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Hydrochemical and Isotopic Study of Water Resources in Khan Al-Baghdadi Area, Al- Anbar Province / West of Iraq

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Abstract

This hydrochemical study of the surface and groundwater in Khan AL-Baghdadi area, western Iraq, included the interpretation of physical, chemical, and biological properties. Water samples were collected from wells (14 samples) and surface water of Euphrates River (6 samples) for the dry and wet periods of October 2018 and April 2019, respectively. The stable isotopes analysis was performed for the dry period only. The surface water samples were characterized by slightly alkaline, fresh, excessively mineralized, Ca-chloride type, and hard to very hard water class. While the groundwater samples were characterized by slightly alkaline, brackish, excessively mineralized, Ca-chloride and Na-Chloride type, and hard to very hard water class. The stable isotopic analysis was used in studying the interaction between water resources of Euphrates River and groundwater. Stable isotopes (δD and δ18O) were used to study the hydrological aspects of water resources in the study area. The results showed that surface and groundwater samples have similar source with a correlation relationship between them, in addition to the clear effect of river recharge on groundwater. The variation in δ2H and δ18O signature of groundwater in the study area is caused mainly by variation in isotopic composition of recharge water zone and mixing water. Using the δ 2H and δ 18O diagram, all surface and groundwater samples were plotted below the global meteoric water line (GMWL) and Local Meteoric Water line (LMWL), indicating the influences of the evaporation processes and seasonal variation.

Keywords: Hydrochemistry**,** Stable isotopes, Water Resources, Khan Al-Baghdadi.

دراسة هيدروكيميائية و نظائرية للمياه السطحية والجوفية في منطقة خان البغدادي ,محافظة الانبار/غرب العراق

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قسم علم الارض، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تتضمن الدراسة الهيدروكيميائية للمياه السطحية والجوفية في منطقة خان البغدادي تفسير الخصائص الفيزيائية والكيميائية والبيولوجية عن طريق 14 بئراً و6نماذج من المياه السطحية لنهر الفرات بمنطقة خان البغدادي ولفترتين ,الفترة جافة في أكتوبر 2018 والفترة الرطبة في أبريل 2019,بينما تحاليل النظائر المستقرة كان للفترة الجافة . تتميز عينات المياه السطحية بالقلوية الخفيفة ، مياه عذبة ، شديدة التمعدن ، ونوع كلوريد الكالسيوم وذات عسرة عالية جدا. في حين تتميز عينات المياه الجوفية بالقلوية الخفيفة ، والمياه المالحة

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،شديدة التمعدن ،ونوع كلوريد الكالسيوم و كلوريد الصوديوم وذات عسرة عالية جدا. تم استخدام تقنية النظائر المستقرة في دراسة تداخل الموارد المائية لنهر الفرات والمياه الجوفية في منطقة خان البغدادي, غرب العراق. النظائر المستقرة تستخدم لدراسة الجوانب الهيدرولوجية والمصادر المائية في منطقة الدراسة. اظهرت دراسة النظائر ان مياه نهر الفرات والمياه الجوفية لهما نفس المصدر وتوجد علاقة ترابط بينهما ,وان تأثير تغذية النهر واضح على المياه الجوفية . الاختلافات في علاقة δ2H مع δ18Oفي المياه الجوفية ناتجة اساسا من الاختلافات في تكوين النظائر والتغذية واختلاط المياه. في الشكل بين δ 2H مع δ 18O جميع المياه السطحية والجوفية تقع اسفل خط المياه العالمي(GMWL) وخط المياه المحلي (LMWL) وهذا يشير الى تأثير عمليات التبخر والتغيرات الموسمية .

