Hydrochemistry and geochemical evolution of unconfined aquifer in Kalal Badrah Basin, Wasit, East of Iraq

Sawsan M. Ali and Ali H. Ali*

Department of Geology, College of Sciences, University of Baghdad, Jadiriyah, IRAQ.
*General Commission of Groundwater, Ministry of Water Resources, Baghdad, IRAQ.
E-mail of the corresponding author: sawsanjaff@hotmail.com

Abstract

Chemical composition of 38 groundwater samples from wells penetrating the unconfined aquifer of the Quaternary deposits throughout Waist governorate, east of Iraq, were analyzed to describe the hydrochemical behavior of this aquifer through the area. The hydrochemical parameters include the major cations and anions, TDS, EC, pH, as well as calculating Na%, Total Hardness (TH), and Sodium Absorption Ratio (SAR). Significant spatial variations in these parameters were noticed and Ca-SO_4 water type was found to be the predominant one. According to the available standards, the present study samples were unsuitable for drinking purposes but adequate for irrigation purposes depending on Na%, TDS, EC, and SAR values. Geochemical modeling approach enabled calculation of the saturation state of some selected minerals i.e. explaining the dissolution and precipitation reactions occurring in the groundwater as well as calculating the amount of mineral mass transfer of the selected mineral phases along some specific flow paths. Based on this approach, the present samples were found to be oversaturated with carbonate minerals and under-saturated with sulfate minerals. Strong correlations between the concentrations of SO_4 and the SI's of sulfate minerals and weak correlation with carbonate minerals were observed. The present study revealed also that calcite precipitation and dissolution of dolomite and gypsum is the main chemical reaction controlling the chemical changes of the groundwater aquifer in the study area.

Keywords: Groundwater, Water Suitability, Saturation Index, Inverse Modeling, Wasit, Iraq.

1. Introduction

Understanding the geochemistry of groundwater is important for maintaining water quality, effective utilization and development of this finite resource (Hirohiko et al., 2006). Chemical and physical parameters of groundwater are an important tool for assessing the water quality and indication of possibility of groundwater contamination.

Geochemical modeling, mostly known as inverse modeling, is a useful tool for studying hydrochemical evolution. It is commonly used to reconstruct geochemical evolution of groundwater from one point in an aquifer to another point located in the inverse direction along the groundwater flow path (Parkhust and Plummer, 1993). Waist area is characterized by semi-arid climate, where groundwater sustains an important component of water supply. Several hydrogeological studies dealing with various aspects in the study area have been achieved such as Al-Furat General Company(2002), Al-Azawi (2002) and Al-Shammary (2008).

The aim of this paper is to investigate the main chemical reactions thought to be responsible for the observed variations in the chemical composition using geochemical modeling approach. Suitability of the groundwater for the different purposes was evaluated as well.

2. Geologic and hydrogeologic conditions of the study area

Kalal Badrah hydrogeological basin locates in Wasit governorate, east of Iraq, between latitudes (32^0 50^-33^0 20^-) N and longitudes (45^0 $30^- – 46^0$ 10^-) E, it is restricted by Iraqi – Iranian border from the east, and covers an area of about 2848.706 km^2 (Figure 1). Badrah city occupies the central part of the basin whereas, Zurbatiyah city is 12 km northeast away from Badrah, near Iraqi-Iranian border line, and Jassan town locates in the southern part of the basin, i.e. 20 km to the south from Badrah city. Topographically the highest elevation points reach about 957 meters above sea level at the northeast of the studied area, while the lowest elevation points reach about 10 meters above sea level, at the southern parts of the studied area as shown in Figure 1.

The streams network within the watershed is delineated from the catchment area. The network contains short exterior links which represent valley side indentation or gully outlets (Figure 2).The network order is used to find the catchments area at the upstream and downstream end of each link (Figure 3). This is used to calculate the direct drainage area, respectively, for each link in the network system within Badrah basin. The predictable relationships are the average stream length, watershed area which increases regularly with the increasing order; average stream gradient which decreases with the increasing order (Figure 4).The flow direction is used to follow each link from its upstream to downstream ends. It flows generally towards southwest (Figure 5). The mean slope is higher for the more turbid streams. It indicates the less time required for water to travel from the higher most distant point of the watershed to the mouth of the primary stream and that the velocity of the flowing water inside the stream will be higher towards the higher order stream thus, less amount of water will be infiltrated into the ground. The surface recharge to the groundwater aquifers is related to the physiographic properties of the basin, the drainage type depends

on the local landforms and the types of rock and the prevailing soil. The streams in the study area follow a dendritic branching drainage pattern.

Geological formations of the basin range in age between Lower Miocene to the Holocene, where the youngest one can be seen along the northeastern border of the basin, whereas the Quaternary deposits cover the central and southern parts of the basin, (Hassan et al., 1977). The Stratigraphic Succession of Kalal Badrah basin composed from Euphrates, Fatha, Injana , Mukdadiya Formations, as well as Quaternary depositions (Figure 6). The latter consists of alluvium deposits, representing a mixture of gravel, sand, silt, clay, and conglomerates of post Pliocene deposits, (Hamza et al., 1989). Structurally, the study area locates within the foothill zone and Mesopotamian plain (Buday and Jassim, 1987).

Hydrological units concentrated mainly in the Quaternary deposits, consisting of gravel, sand, silt, and clay representing surface unconfined aquifer. The depth of groundwater of the wells tapping these deposits ranged from 30 to 90 meter below ground surface. Al-shammary, (2008), gave the following values for the hydraulic properties, transmissivity of (228.43) m^2/day, hydraulic conductivity of the range (0.103-45.024) m/day, specific capacity values ranged from (4.57-1555) m^3/day and Specific yield ranged from (0.01-0.073). Groundwater flow in the study area is towards the southwest as show in Figure 7. The climate of the studied area is characterized by a cold, arid winter and long, hot, dry summer. Precipitation begins in October and ends in May, where the mean monthly precipitation values for the period (1995–2012) of Badrah station, range from 0.03,(August) to 40.78 mm (January) whereas, the mean monthly class A pan evaporation values have a range from 65.4 mm (January) to 496.4 mm (July). The mean, minimum and maximum monthly temperature values have range from $5.96\,^\circ$c (January) to $35.7\,^\circ$c (June) and from $16.32\,^\circ$c (June) to $45.73\,^\circ$c (July). The mean monthly values of relative humidity and wind speed range from 20.56% (July) to 71.76 %(January) and from 2.0 m/s (November) to 3.92 m/s (June), respectively, (Iraqi Meteorological Agency, 2013).
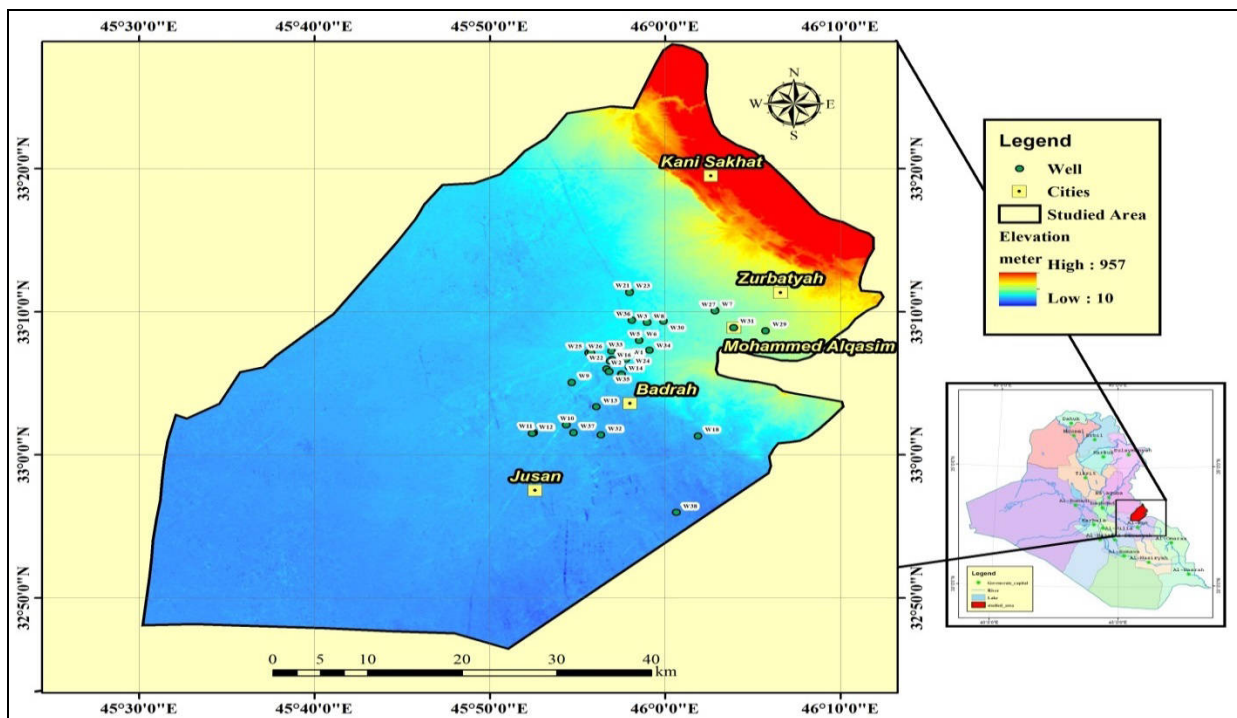

