation (Kattan, 2006; Ghalib, 2014). The groundwater in the Quaternary Sediments probably recharged from Mediterranean precipitation and continental water of meteoric origin. The stable isotope similarity between the two aquifers is probably related to the hydraulic interconnection between confined and unconfined aquifer. This indicates that Water from the confined aquifers is more depleted in the stable isotope ratios, suggesting a cooler climate at the time the water was recharged. The stable isotopes content decreases from the north western part towards the south eastern part of studied area which indicates poorly modern recharge.

Stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) are successfully and suitable method for determine the mechanisms of groundwater salinity, also estimate origin of salinity (IAEA, 2010; Al-Charideh, 2010). The Sources of salinity are from the dissolution processes, the isotopic concept is not changes in the composition of ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) based on sources of salinization. The changes in stable isotopic composition ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) under mixing or evaporation processes are sensitive (IAEA, 2010, Al-Charideh, 2010).

## 6. Conclusion

Study area (Ali Al-Gharbi) approximately 760 km<sup>2</sup> covering the north east of Missan Province of Iraq. The topographic map elevation (DEM) is between (0–160) m, high elevation is Hemrin hills. The sediments of study area are quaternary deposits. Calculation results of saturation indices of mineral phases indicate that there are changes in these values in the study area for two periods. Major minerals such as calcite, dolomite, gypsum and sylvite show significant spatial and temporal changes and no significant change in other minerals. Also, the calculations show us precipitation and dissolution processes of minerals in study area. The situation in wet period shows a significant difference compared to December dry period. The complex flow path system affects both of the precipitation and dissolution rates, and will be heterogeneous distribution of the above process.  $\text{PCO}_2$  has an important role in saturation control of some carbonates; submit to atmospheric effects in free aquifer (partly open system). The different trends of  $\text{PCO}_2$  with all minerals also explain the complex structure of the aquifer. The results of flow path reactions are various both in two periods, also the nature of these reactions is different during working (periods) with time. The processes both of dissolution and precipitation of carbonate minerals often influence in the control of chemical composition changes. Reaction path models show that there are different chemical reactions related to selected flow paths for two periods. The main sedimentation mineral was calcite, while dolomite dissolved except the flow path 4. Gypsum and halite reactions have same behavior for both (precipitation & dissolution) results, while hematite and sylvite are various

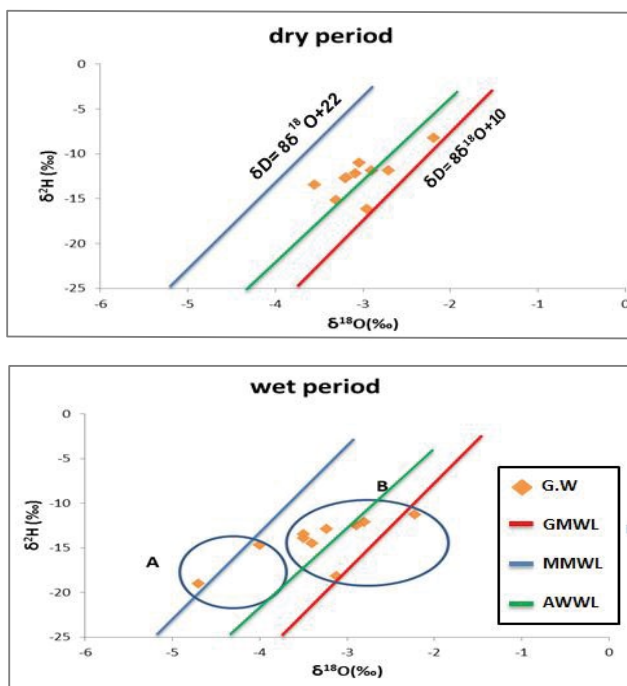
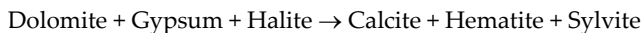


Fig. 6. diagram ( $\delta^2\text{H}$ - $\delta^{18}\text{O}$ ) of groundwater sample for study area.



in precipitation/dissolution. According to these facts, the basic reaction for two periods can be explained as follows



The applied models are the dominant geochemical process of d-dolomitization involving dolomite, gypsum and halite dissolution and calcite precipitation of groundwater in study area.

Confined part located in eastern part of study area and most of sediment of this aquifer is gravel, while unconfined part located in western part of study area and most of sediments are sand with silt. The hydraulic connections between the aquifers in middle part of study area. According to stable isotope data  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , most wells of groundwater are of meteoric origin and exposed to evaporation, also presence hydraulic connection between to water type. Stable isotopes are explaining that recharge groundwater undergoes significant evaporation through it transit to the aquifer. The variation in the isotopic composition in all points indicates that groundwater is affected by different degree of evaporation. The Stable isotopes for all samples of groundwater are located between GMWL and MMWL, this indicate that these samples are mixture of two types. Amara meteoric water line (AMWL) is near to GMWL and away from MMWL, this indicates climate of study area is affected by Arab Gulf climate.

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