Introduction

The quality of groundwater is important according to the purpose of use. The needs for drinking, industrial, and irrigation water vary widely [1]. The use of stable and radioactive natural isotopes has become a useful tool for hydrological research, particularly in the study of meteoric water, surface water and groundwater [2]. Values of δ2H and δ18O in water, especially combined with conservative solute concentrations, are the best geochemical indicators of the source, recharge locations, and flow paths. Precipitation and seawater were the main topics of studies on isotopes of water [3]. In this study, stable isotopic analysis (δ18O and δ2H) was used to observe the intermixing between the different water resources (wells and Euphrates River.) in western Iraq. LMWL was previously plotted from data obtained from isotopic analysis (2H and 18O) for rain water samples collected from five stations in Baghdad city in 2017 [4]and five stations in Baghdad city in 2012 [5]. In addition to data obtained from other previous studies [6, 7]. Moreover, this analysis was applied to test data from 3 stations in Baghdad and 2 stations in Samawa city, collected during 2014 [8]. The average d-excess of all these data showed a value of 14.3 ‰. The present study area is located in the northwestern part of Al-Anbar governorate, between the latitudes 33 º 47 ' - 34 º 0 ' N and longitudes 42º 28'- 42 º 45' E. Khan Al-Baghdadi represents the main area in the present research (Fig.1), located parallel to Euphrates River.