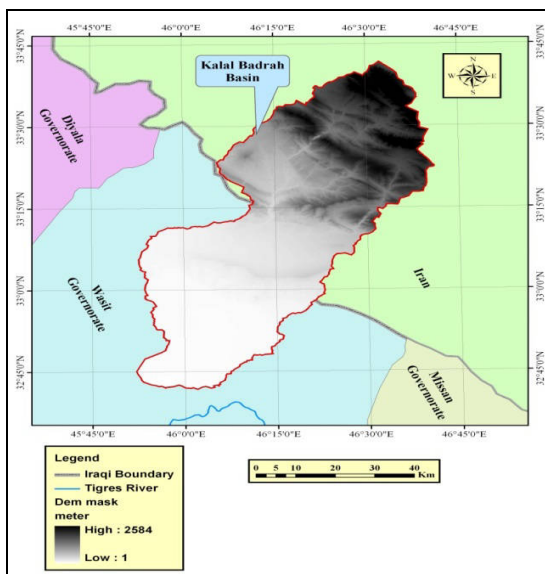Figure 1. Location map of study area.

Figure2. Watershed of Kalal Badrah basin.
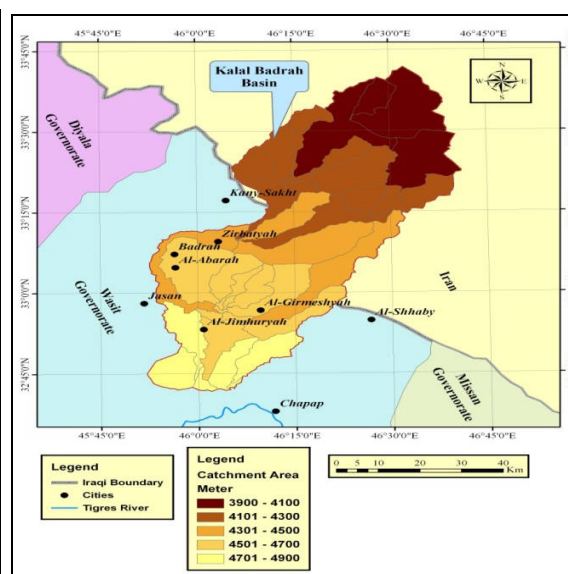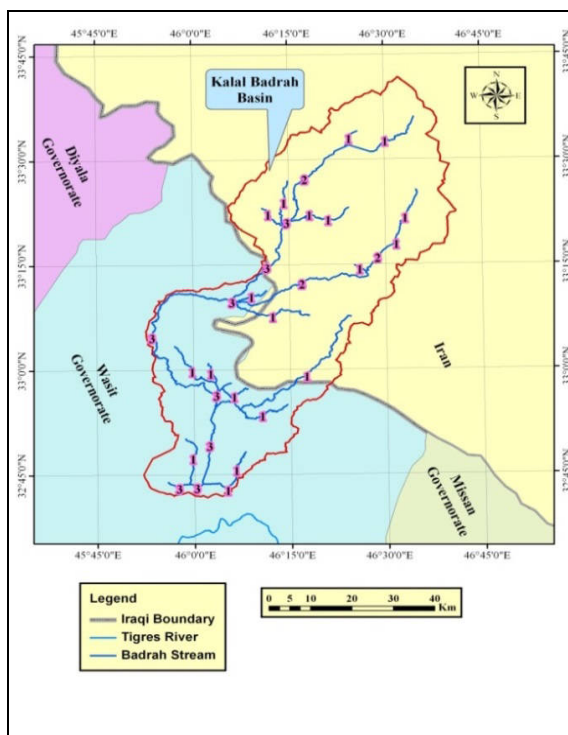

Figure3. The main surface basin of Kalal Badrah.

