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Geochemical Evolution of Groundwater in Ravar-Naybandanarea, Central Iran

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Abstract

Hydrochemical investigations were carried out in Ravar-Naybandan area, central Iran, to assess chemical composition of groundwater. Identification of hydrogeochemical processes has been performed by studying a series of ionic ratios on eighteen samples including were collected from pimped well. Groundwater of the study area is characterized by the dominance of Na-Cl water type. The Na^+,Ca^{2+},Mg^{2+},SO_4^{2-} and HCO_3^- were mainly derived from the dissolution of evaporates and carbonates.

Keywords: Hydrogeochemical, Groundwater, Dissolution, Ravar- Naybandan

Introduction

Throughout the world, sustainable socioeconomic development of every community depends on the sustainability of available water resources. Groundwater has become the major source of water supply for domestic, industrial and agricultural sectors of many countries. Water shortages have become an increasingly serious problem in Iran, especially in the arid and semi-arid regions of Iran [1]. Iran is located in a semi-arid area with an average annual precipitation less than one-third of that of the world [2]. The quality of groundwater at any point below the surface reflects the combined effects of many processes along the groundwater flow path. Chemical reactions such as weathering, dissolution, precipitation, ion exchange and various biological processes commonly take place below the surface. Hydrogeochemical study is a useful tool to identify these processes that are responsible for groundwater chemistry [3]. Groundwater occurs almost everywhere beneath the earth surface not in a single widespread aquifer but in thousands of local aquifer systems and compartments that have similar characters. Knowledge of the occurrence, replenishment and recovery of groundwater has special significance in arid and semi-arid regions due to discrepancy in monsoonal rainfall, insufficient surface waters and over drafting of groundwater resources [4]. Increased knowledge of geochemical evolution of groundwater in these arid regions could lead to improved understanding of hydrochemical systems in such areas, leading to sustainable development of water resources and effective management of groundwater resource [5]. The main objectives of this paper were to presents a comprehensive regional hydrogeochemical study, allowing the origin of groundwater to be determined, and give a qualitative and quantitative understanding of the main geochemical processes controlling the geochemistry and spatial evolution of groundwater of the Ravar-Naybandan region as an arid area in Iran.

Study Area

The study areas are located in the Central Iran (Figure 1). The climate of the study area is considered semi-arid to arid; the annual average precipitation being approximately 250 mm. Rainfall occurs from November to April, with maximum during January and February, each year. The mean monthly temperatures are high, varying between -2°C in December-January, 50°C in July. The Central Iran is a segment of the Iran Plate, Which, in turn, is part of the Cimmerian Continent collage [6]. This micro-continent, which is a part of a magmatic island arc complex, separated from Gondwana at the beginning of the Triassic period to collide with Eurasia, more specifically with the Turan plate, in the Late Triassic. Sedimentation on the blocks during the Mesozoic was partly shallow marine, partly terrestrial in nature [6]. The study area consists of different lithology with of Triassic and Quaternary age. The surface geology map shows that 50% of the land is covered by Quaternary deposits (Figure 1) and basement rocks in the study area mainly consist of sandstone, conglomerate, evaporite and carbonate rocks [7-9]. The western part of the study area is represented from other by evaporate and coal seam layers, and eastern part with volcanic rock outcrops.

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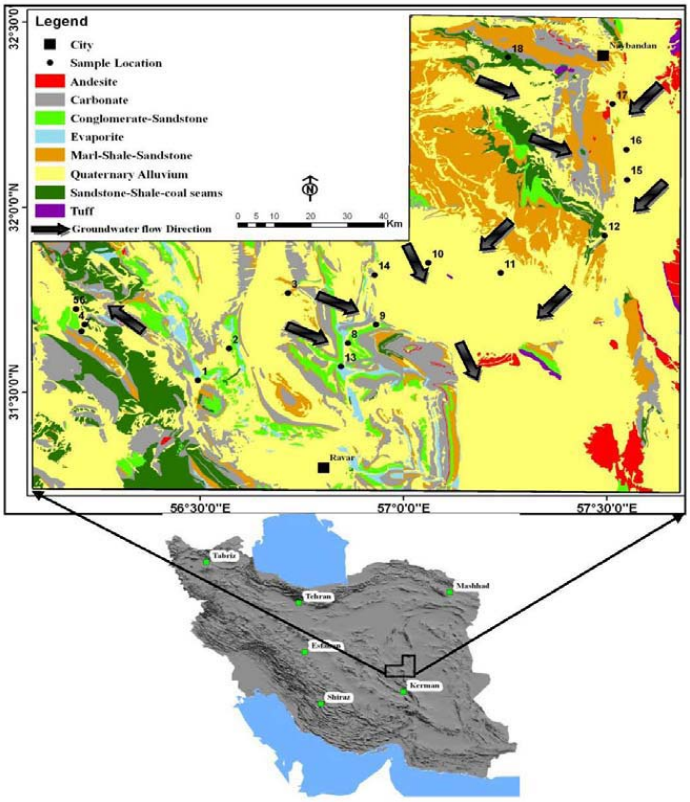