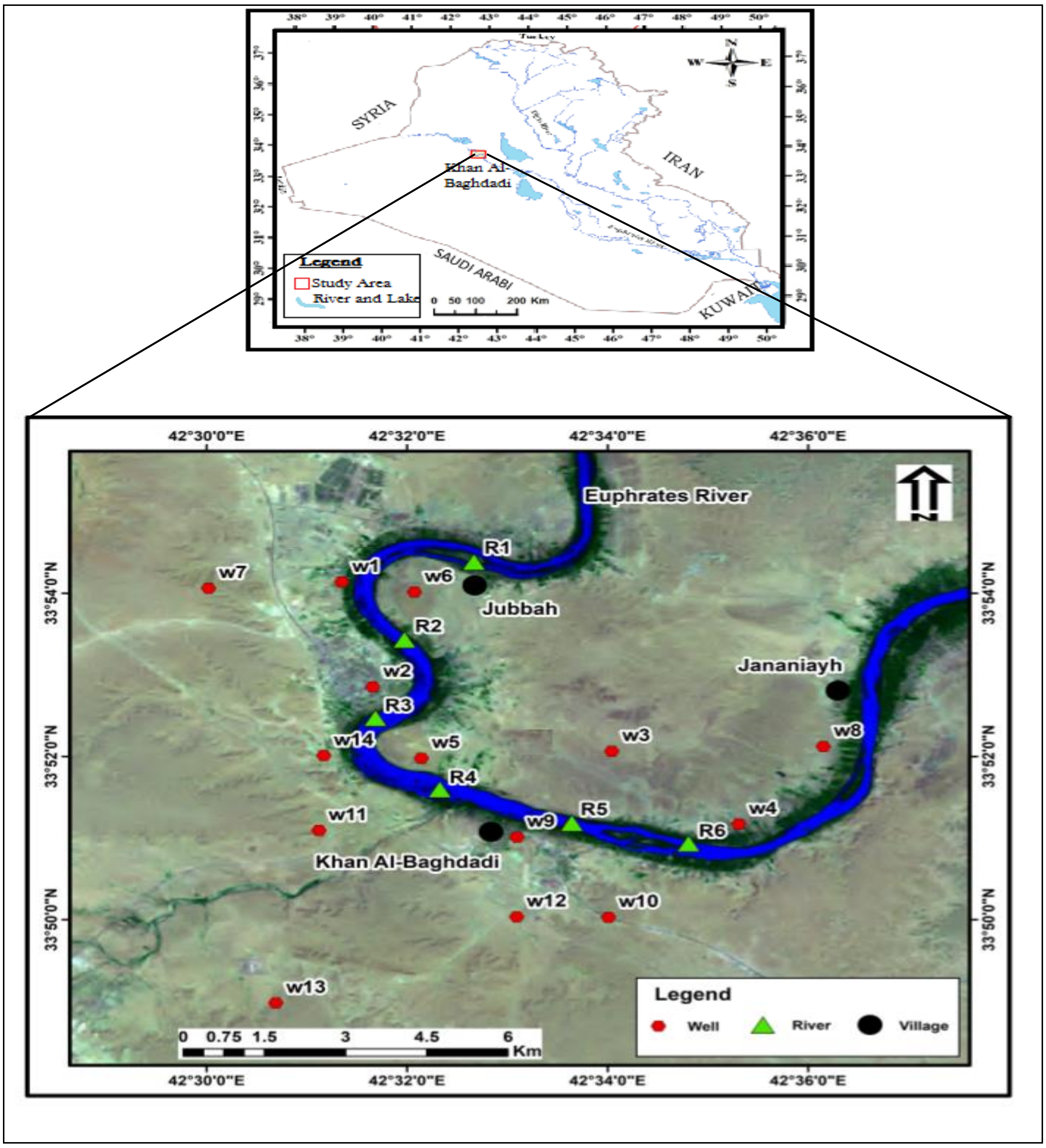


Figure 1-Location map showing the study area and water sampling locations.

Geological Setting

The exposed formations within the map area range in age from the Oligocene to Pliocene, with different types of Quaternary deposits. The western shoreline receded towards the area of the present day the Euphrates River. Euphrates River in Iraq crosses many geological formations within the stable shelf of the Nubian- Arabian carton. Oligocene sediments are absent over most of Rutba subzone, the Salman zone and on the Zubair and Euphrates subzones of the Mesopotamian [9]. The exposure formations of the study area can be described as follows.

Anah Formation (Lower Oligocene)

The formation consist of massive, coralline, creamy, and very hard limestone as well as dolomite limestone [10].

Euphrates Formation (Lower Miocene)

The Euphrates Formation is composed of two Members, as described below[11]:

- Lower Member: The pebbles are composed of limestone, dolomite, and fine crystalline, hard, and angular, subangular to rounded splintery grains.
- Upper Member: It consists of marl, brecciated limestone, dolostone, marly limestone, and dolomite limestone.

Fatha Formation (Lower Fars, Middle Miocene)

The formation to the east of Euphrates River is developed in its normal lithological constituents of cycle nature (marl, limestone, gypsum and claystone) [11].

Materials and Methods

The laboratory works include the physical and chemical analysis of water samples in the laboratory of the Ministry of Science and Technology . A total of 14 well and 6 surface samples were collected in October, 2018 and April, 2019. The measurements were conducted according to the published standard methods [12]. The measurements included hydrogen number (pH), electrical conductivity (EC), total dissolved solids (TDS), and temperature (T), which were analyzed using TDS-EC-pH and T meter. Calcium, magnesium, chloride and bicarbonate. Sodium and potassium were analyzed using flame photometer. Sulfate was determined by spectrophotometer. Trace elements were determined by atomic absorption spectrometer. Rock Ware AqQa version 1.1 software was used for water classification and determination of water type. The coordinates for each sample location, including longitude, latitude, and elevation, were measured using GPS. The isotopic analyses with the values of deuterium excess (d) concentration of water samples were achieved in the laboratory of the Ministry of Science and Technology. These analyses were conducted on all samples collected in October, 2018. Sampling procedure was carried out according to the instructions of the IAEA [13]. Fifteen ml of water was collected in glass bottles for each sample. All bottles were labeled with code number, identification name, sampling date, coordinates, and physical properties (EC, T, pH), which were measured on site. LWSIA was used to determine the stable isotopic composition of the water samples with an analytical precision of ±0.8 range. The results of the measurements of hydrogen and oxygen isotopes are expressed as delta notes (δ18O, δ2H) in relation to the Vienna Standard Mean of Ocean Water (VSMOW).