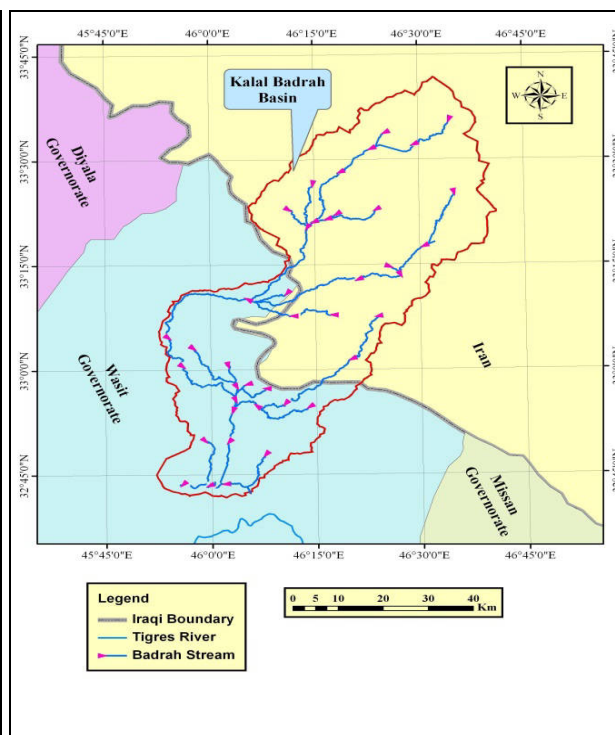Figure 4. Stream order classification in Kalal Badrah basin.
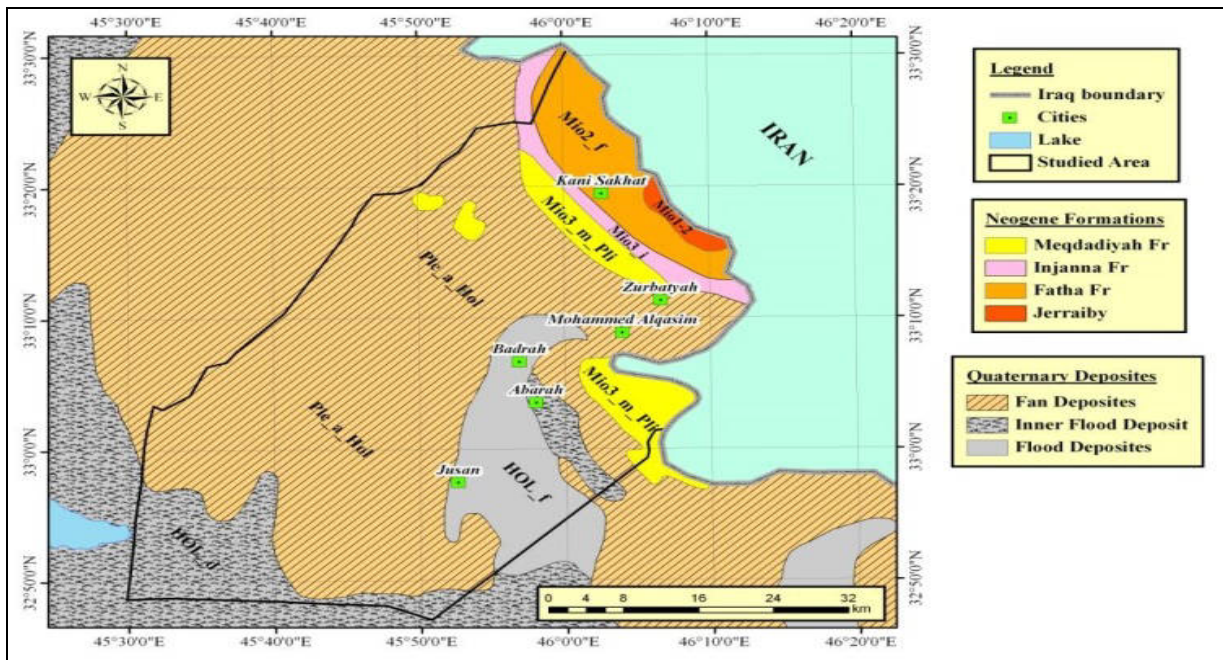

Figure 5. Stream flow direction in Kalal Badrah basin
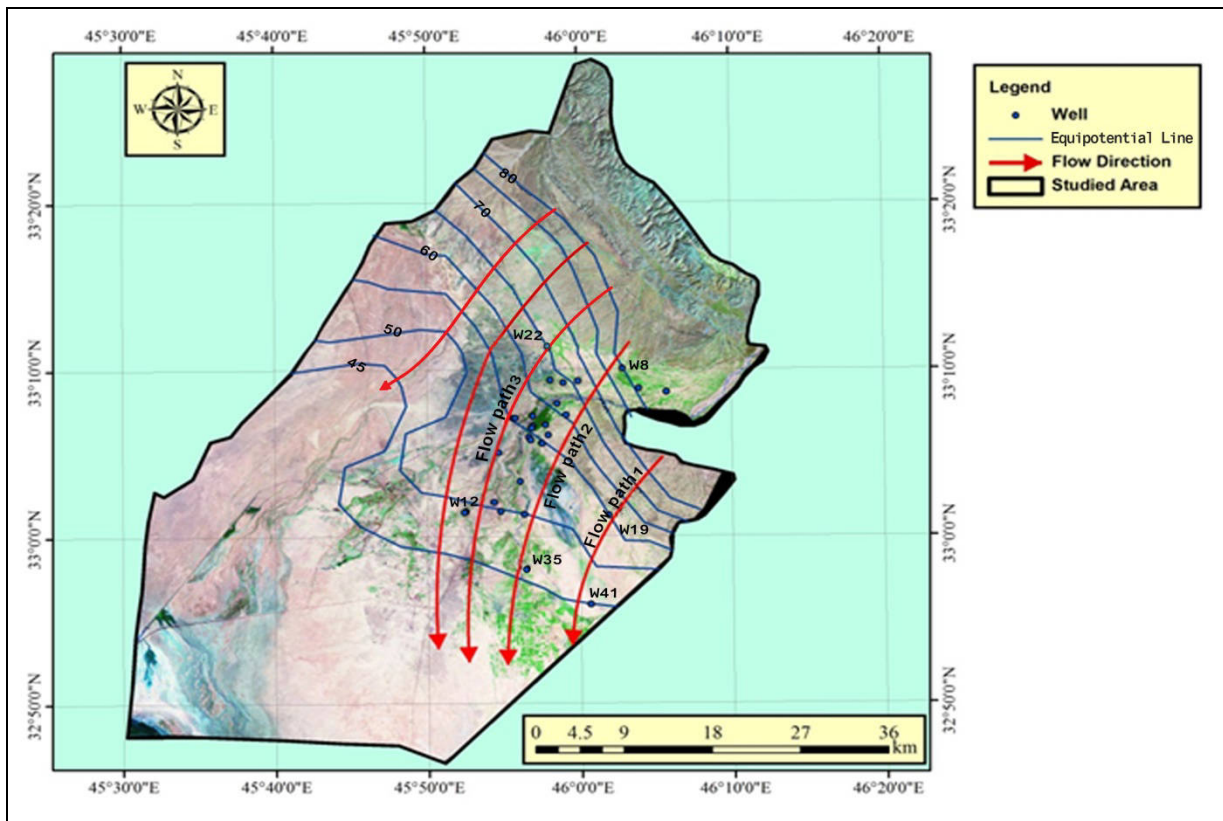
Figure 6. Geological map of the study area.

Figure7. Groundwater flow map (meter above sea level) of the study area.

3. Materials and Methods

A total of 38 water well samples were collected from the unconfined aquifer of the Quaternary deposits for the period 2012-2013, (Figure 1). pH ,temperature ,TDS and EC were measured in the field whereas the concentrations of the major cations and anions were analyzed at the laboratories of the General Agency of Groundwater using standard analytical procedures (APHA,1998). Sodium and potassium were analyzed using flame photometer. Calcium, magnesium, chloride, carbonate and bicarbonate were determined by titrimetric method using the relevant reagent. Sulfate concentration was determined following the turbidity method by using of spectrophotometer.

Statistical analyses were performed using SPSS computer software. A combination of WATEQ4F speciation calculations program developed by Ball and Nordstrom (1991, 2001) and NETPATH Code developed by Plummer et al. (1994) were used to investigate the major geochemical processes controlling the quality of the aquifer chemistry and the evolutionary trend of selected flow paths in the area.

4. RESULTS AND DISCUSSIONS

4.1 Hydrogeochemical parameters

The hydrochemical data of the investigated groundwater samples are summarized in Table 1 .The result of these data were presented statistically in form of minimum, maximum, mean, median and standard deviation in Table 2. Almost, all the parameters except pH and NO_3 showed wide ranges. Groundwater of the study area is slightly alkaline with pH values ranging from 7.1 to 7.8.

As groundwater moves or stays for a long period along its flow path, there is normally an increase in TDS values which determined the suitability of these waters for the different uses (Freez and Cherry, 1979). According to the classification of groundwater, (Table 3), the majority of the present samples fall in slightly-brackish water class. According to Detay, (1997), in table 4, the present water samples represent slightly to moderately mineralized water. Total hardness (TH), expressed as the equivalent quantity of calcium carbonate showed that all groundwater samples of the study area are very hard (Table 4).

Spatial distribution of TDS, EC and the concentrations of the cations and anions through the studied area are presented in Figures (8 and 10). No specific trends of changes could be noticed, but it could be shown that the groundwater properties are considerably differs from site to another, due to the lithological variations in the area.