Figure 1: Geology map and sample location of the study area (Simplified after [7-9]).

Material and Methods

Eighteen samples including were collected from pimped well in January 2009. Water samples were filtered through 0.45 μm millipore filter paper (Except for analysis of alkalinity) [5]. The samples were collected in three new 250 ml polyethylene bottles. Conductivity, pH, Eh and temperature were determined in the field using portable pH meter. The cations were measured with Inductively Coupled Plasma and Mass Spectrometry (ICP–MS). The anions (Cl, F, Br, SO_4 and NO_3) were analyzed using ion chromatography. Total Dissolved Solids (TDS) were measured by sample evaporation techniques and HCO_3 was analyzed by potentiometric determination.

Results and Discussion

Physicochemical data and major ionic concentrations of 18 analyzed groundwater samples are summarized in Table 1. The total dissolved solids as a function of mineralization characteristics of the groundwater range from 719.49 to 27546.30 mg/l. It indicate that except sample 18 (with TDS<1000 mg/l as Fresh) and samples 3 and 14 (with TDS >10000 mg/l as Saline) other groundwater are brackish.

The pH of the s water ranged from 5 to 8.25 (Table 1), and these waters were, therefore, acidic to alkaline. Sample contains widely variable Eh and seems mostly oxidizing in western part and reducing in east and northern-east part of area. Under arid/semi-arid conditions, strong evaporation would have dramatically affected the groundwater chemistry; therefore, the groundwater from the discharge area contained more Na^+ and Cl^- [10]. The results of the chemical analyses shown in the Piper diagrams (Figure 2) show that Na-Cl water type is dominated in the most part of the studied area except for five samples (number 4,5, 6,7 and 8)that placed in Ca–Mg–SO_4–Cl type and one sample (number 17) that placed in Ca–SO_4 type.

The relative major ion compositions are remarkably similar to each other (Figure 3). All of the groundwater types are dominated by Na^+ and Cl^-, with lesser amounts of K^+, Mg^{2+}, NO_3^- and HCO_3^- , reflecting the meteoric and ultimately oceanic origins of their dissolved solutes.

Chloride and bromide ions move conservatively in water and (Cl/Br) have been used by several studies to distinguish pristine groundwater from waste water sources and other anthropogenic and natural salinity sources such as road salt, seawater, and deep basin brines [11-13]. The Cl/Br ratio in study are arranged from 14.39 to 1172290. Variations in Cl/Br ratios in rainfall and recharge waters have been extensively studied and are close to or below the Cl/Br ratio in seawater (290±4) [14,15]. This water types in study area are seen in west, central and northern part of area and closed to alluvium and sandstone-shale-coal seamlithology (Figure 1 and 4). The high Cl/Br ratio in the wells number 3,9,13 and 14, can be seen and are associated with evaporate in study area. The high Cl/Br ratio may be due to results from the depletion of bromide inhalite [16] and dissolution and subsequent saturation with respect to halite in groundwater.

If halite dissolution is responsible for sodium, the Na/Cl ratio should be approximately equal to 1, whereas a ratio greater than 1 is typically interpreted as Na released from silicate weathering reactions [3]. In the present study, the Na/Cl ratio of groundwater samples generally varies from 0.13 to 1.17 (Figure 4). Samples having Na/Cl ratio approximately equal and less than 1 in the study area and hence sodium might have come from irrigation return flow, anthropogenic activity and halite dissolution, but not from silicate weathering. The

Table 1: Physicochemical parameters of groundwater samples.