Table 1-Coordinates of the studied samples

Samples No.	Latitude	Longitude	Well depth(m)
W.1	33.9022	42.5225	58
W.2	33.8808	42.5275	80
W.3	33.8681	42.5675	42
W.4	33.8525	42.5850	32
W.5	33.8669	42.5356	31
W.6	33.9006	42.5342	40
W.7	33.9014	42.5000	70
W.8	33.8686	42.6022	50
W.9	33.8508	42.5517	35
W.10	33.8344	42.5667	30
W.11	33.8519	42.5186	50
W.12	33.8333	42.5519	70
W.13	33.8169	42.5114	50
W.14	33.8672	42.5189	55
R.1	33.9059	42.5446	_
R.2	33.8899	42.5326	_
R.3	33.8744	42.5272	_
R.4	33.8588	42.5388	_
R.5	33.8527	42.5604	_
R.6	33.8485	42.5798	_

W:groundwater, R:surface water

Results and discussion

Hydrochemistry

The results of water samples collected from the study area were plotted on Durov diagram. Plots of groundwater indicate that most samples have the (Na-Mg-Ca-Cl-SO4) water type, pH values less than 7.6, and TDS range of 1000-5000 mg/l, for both the dry and wet periods. Surface water plots indicate that most samples have the (Na-Ca-Cl-HCO3) and (Na-Ca-HCO3-Cl) types for the dry period and (Na-Ca-HCO3-Cl) type for the wet period, as shown in Figures- 2 and 3. Stiff diagrams for all samples in the study area during the two periods appear to be fit with the hydrochemical formula . Ca^{+2} and Na^{+} appeared to be prevailing as cations whereas Cl^{-} and SO_4^{-2} were the prevailing anions, as shown in Figures-(4, 5, and 6). The variability in the different types of water points was possibly due to the interaction of several factors, such as lithology, recharge, aquifer geochemistry, and well depth [14]. Through the comparison between the type of groundwater and surface water, we find that both types of water were similar in terms of the studied isotopes.