Presentation of geochemical data in the form of graphical charts such as Piper diagram (Piper, 1948) helps us in recognizing hydrogeochemical types of groundwater samples based on the ionic composition of different water samples (Figure 11) . Based on this diagram, the predominant water type is $CaSO_4$, reflecting the great effects of the evaporates dispersed in the aquifer matrix.

4.2 Suitability of groundwater

The suitability of water for different purposes such as drinking and irrigation is related to its physical-chemical and biological properties. According to WHO (2008) and Iraqi standards (2009), all of the selected groundwater samples found to be unsuitable for drinking purposes, (Table 5).

The suitability for irrigation purpose is determined by TDS, EC, Sodium Adsorption Ratio (SAR) and sodium percent Na%, in addition to the major and minor elements concentrations. The most influential water quality parameter on crop productivity is the water salinity as measured by electrical conductivity.

Calculation of Na% can be done by using the equation of Todd (1980):

Na% = [Na+ k] ×100/ [Ca+ Mg+ Na+ K] --------1

All ionic concentrations are expressed in meq/l.

Sodium hazard can be determined by the absolute and relative concentrations of the cations and can be evaluated through the sodium adsorption ratio (SAR), because of its direct relation to the absorption of sodium by soil (Todd, 1980). It is defined by:

SAR = r Na / [r (Ca+Mg) /2]0.5------------   2

Where, r represent meq/l

Classification of irrigation water based on SAR and Na% values is shown in Table 6, (Todd, 1980). On the basis of this classification, all of the present samples belong to excellent water class according to SAR values except the sample w34 which classifies as good water class. 81.5% of the groundwater samples of study area are classified as permissible water class according to Na% values while 13.2% of them are good water class. The remaining 5.3% samples belong to doubtful water class.

4.3 Water- rock interaction processes

The interaction between groundwater and the hosting rocks though to be the main affecting factor for the observed chemical characteristics variation of groundwater of the study area. Mean, median, minimum, maximum and

standard deviation of the saturation indices (SI) of selected minerals in the study area as calculated by WATEQ4F code are listed in Table 7. The use of the SI values showed that, all the samples were undersaturated with respect to the evaporate minerals, anhydrite and gypsum, and saturated to oversaturated with respect to carbonate minerals, calcite, dolomite and aragonite (Figure12). The computed log P_{CO2} values for all present samples in the study area vary between $10^{-2.5}$ and $10^{-1.4}$ atm being significantly higher than that of the atmosphere ($10^{-3.5}$ atm) reflecting that the aquifer can be regarded as partially open system (Suarez, 1995).

 Strong correlations between the concentrations of SO₄ and the SI's of gypsum and anhydrite can be noticed in which R values are around 0.85. Weak correlation between SO₄ and carbonate minerals can also be observed (Figure 13). These relationships suggest that the precipitation of the carbonate are highly affected by the dissolution of evaporate minerals. Concerning the correlation among SI's of the selected minerals (Figure 14), it is clear that the carbonate minerals are strongly correlated, whereas there are weak inverse

 Relationships of the SI's of these minerals with the of evaporates. This assures, also that the precipitation of carbonate minerals are highly related to the dissolution of evaporates which will be further investigated and quantified using the inverse geochemical modeling based on mass balance concept as in the fallowing paragraph.

Table 1. Hydrochemical parameters of the study area samples.

Well No.	Ca²⁺ ppm	Mg²⁺ ppm	Na+ ppm	K+ ppm	Cl⁻ ppm	SO₄²⁻ ppm	HCO₃⁻ ppm	NO₃⁻ ppm	pH	TDS ppm	EC µmos/cm	T.H ppm	SAR ppm	Na% meq
W1	126	89	130	12	245	448	110	3.5	7.18	1250	1890	679.9	2.17	30.5
W2	340	210	720	110	941	1801	232	2.0	7.51	4400	5100	1714.3	7.57	50.0
W3	281	134	529	79	649	1175	479	3.0	7.23	3400	3950	1252.9	6.50	50.0
W4	264	171	280	8	442	1016	268	4.3	7.31	2865	3500	1361.9	3.30	31.2
W5	200	97	369	4	467	680	352	5.5	7.51	2469	3010	897.7	5.35	47.3
W6	271	121	420	170	590	1067	248	3.5	7.23	2950	3570	1174	5.33	49.1
W7	411	191	721	12	914	1569	537	2.0	7.50	4800	5500	1813.4	7.37	46.7
W8	259	160	380	8.9	650	950	262	8.0	7.43	3120	3810	1304.4	4.57	39.1
W9	140	125	365	6.5	470	673	350	4.0	7.25	2528	2884	863.2	5.40	48.2
W10	452	241	800	11	1060	1700	550	7.0	7.13	5550	6120	2122.5	7.56	45.3
W11	137	115	370	3	468	670	320	6.0	7.61	2151	2974	814.5	5.63	49.8
W12	369	185	603	109	719	1600	509	2.0	7.41	4112	5100	1683.4	6.40	46.3
W13	190	76	550	5.1	530	864	357	8.2	7.41	2760	3550	786.6	8.52	60.5
W14	271	130	390	17	550	990	241	3.1	7.21	2670	3630	1210.8	4.87	41.8
W15	281	128	410	81	545	990	452	6.1	7.44	2949	3720	1227.8	5.09	44.8
W16	332	157	536	117	716	1296	509	4.0	7.20	3736	4510	1475.2	6.09	47.2
W17	301	139	478	89	645	1121	465	3.0	7.22	3493	4210	1323.3	5.71	46.6
W18	300	138	480	85	650	1123	460	2.0	7.18	3300	4210	1316.7	5.75	46.7
W19	332	157	536	117	716	1296	509	3.0	7.26	3725	4180	1575.2	6.07	47.2
W20	360	230	740	115	994	1921	240	0.1	7.31	4700	5600	1847	7.50	48.8
W21	349	177	609	101	709	1520	510	4.5	7.33	4320	5100	1600.4	6.62	47.6
W22	270	130	510	85	639	1104	455	2.1	7.17	3408	3985	1208.8	6.38	50.2
W23	351	178	587	102	708	1530	508	3.5	7.33	4320	5100	1609.5	6.37	46.7
W24	325	154	529	113	650	1180	706	3.0	7.15	3792	4520	1445.4	6.05	47.3
W25	325	150	530	113	640	1180	706	3.0	7.61	3800	4490	1428.9	6.10	47.6
W26	261	126	415	78	548	1003	428	5.0	7.72	3085	3800	1169.6	5.28	46.2
W27	332	162	567	102	684	1413	492	2.0	7.82	3872	4600	1495.9	6.38	47.7
W28	494	211	860	61	1087	1820	740	3.0	7.63	5500	6350	2104.5	8.17	48.1
W29	275	130	417	159	580	1059	250	3.0	7.52	2883	3500	1221	5.19	47.6
W30	250	141	216	12	500	730	204	7.1	7.71	2200	3100	1203.2	2.71	28.7
W31	169	114	450	27	563	960	108	1.5	7.22	2850	3350	890.4	6.55	53.2

W32	241	106	369	15	486	925	240	4.0	7.24	2400	3130	1037.1	4.98	44.2
W33	315	144	484	103	662	1150	520	7.5	7.41	3420	4100	1379	5.67	46.2
W34	70	37	428	15	359	511	267	4.0	7.44	1827	2370	326.6	10.3	74.4
W35	253	140	215	11	443	793	203	8.0	7.11	2088	3100	1206.5	2.69	28.5
W36	332	157	538	118	718	1289	500	2.0	7.41	3675	4330	1475.2	6.09	47.2
W37	350	171	589	100	704	1510	506	1.1	7.12	4119	4730	1578.1	6.45	47.2
W38	225	106	374	3.5	530	770	310	6.0	7.21	2400	3200	997.1	5.15	45.1