Sample	EC	pH	Eh	T	F	Cl	Br	NO_3	SO_4	HCO_3	Ca	K	Mg	Na	TDS
	mS/cm		mV	^{0}C	Mg/l										
1	5.14	6.54	312.10	21.20	0.05	1183.71	3.34	13.80	646.19	222.58	134.80	6.90	62.67	887.25	3904.47
2	7.14	7.03	330.70	17.00	0.06	1761.62	3.41	12.91	1034.96	223.49	179.89	11.64	94.07	1357.70	8607.97
3	20.19	7.06	158.50	22.00	0.06	5861.45	0.01	88.62	2458.34	124.56	605.00	14.30	211.70	3777.06	14005.63
4	2.58	8.29	205.20	19.00	2.35	279.53	13.44	20.76	1039.02	260.95	231.33	4.95	50.37	285.01	2301.31
5	2.71	8.15	137.20	21.50	2.65	308.72	18.62	6.57	1155.18	187.84	226.11	2.69	49.78	336.41	2425.35
6	2.71	8.15	136.30	21.50	2.82	307.55	17.58	7.97	1147.15	191.83	230.51	2.74	49.61	334.44	2405.63
7	1.34	7.99	217.30	23.00	1.70	105.10	6.46	6.17	456.63	208.31	131.80	2.85	24.63	122.60	1099.72
8	1.51	6.18	20.70	19.00	0.85	174.84	12.15	4.05	449.10	149.42	97.00	4.90	29.90	163.00	1103.96
9	9.59	5.35	39.50	25.50	0.05	2254.68	0.01	41.19	2343.18	40.46	600.80	8.90	105.94	1707.50	7402.64
10	6.54	5.00	63.00	20.00	0.79	196.25	13.55	4.24	475.12	145.47	101.00	5.80	31.25	177.00	1162.86
11	1.51	5.77	140.00	20.00	0.81	181.28	12.58	4.01	456.76	135.56	97.60	4.86	30.32	167.40	1104.77
12	4.68	6.08	-21.00	21.10	0.05	1210.34	3.90	14.20	619.87	111.75	162.60	43.87	37.84	849.24	3146.98
13	6.19	5.33	33.40	20.30	0.07	1098.00	0.01	36.42	2060.62	49.40	590.88	12.19	74.25	922.21	5050.03
14	36.32	7.10	25.60	16.00	0.08	13336.00	6.64	29.89	370364.00	95.12	923.90	29.33	369.20	12006.57	27546.30
15	4.58	6.07	-3.40	21.70	2.11	1075.30	2.08	7.13	576.76	121.22	158.25	43.79	34.99	1028.45	2913.69
16	0.03	5.08	-36.00	21.00	0.06	3617.21	5.97	15.11	1289.28	202.98	252.40	103.16	145.04	3099.20	8157.37
17	7.50	6.11	8.20	20.40	0.06	1973.44	3.28	23.60	1234.81	203.18	247.75	24.37	129.17	247.75	5329.27
18	0.97	6.01	1.70	26.70	0.56	124.32	7.63	6.29	190.74	185.07	56.36	3.32	17.25	124.40	719.49

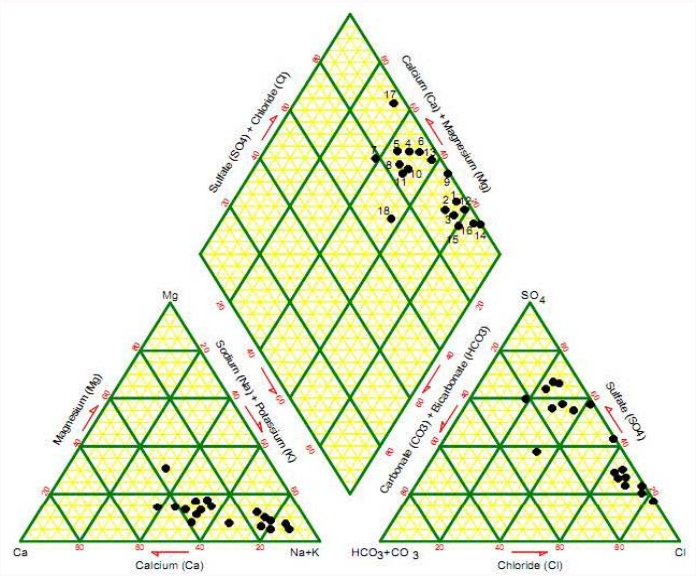

Figure 2: Piper trilinear plots for the chemical compositions of groundwater samples in the study area.