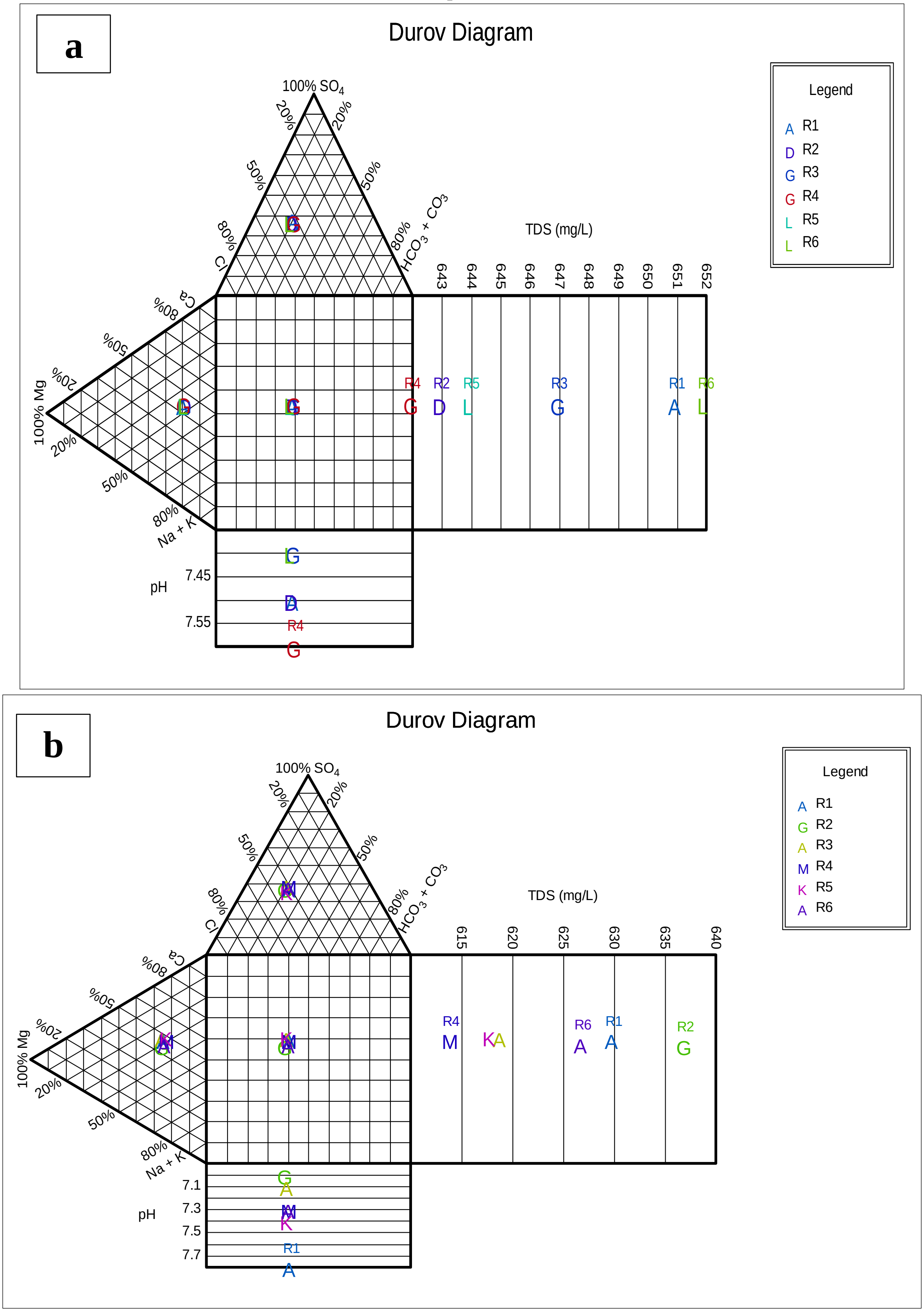


Figure 2-Durov diagram of surface water during a: dry period b: wet period.