Table 2. Statistical characteristics of hydrochemical parameters in the study area

	Ca	Mg	Na	K	Cl	SO$_4$	HCO$_3$	NO$_3$	pH	TDS	EC	TH	SAR	Na%
mean	284.3	145.5	486.7	65.2	636.1	1142.0	397.5	3.9	7.4	3339.1	4049.3	1311.1	5.9	46.3
median	281.0	140.5	482.0	80.0	642.5	1112.5	440.0	3.5	7.3	3350.0	3967.5	1310.6	6.1	47.2
minimum	70.0	37.0	130.0	3.0	245.0	448.0	108.0	0.1	7.1	1250.0	1890.0	326.6	2.2	28.5
maximum	494.0	241.2	860.0	170.0	1087.0	1921.0	740.0	8.2	7.8	5550.0	6350.0	2122.5	10.3	74.4
Std.deviation	87.6	41.2	157.3	50.8	181.1	369.9	159.4	2.1	0.2	971.7	993.0	377.8	1.6	7.9

Table 3. Classification of water salinity according to the TDS (ppm).

	Drever (1997)	Todd (2007)	Water class
0-1000	< 1000	10-1000	Fresh water
1000-3000	1000-2000	--------	Slightly water
3000-10000	2000-20000	1000-10000	Slightly-Brackish water
10000-100000	------	10000-100000	Brackish water
------	20000-35000	------	Saline water
>100000	>35000	>100000	Brine water

Table 4. Water classification based on electrical conductivity (Detay,1997)
and total hardness (Todd,1980)

	Mineralization	Total well	Total Hardness	Water class
<1000	Very weakly mineralized water		< 75	Soft
1000-2000	Weakly mineralized water	1	75-150	Moderately hard
2000-4000	Slightly mineralized water	19	150-300	Hard
4000-6000	Moderately mineralized water	16	>300	Very hard
6000-10000	Highly mineralized water	2		
>10000	Excessively mineralized water			

Table 5. Measured values of present study compared with IQS,
2009 and WHO, 2008, permissible limits for drinking water

parameters		Present study Range ppm	IQS,2009 ppm	WHO,2008 ppm
		7.1-7.8	6.5-8.5	6.5-8.5
TDS	ppm	1250-5550.0	1000	1000
Ca	ppm	70.0-494.0	150	75
Mg	ppm	37.0-241.2	100	100
Na	ppm	130.0-860.0	200	200
K	ppm	3.0-170.0		12
Cl	ppm	245.0-1087.0	350	250
SO$_4$	ppm	448.0-1921.0	400	250
NO$_3$	ppm	0.1-0.8	50	50

Table 6. Classification of irrigation water based on SAR and Na%
values (Todd, 1980)

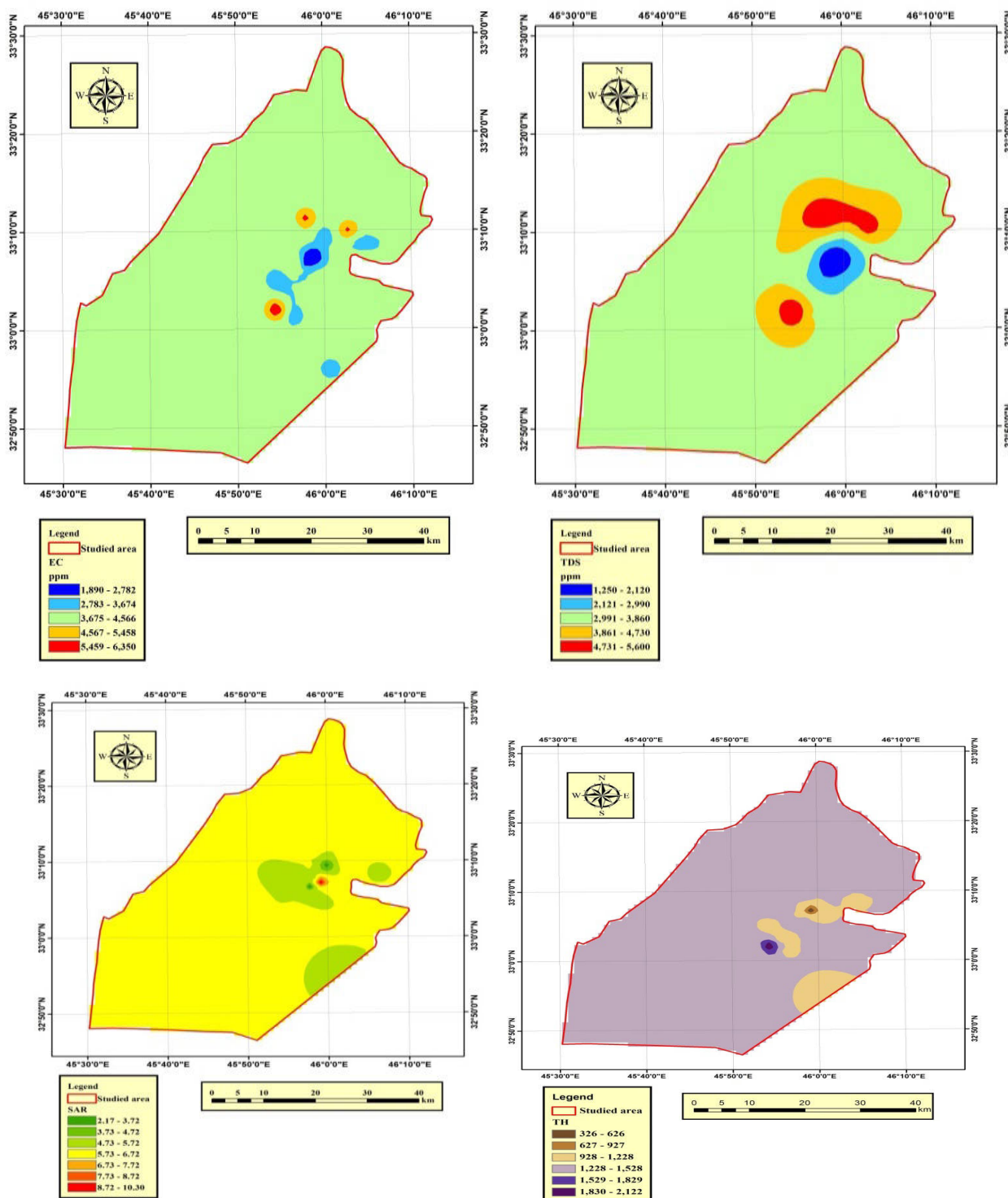| EC μc/cm	Na%	Classes of water	Total well	SAR	Water classes	Total well
<250	< 20	Excellent		<10	Excellent	37
250-750	20-40	Good	5	10-18	Good	1
750-2000	40-60	Permissible	31	18-26	Fair	
2000-3000	60-80	Doubtful	2	>26	Poor	
>3000	>80	Unsuitable				

