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Isotopic and Hydrochemical Study of Groundwater in an Area Between the Lesser Zab and Tigris River, Northern Iraq

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Abstract

Stable isotopes (^2H , ^{18}O) in the water cycle can carry all the information about the movement of water molecules, their ratio different from one place to another in rainfall. Stable isotopes are the function of evaporation, relative humidity, temperature and different longitude, latitude and altitude. On this base. A total of 28 water sample (20 samples were analyzed for major ions and 8 samples for stable isotopes) were collected for two periods to study the origin and the type of groundwater in the area between Lesser Zab and the Tigris river. The Results indicated that groundwater samples in the study area are brackish saline water and excessively mineralized water. The average groundwater was classified as Mg-Na-Calcium: Cl-Sulfate for two periods. The groundwater samples represent earth alkali with privilege sulfate and chloride according to the piper diagram. The mean values of ^{18}H and ^{20}O in the groundwater sample are -27.7 and -4.9, respectively for the dry period, and -29.8 and -5.2, respectively, for the wet period. The d-excess varies significantly depending on the humidity and temperature at the vapor source. Isotopic analysis of ^2H - ^{18}O for groundwater in the study area shows that the origin of groundwater in the study area is of meteoric origin from global source and rain from a local source. The downward shifting of the regression line on the ^2H - ^{18}O diagram indicates that the samples have undergone evaporation events.

Keywords: Groundwater, Lesser Zab, Hydrochemistry, Stable isotopes

1. Introduction

In the last decades, groundwater starts to play a vital role in arid and semi-arid regions to sustain economic development and to ensure water security for rural communities (Liu et al., 2015). The main reason for the large water demand is human growth population, increasing land used for agriculture and industrial projects as well as the decreased amount of rainfall and water supply in the last years (Awadh and Al-kilabi, 2014). Groundwater is affected by many ecological processes that might cause groundwater disruption. Thus, a sustainable groundwater strategy plan and deep understanding of the geochemical evolution of groundwater is needed in order to guarantee the sustainability of groundwater (Fu et al., 2018). Groundwater characteristics can be utilized in addressing different geochemical problems, where the groundwater contains many soluble minerals derived from several factors such as the interaction between rocks and water (Awadh et al., 2016) and soluble product of rock weathering

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(Chenini et al., 2010). Hydrochemistry plays a key role to understand groundwater management (Ali et al., 2021). Globally, physio-chemical parameter is of great important to assess the groundwater quality. The physical parameter is represented by total dissolved solids (TDS), hydrogen ions concentration (pH) and electrical conductivity (Ec), whereas the chemical parameters are defined by the major cations (Na^+ , Mg^{2+} , Ca^{2+} , K^+) and the major anions (Cl^- , SO_4^{2-} , HCO_3^-) (Fetter, 2001). However, it is never enough to determine the origin of water (Tweed et al., 2019). Therefore, isotopes composition has been used commonly in hydrology as a tool to investigate and understand different hydrogeological process such as rainfall, groundwater recharge and surface water-groundwater interactions (Al-paruany et al., 2017). As well as, determine the origin and give answer about the change in the pathway, such as the interaction between the groundwater and surface water, determine groundwater velocity and to determine the residence time of groundwater (Ali et al., 2015). The use of stable isotopes (^{18}O and ^2H) has gained a wide acceptance between hydrological professionals, especially when it comes to water investigation (Mazor and Dekker, 1997). The ratio between $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ in stable isotopes is expressed by $\delta^2\text{H}$ and $\delta^{18}\text{O}$. where $\delta = (\text{R sample}/\text{R SMOW} - 1) \times 1000$, $\text{R} = ^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ the last is taken from SMOW or V-SMOW (Craig, 1961). In Iraq demand for water has increased dramatically due to human growth population and newly established land for agriculture, therefore, the main objective of This study aims to and investigate the groundwater source by using stable isotopes (^2H and ^{18}O), assess the hydrochemistry of groundwater by determining the dominant cations and anions groups, and its suitability for drinking water.