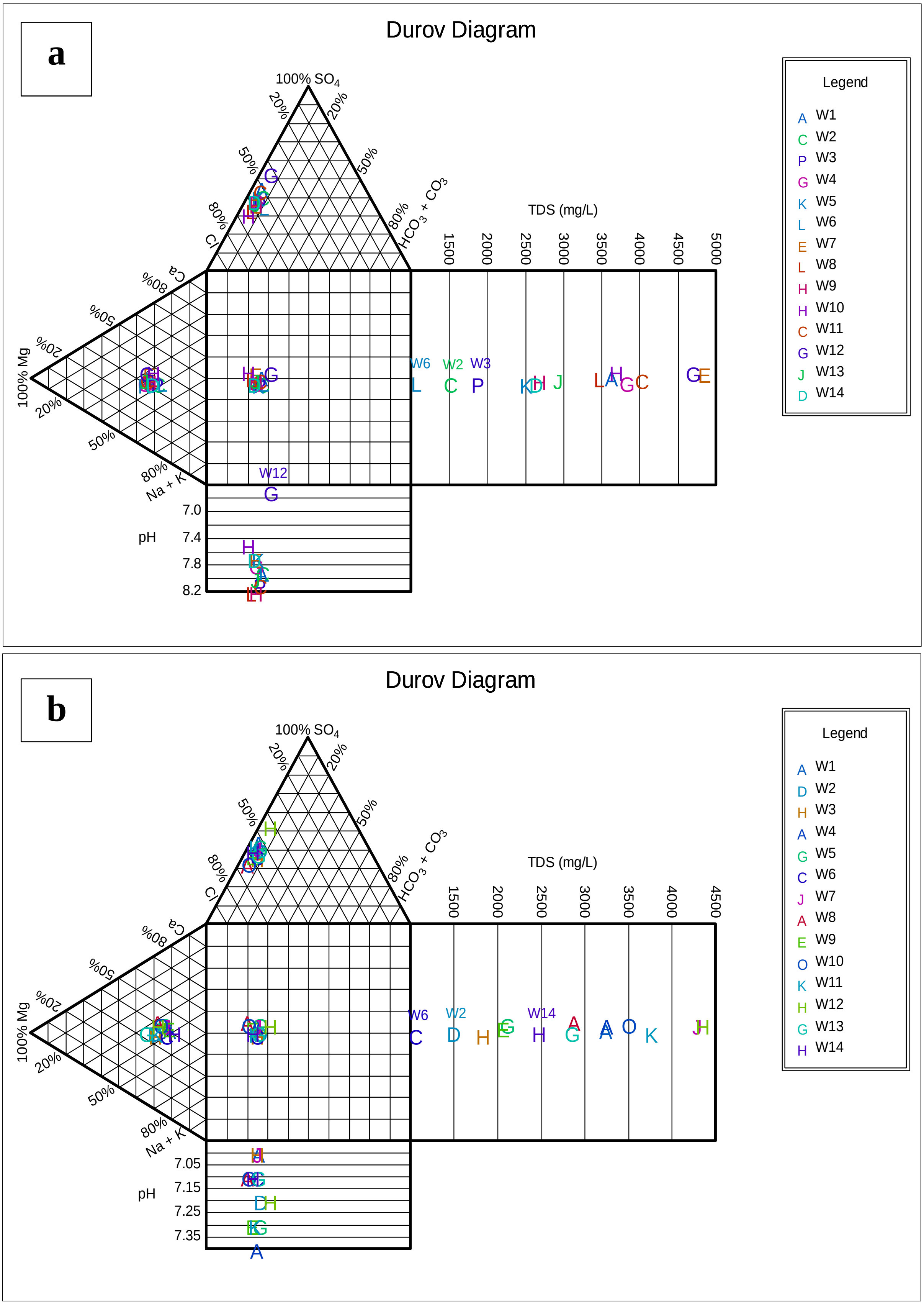


Figure 3-Durov diagram of groundwater during a: dry period b: wet period.