Figure 8. Spatial distribution of TDS, ES, TH and SAR, values of the study area.
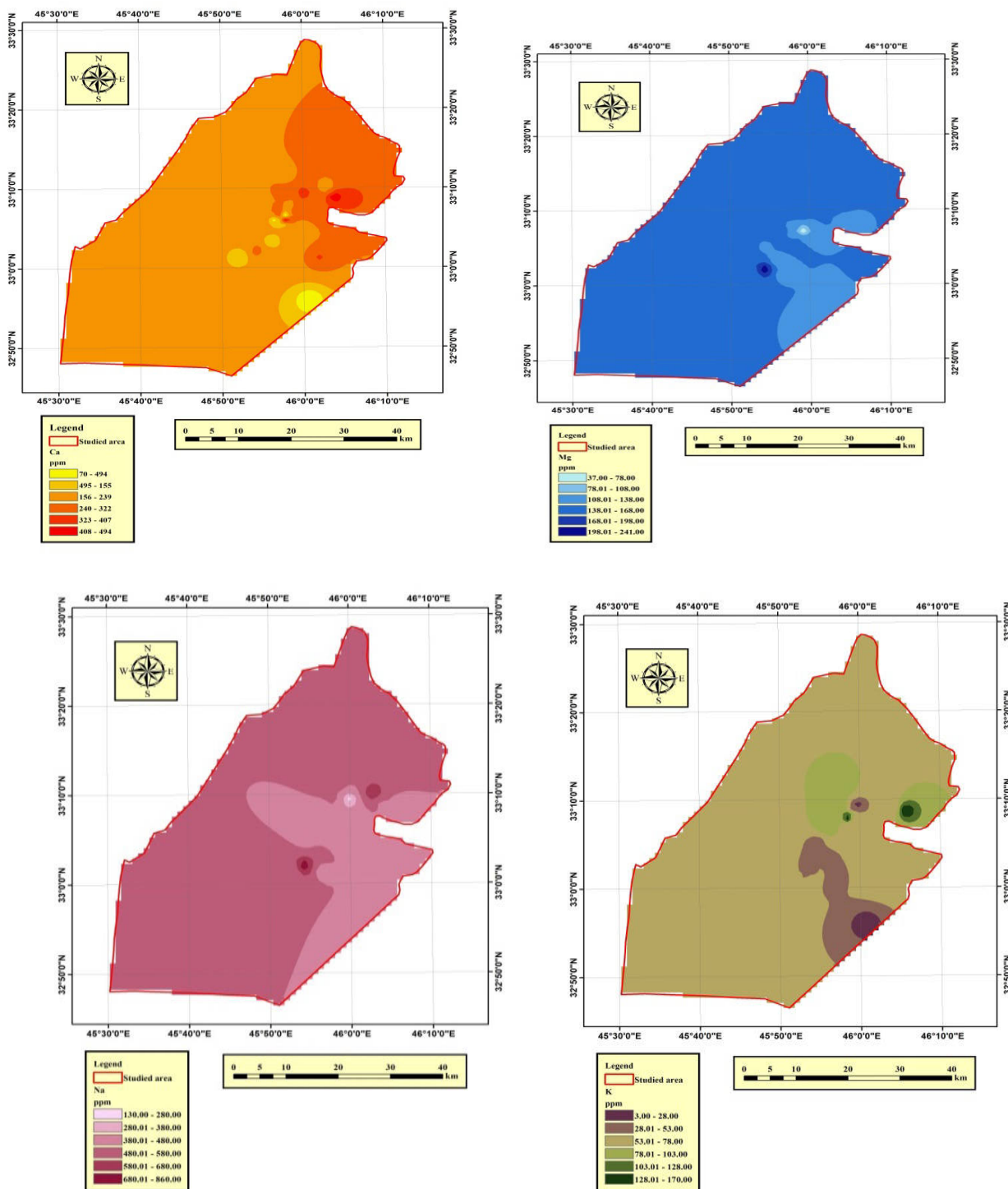
Figure 9. Spatial distribution of Ca, Mg, Na, and K values in the study area.
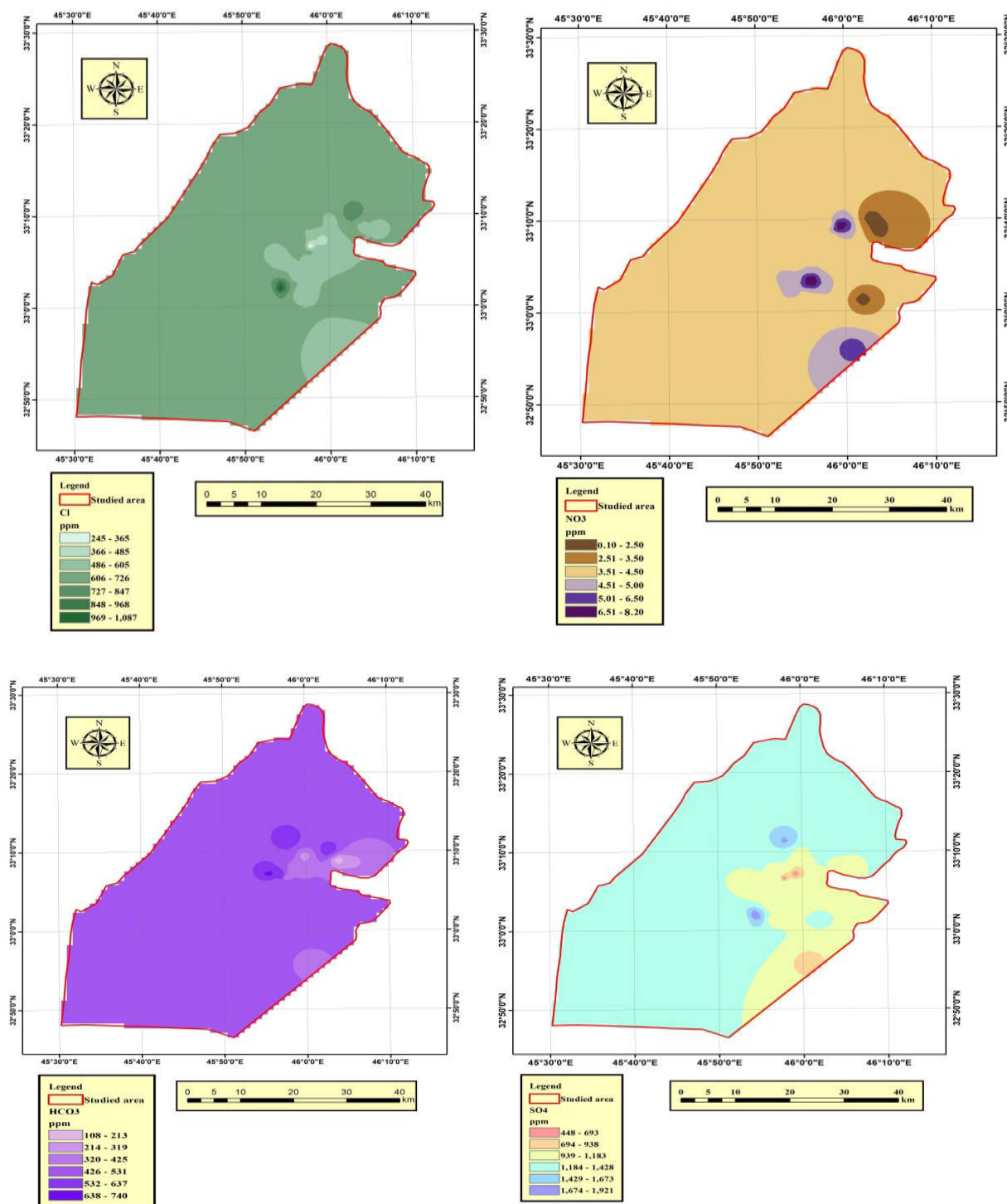
Figure 10. Spatial distribution of Cl, HCO_3, SO_4 and NO_3 values in the study area.
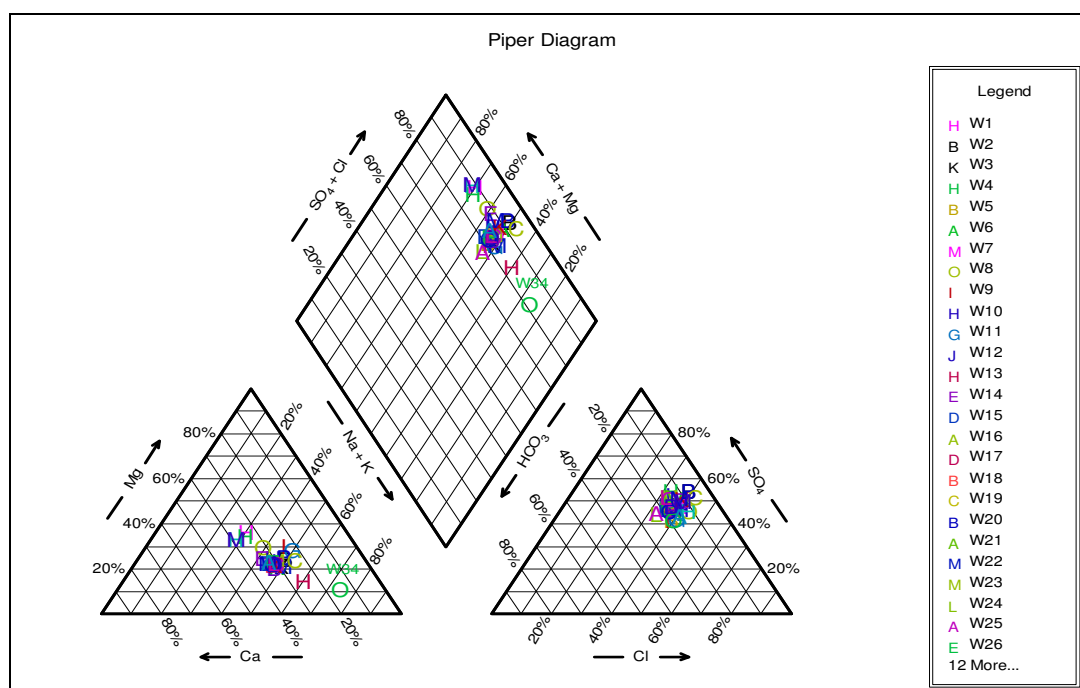
Figure11. Piper diagram of groundwater of the present study samples.