2. Location and Geological Setting

The study area located in the north east of Salah Al-Din and west of Kirkuk between Longitude ($35^\circ 27' 00'' - 35^\circ 15' 00''$ N) and latitude ($43^\circ 14' 40'' - 43^\circ 36' 00''$ E) (Fig. 1), it is bounded from the east by the Tigris River and from the west by Lesser Zab river covering an area of about 600 km^2 approximately. The climate in this area is arid-semi arid with an average annual temperature, relative humidity, wind speed, rainfall and evaporation of about 22.29°C , 48.1 %, 1.7 m/s, 15.9 mm and 213.8 mm, respectively. The study area is located in the Himreen-Makhul Subzone (Jassim and Goff, 2006). The outcropping geologic formations in the study area and surrounding from the oldest to the youngest are Azkand (upper Oligocene), Euphrates (lower Miocene), Fatha (middle Miocene), Injana (Upper Miocene), Mukdadyia (lower Pliocene), Bai Hassan (upper Pliocene), and Quaternary deposits (Pleistocene-Holocene). The latter is almost fully cover the study area (Fig.1). The groundwater flow direction trend in the study area runs from the north east part toward the south east part in the study area following the topography of the area. Therefore, the north east part is representing the recharge zone. while, south eastern part representing discharge zone (Jassim and Guff, 2006).

3. Materials and Methods

From different location a total of 28 groundwater samples (20 samples were analyzed for major ions and 8 samples for stable isotopes) were collected for two periods, the first was carried out during Oct, 2019 (dry season) and the second was carried out during Mar, 2020 (wet season). Some parameters were measured in site (TDS, pH and Ec). 50 ml volume glass bottles were used for major ions and 500 ml volume polyethylene bottles were used for stable isotopes sample collection. All the samples were sealed immediately, labeled and sent to analyzed at the laboratory of the ministry of science and technology. The major ion were measured according to APHA (2012), while stable isotopes (^{18}O and ^2H) were measured using liquid stable isotope analyzer (LWSIA) (Nada et al., 2020) Table 1.

Fig.1. Geological map shows the location of the study area and the location of studied wells

Table 1. Locations of groundwater sampling stations

Well	Easting	Northing	depth(m)	Elevation(m)	S.W.L(m)
W1	345140	3926653	9	163	----
W2	353446	3923085	60	193	11.5
W3	357427	3922121	14	190	10.5
W4	361158	3923851	40	201	15.5
W5	364795	3923452	37	193	----
W6	368200	3922077	40	187	9.2
W7	346071	3916966	35	156	2.6
W8	349344	3913784	10	151	3.1
W9	351275	3914017	----	165	12.46
W10	353067	3914983	90	175	----
W11	351678	3910375	14	152	----
W12	352103	3909964	9	149	----
W13	352195	3908553	13	151	----
W14	354644	3906649	24	142	6.2
W15	359548	3904128	41	165	6.43
W16	360409	3904355	36	168	12.95
W17	363782	3906197	50	158	12.83
W18	366850	3908476	40	165	8.7
W19	359904	3905880	30	170	6.81
W20	353236	3918336	----	180	8

4. Results and Discussion

4.1. Hydrochemistry

The results of the groundwater hydrochemistry are listed in Table 2. The TDS value can be used to reflect the water quality, the last represents a comprehensive hydrochemical parameter (Zhang et al., 2020). TDS values permissible limits in drinking water is 1000 mg/L (RS2, 2012). The TDS values in the study area range between 1200 and 4650 mg/L with an average of 2650 mg/L in the dry period, while it varies from 1132 to 4561 with an average of 2336 mg/L in the wet period according to (RS2, 2012) the TDS values are exceeding the permissible limits, while groundwater in the study area are classified as brackish-saline water (Altovisky, 1962). The Ec values ranges between 2055 and 8340 with an average of 4262 in the dry period while it ranges between 2030-8290 with an average of 4219 in the wet period, according to Detay (1997) the groundwater samples are excessively mineralized water for two periods. The dominant cations and anion concentration in the groundwater samples follow the order (Ca^{2+} , Na^+ , Mg^{2+} , K^+) cation (SO_4^{2-} , Cl^- , HCO_3^-) anion, the average groundwater type for two periods in the study area are Mg-Na-Calcium: Cl-Sulfate. Piper diagram shows that the groundwater samples in the study area evolved toward the SO_4 and Ca + Mg pole which represent earth alkali with privileged sulfate and chloride, as shown in Fig. 2.