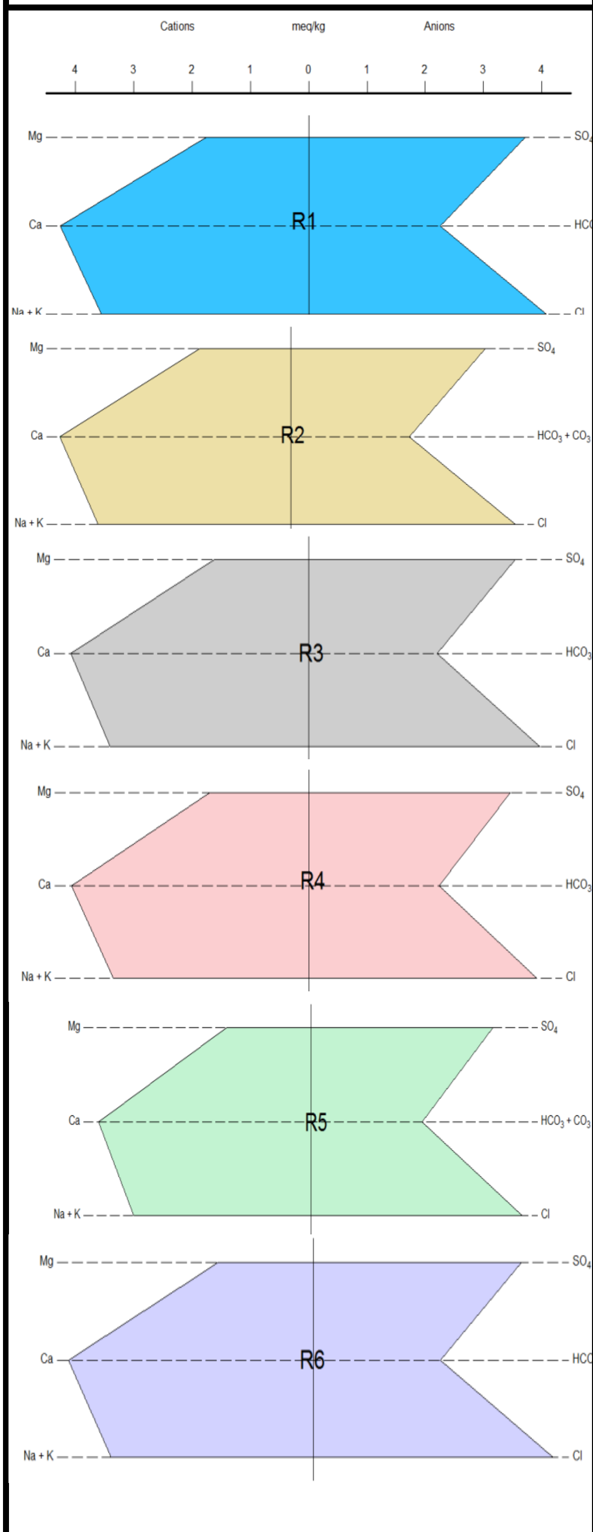
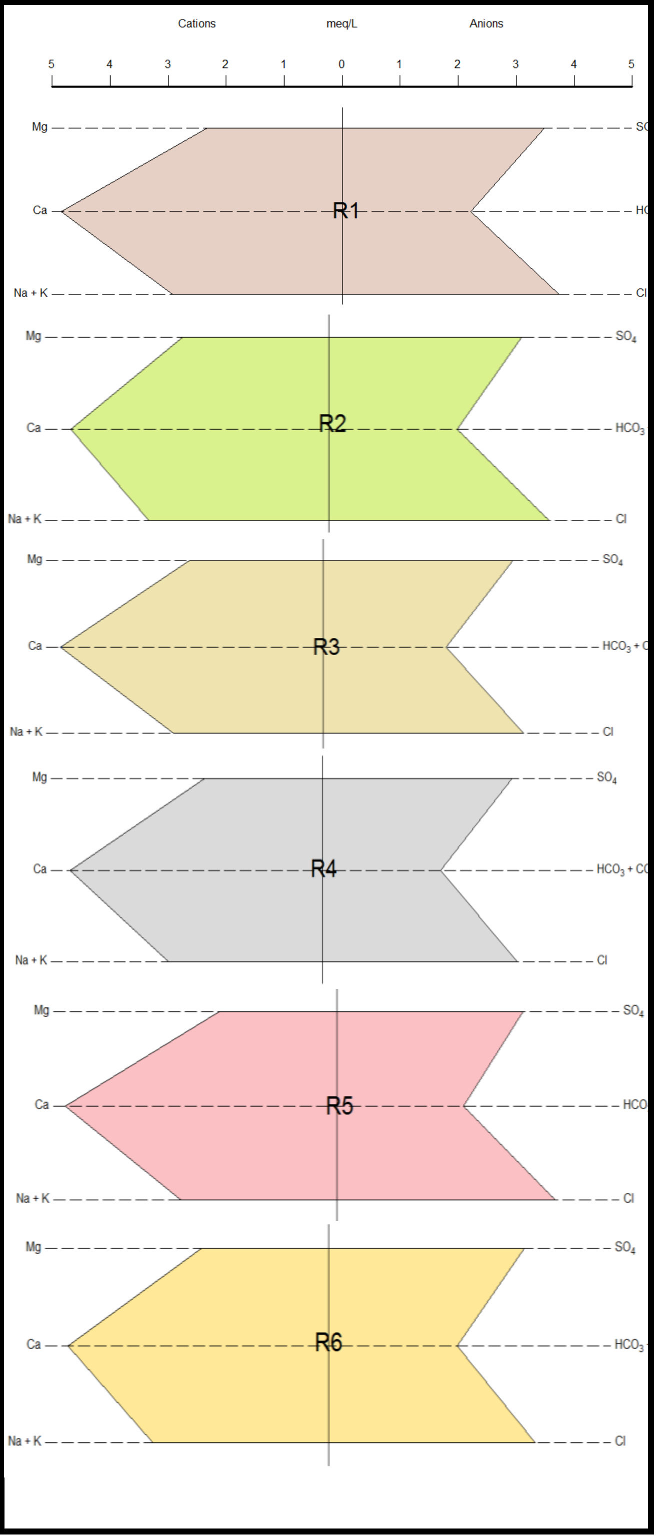
Stiff Diagram for Dry Period	**Stiff Diagram for Wet Period**
	

Figure 4-Stiff diagram for surface water in the two periods.