4.4 INVERSE MODELLING

Invers modeling technique is based on the mass balance concept in which several constraints should be impose on the system to obtain the best model describing the chemical reactions controlling the geochemical processes in it. For the purpose of the present study NETPATH code developed by Plummer, et al. (1994) was used to investigate the best model expressing the overall process in the aquifer under consideration. The best or "unique" model should be selected by comparing the results of the inverse modeling obtained from NETPATH with the results of saturation indices calculated byWATAQ4F in which only the compatible results can be adopted. Mineralogical, lithological, major ions concentrations and the other parameters were used as constraints (inputs) into the geochemical inverse model. For the present study, three flow paths were selected to detect the main chemical reactions along them (Figure 7). Mass transfer of the selected mineral phases (in mmole/kg H_2O) along these flow paths were presented in (Table 8).

 For these flow paths, calculations show that the precipitation of calcite and dissolution of dolomite, gypsum and anhydrite is the main reaction in the aquifer as explained in Table 8.

   No other processes were detected and hence it could be say that the present aquifer is characterized by a simple process represented by the above reaction but with variable degree along the selected different flow paths.

5.Conclusions

Several conclusions can be drawn from the present study as follows:

1- The hydrochemical analysis demonstrates that the groundwater under consideration is slightly-brackish and of $CaSO_4$ type. Spatial distribution of TDS ,EC and the cations and anions values through the studied area revealed that the groundwater properties is considerably differs from site to another mainly due to the lithological variations of the area.

2- Groundwater of the study area shown to be unsuitable for drinking purpose according to IQS,2009 and WHO,2008 whereas it is suitable, in general, for irrigation. However, it is unsuitable for irrigation at a few places.

 3- Geochemical modeling results show that groundwater samples are under-saturated with respect to the evaporate minerals and saturated to oversaturated with respect to carbonate minerals, the relationships between the SI' s of these minerals and SO_4 suggest that the precipitation of carbonate minerals are highly related to the dissolution of evaporate minerals.

4- The main reaction controlling the chemical composition changes throughout the study area is the calcite precipitation associated with dissolution of dolomite and gypsum.

Table7: Statistical characteristics values of the SI of the
selected minerals and log P_{CO_2} in the study area

	Saturation index					
	Calcite	Dolomite	Gypsum	Aragonite	Anhydrit	$LogP_{CO_2}$
mean	0.47	0.96	-0.52	0.32	-0.75	-1.92
median	0.48	0.98	-0.49	0.33	-0.72	-1.95
Minimum	-0.40	-0.65	-1.18	-0.54	-1.42	-2.50
Maximum	1.21	2.35	-0.20	1.06	-0.43	-1.41
Std. deviation	0.35	0.66	0.21	0.35	0.22	0.24

Table 8. Mass transfer (mmol/kg H_2O) result for flow Paths
in the study area.

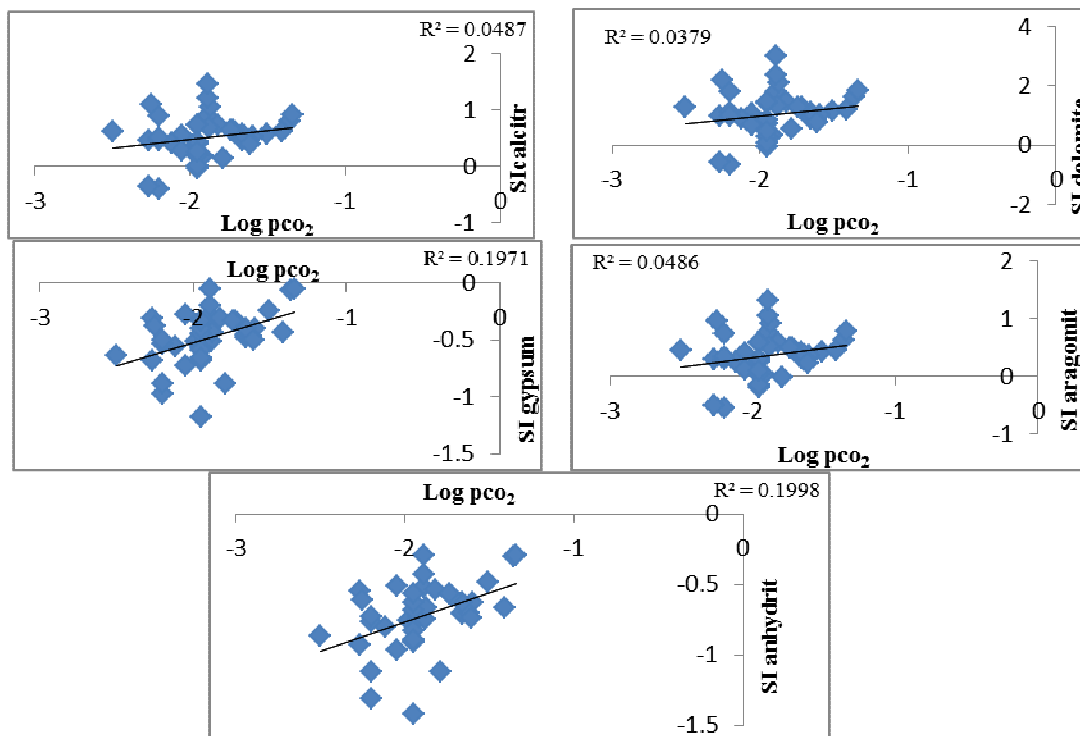| Flow path			Mass transfer mineral phases (mmol/kg H_2O)		
Flow path no.	Initial well no.	Final well no.	Calcite	Dolomite	Gypsum
1	W19	W41	-153.8	100.6	182.6
2	W8	W35	-1.06	0.40	1.79
3	W22	W12	-261.3	151.67	215.8
Negative values indicate precipitation and positive ones indicate dissolution					