two chloro-alkaline indexes, is suggested by Schoeller (1977) [17], which indicate the ion exchange between the groundwater and its host environment:

$$CAI\ 1 = Cl^- - [(Na^+ + K^+) / Cl^-] \quad \text{……..(1)}$$

$$CAI\ 2 = Cl^- - [(Na^+ + K^+) / SO_4^{2-}] + HCO_3^- + CO_3^{2-} + NO_3^- \quad \text{……..(2)}$$

If ion exchange between Na^+ in the groundwater and Ca^{2+} or Mg^{2+} occurs in the alluvium or in weathered materials, both indices are positive. CAI 1 and CAI 2 were positive in all the groundwater samples (Figure 4) indicating that cation exchange mainly took place in the study area.

To understand the spatial control of major ions concentration, the relationships between TDS (as a useful indicator of anthropogenic contamination) and major ions are illustrated in Figure 5. The Cl^- and Na^+ concentrations increased with increasing TDS represent the intensity of evaporation [5]. This suggests that the dissolution of halite is a considerable control on the Na^+ and Cl^- concentrations. The TDS and SO_4^{2-} concentrations were strongly and significantly correlated, suggesting that weathering of gypsum ($CaSO_4.2H_2O$) occurred in area (Figure 5). Potassium shows somewhat weak correlation with TDS indicating that weathering possible sources of K^+ in groundwater

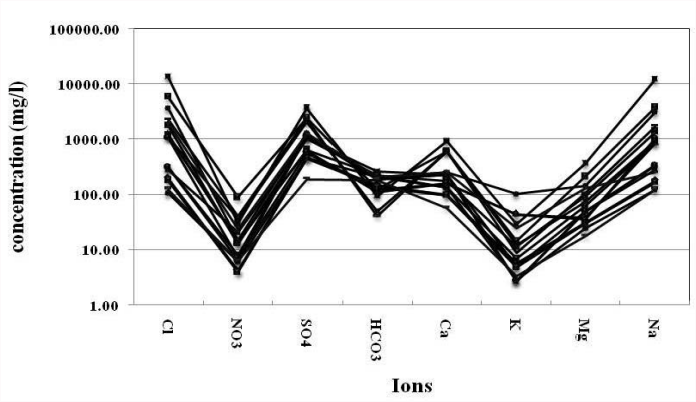

Figure 3: Anion and cation concentrations in groundwater samples.

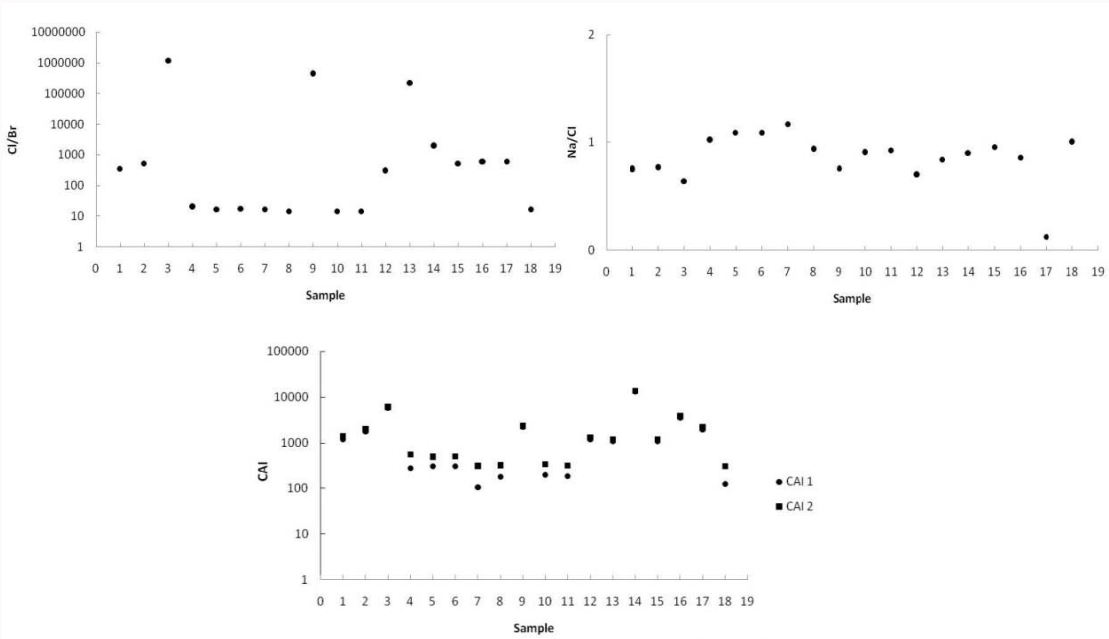

Figure 4: Na/Cl, Cl-Br ratios and CAI index of well samples in the study area.

such as K-feldspars and K-bearing minerals are rare in the studied area [5].