Table 2. Results of groundwater hydrochemistry for the dry (Oct. 2019) and wet (Mar. 2020) periods

Variable	Dry period			Wet period		
	Minimum	Maximum	Average	Minimum	Maximum	Average
pH	6.9	7.9	7.67	6.8	7.8	7.56
TDS	1200	4650	2427	1132	4561	2336
EC	2055	8340	4262	2030	8290	4219
Ca	185	689	370	175	683	353
Mg	60	284	114	55	276	109
Na	123	511	281	112	499	269
K	6	10	7.7	5	9	6.9
HCO_3	92	464	219	63	425	193
Cl	230	1168	581	220	1170	568
SO_4	396	1670	896	381	1650	865

4.2. Isotope Composition of the Groundwater Samples

Stable isotopes composition of the groundwater samples are shows in Table 3. Isotopes and d-excess values of the groundwater samples at the dry and wet period,s the δ ranges between -42.2 to -20.14 with an average of -27.7, and it ranges between (-7.26 and -3.08) with an average of -4.9) for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively for the dry period. It ranges between 42.2 and -18.14) with an average of -29.8, and it ranges between -7.26 and -3.08) with an average of -5.2 for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively in comparison the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the groundwater for two periods, the isotopic composition of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ was more enriched in the dry period due to evaporation effect in arid regions (Boschetti et al., 2018) . It appears that there is a low variation between the studied periods due to difference in the groundwater conditions (water temperature, water level and climate effect).

Fig. 2. Piper classification of groundwater samples in the study area for two periods

Well No.	^2H (permil)	^{18}O (permil)	d-excess	^2H (permil)	^{18}O (permil)	d-excess
	dry period			wet period		
W2	-18	-4.34	16.72	-20.14	-4.79	18.18
W4	-16.2	-2.83	6.44	-18.14	-3.08	6.5
W6	-23	-4.32	11.56	-25.46	-4.59	11.26
W7	-39	-7	17	-42.2	-7.26	15.88
W10	-33.4	-5	6.6	-34.52	-5.23	7.32
W12	-39.4	-6.41	11.88	-41.5	-6.91	13.78
W15	-34.42	-6.31	16.28	-36.26	-6.38	14.78
W17	-18.4	-3.14	6.72	-20.48	-3.44	7.04

Fig. 3. Isotopes composition of the groundwater in the study area compared with GMWL and LMWL

Fig. 3 illustrates the relationship between $\delta^2\text{H}$ - $\delta^{18}\text{O}$. It shows that most of the isotopes values in the study area lie close to the global meteoric water line (GMWL) (Craig, 1961) and Local meteoric water line (LMWL) (Ali and Ajeena, 2016), this indicate that the groundwater source is of meteoric origin from global source and rain from local source. Moreover, the downward shifting of the regression line indicates evaporation event. That means groundwater effected by evaporation and/or the rain water that recharge the groundwater effected by secondary evaporation (evaporation during event). The deuterium excess is a typical character showing the origin of air. Dansgaard (1946) first proposed the use of the value ($d=2\text{H} - 818\text{O}$). to characterize deuterium excess in global precipitation. Deuterium excess was used frequently as a powerful tool to investigate the origin of water vapor, such as humidity and source of water vapor as well as secondary evaporation (evaporation during event) (Zhao et al., 2018). Values of excess ('d') below 10 indicate an evaporation process. Fig. 4 show that most of the d-excess value in the study area (w2, w6, w7, w12 and w15) are higher than the intercept of (GMWL) 10‰. this indicate that groundwater is affecting by moisture. Whereas, the rest of sample (w4, w10 and 17) seems to be fall below the intercept of (GMWL) 10‰, which indicate that low-humidity conditions controlling the evaporation at the vapor source region (Zhao et al., 2018).

Fig 4. The d-excess values in the groundwater samples in the study area during the dry (Oct. 2019) and wet (Mar. 2020) periods

5. Conclusions

The groundwater flow direction trend is from the north eastern part to the south west in the study area following the topography of the area. Concentrations of EC and TDS indicated that the groundwater samples for two periods are brackish saline water excessively mineralized water. The average groundwater type for two periods in the study area are (Mg-Na-Calcium: Cl-Sulfate). Piper diagram shows that the groundwater samples in the study area which represent earth alkali with privilege sulfate and chloride. Isotopic analysis of ^2H - ^{18}O for groundwater in the study area shows that the origin of groundwater in the study area is of meteoric origin from global source and rain from local source. groundwater effected by evaporation and/or the rain water that recharge the groundwater and affected by secondary evaporation (evaporation during event).

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