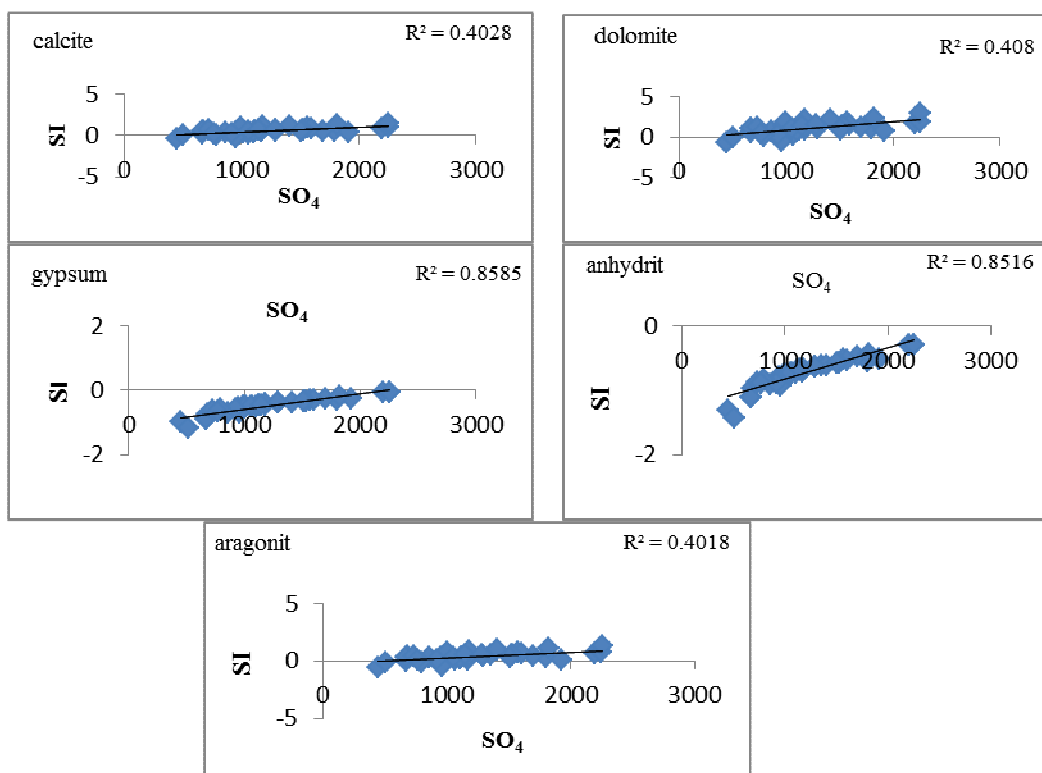Figure 12.Relationships between Log Pco₂and the SI of the selected minerals in the study area.

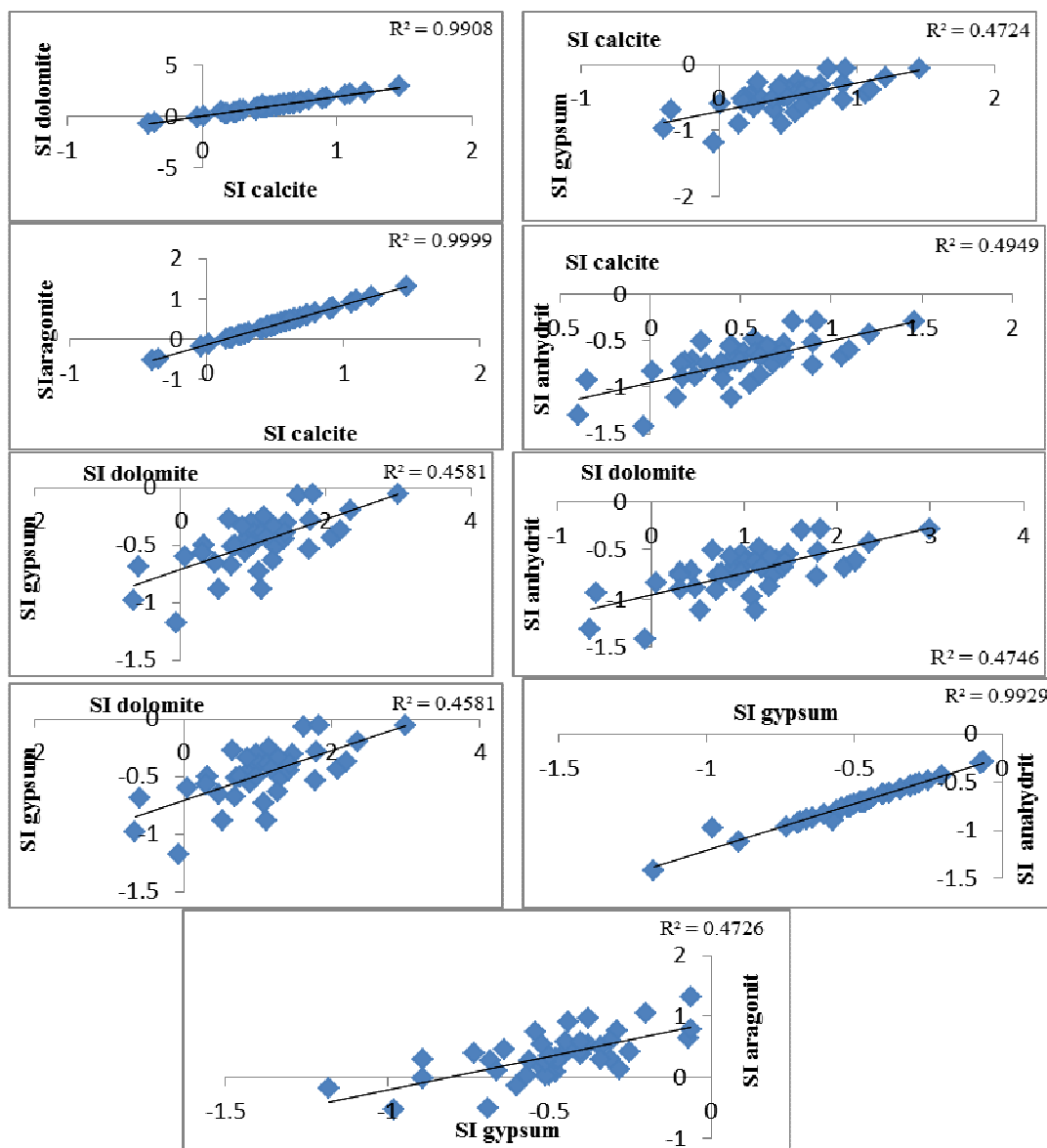Figure 13. Relationships between the concentration of SO₄ and the SI of the selected minerals in the study area.

Figure 14. Relationships between the SI of the selected minerals of the study area.

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