Following rainwater recharge, the infiltrating water reacts with the major mineral phases in the aquifer, namely calcite, dolomite and gypsum. Dissolved Ca^{2+} concentrations may increase through the dissolution of carbonate minerals and/or gypsum [18]. Study of the bedrock geology of the basin (Figure 1) suggested that carbonate and gypsum dissolution was happening mainly in the study area. The dissolution reaction of gypsum is:

$$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-} \quad \text{.....(3)}$$

By assuming that all the SO_4^{2-} in the groundwater of the study area is derived from gypsum dissolution the non-gypsum Ca^{2+} source can be determined by subtracting the amount of Ca^{2+} equivalent to the amount ofSO_4^{2-} from the total Ca^{2+} concentration and expressed as $\{Ca^{2+}\}-\{SO_4^{2-}\}$(in mmol/L) [19]. The non-gypsum source Ca^{2+} is mainly from carbonate mineral dissolution as:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad \text{.....(4)}$$

The plot of HCO_3^- and SO_4^{2-} versus Ca^{2+} shows a strong relationship between Ca^{2+} and HCO_3^- in group 1 samples (samples 12,15,16,17 and 18) that placed in northern east part of study area and between Ca^{2+} and SO_4^{2-} (Group 2: 1,2,3,4,5,6,7,8,9,10,11,13 and 14) in other parts of area (Figure 6). It suggested that carbonate dissolution was happening mainly in northern-east and gypsum dissolution in other parts is dominant.

Dedolomitization driven by gypsum dissolution is a well recognized process, especially in carbonate systems containing evaporate sulphates (gypsum, anhydrite) [4]. The systematic increase between the recharge zone towards the discharge zone in both Ca^{2+} and Mg^{2+} in conjunction with a SO_4^{2-} and decrease in HCO_3^- is also a result stemming from the evolutionary paths following the dedolomitization reaction [18]. This process occurs in Ravar-Naybandan area (Figure 7). The dissolution of both gypsum and dolomite will promote calcite supersaturation:

$$CaMg(CO_3)_2 + CaSO_4.2H_2O + CO_2 \leftrightarrow CaCO_3 + (Ca^{2+}+Mg^{2+}) + 2HCO_3^- + SO_4^{2-} + H_2O \quad \text{.....(5)}$$

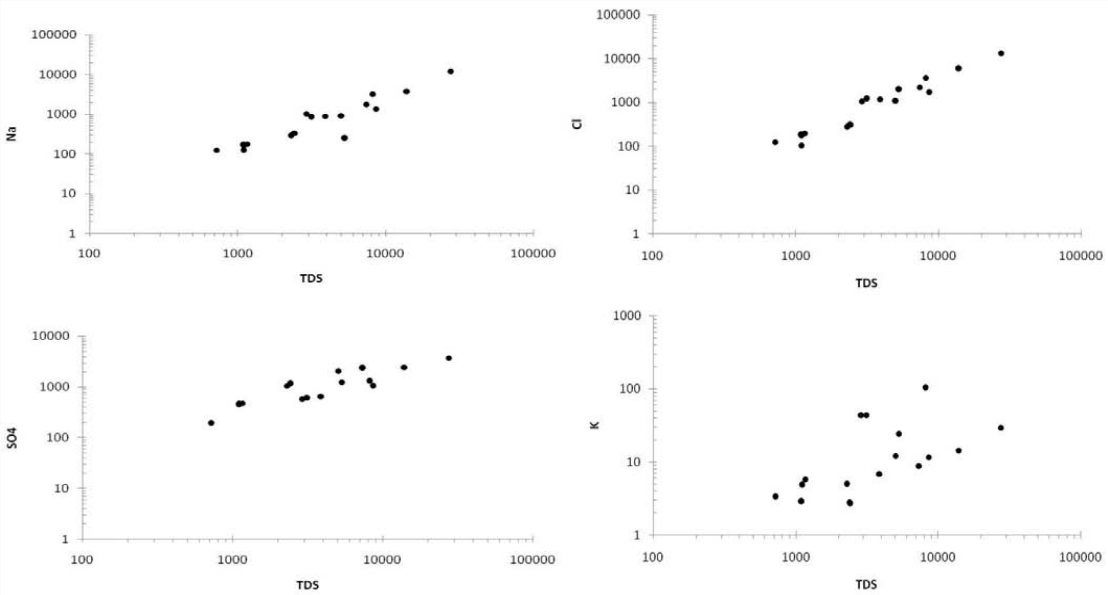

Figure 5: Relationships between ion concentrations for Na^+,K^+,Cl^- and SO_4^{2-} with TDS.

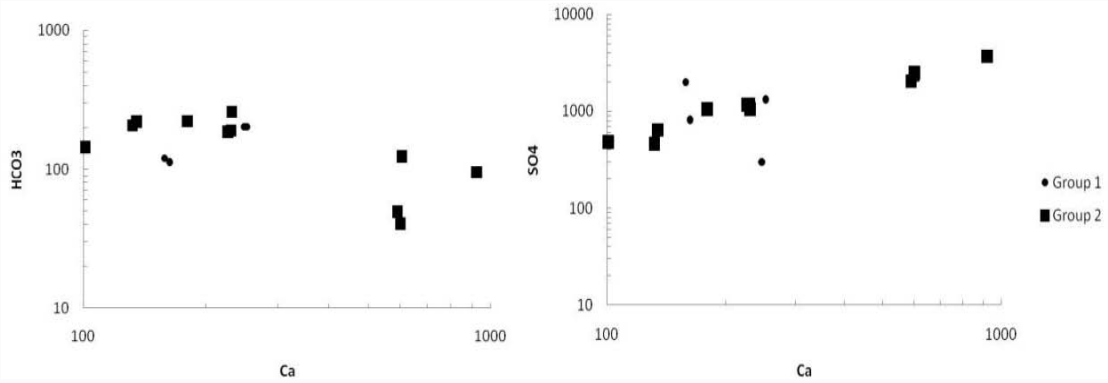

Figure 6: Relationships between HCO_3^- and SO_4^{2-} with Ca^{2+}.

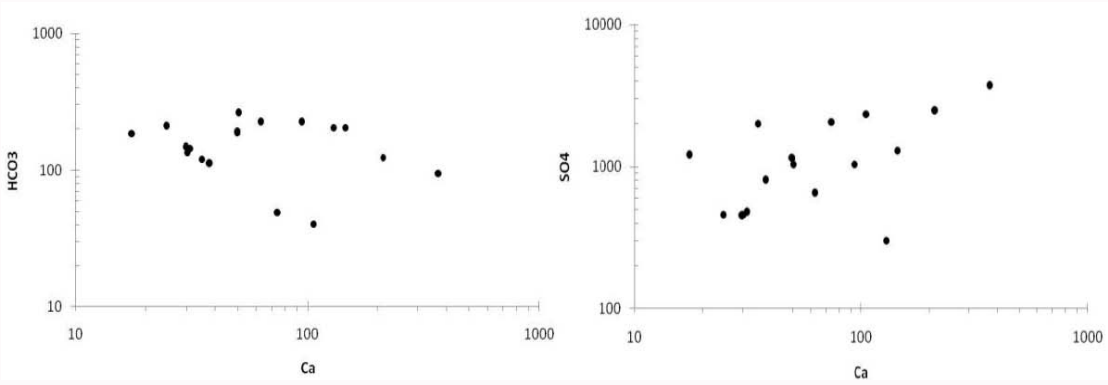

Figure 7: Relationships between HCO_3^- and SO_4^{2-} with Mg^{2+}.

Conclusions

The weathering of minerals is of prime importance in controlling the groundwater chemistry. In study area most water samples were brackish and classified according to major ion contents that indicate Na-Cl water type is dominated. The ion exchange between Na^+ in the groundwater and Ca^{2+} or Mg^{2+} occurs in the alluvium and in weathered materials but weathering possible sources of K^+ in groundwater are rare in the studied area. Evaporates have a great effect on the geochemistry of the water in study area. The evolution of the groundwater hydrogeochemistry is affected by both carbonate dissolution/precipitation and gypsum dissolution.

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