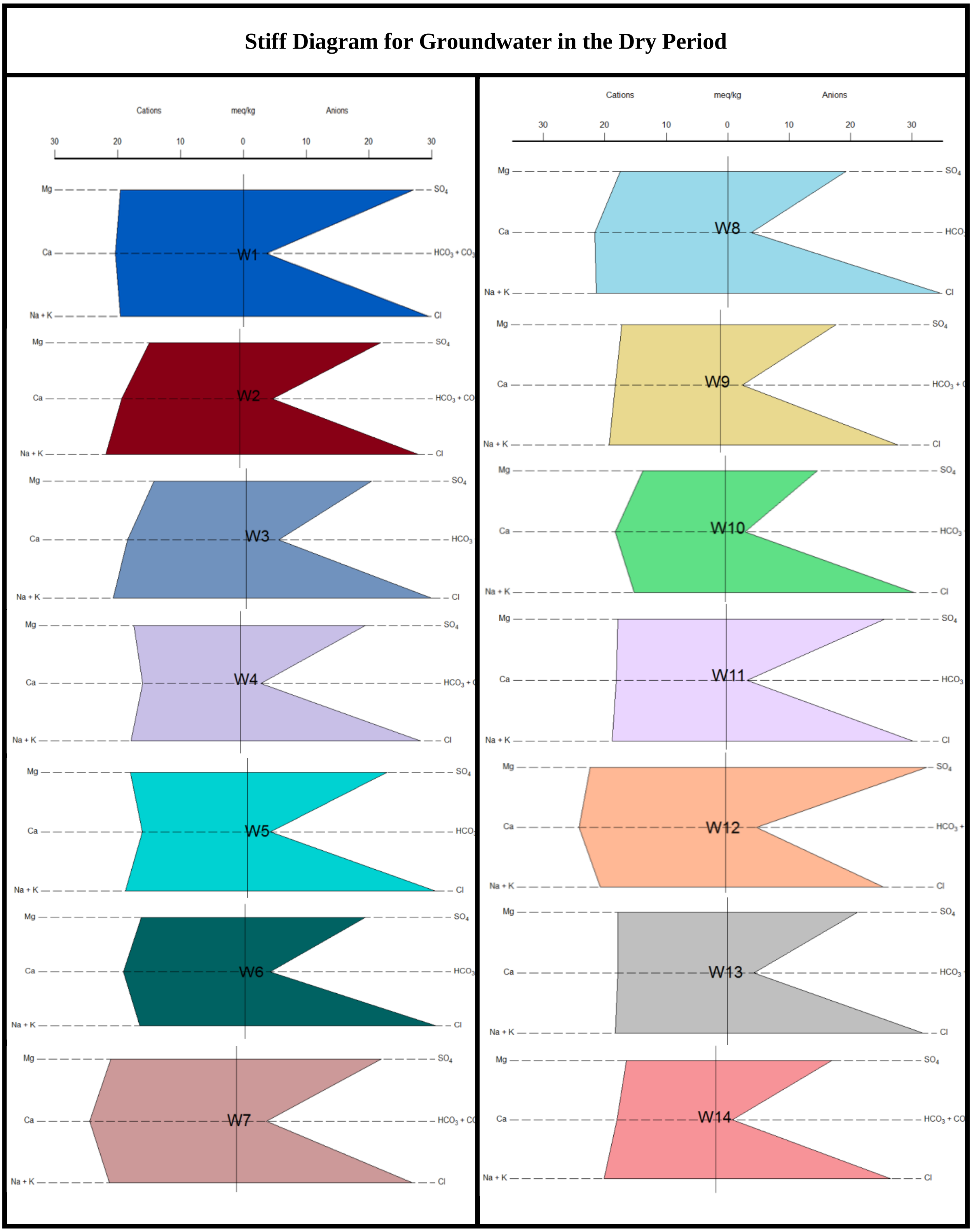


Figure 5-Stiff diagram for groundwater in the dry period.

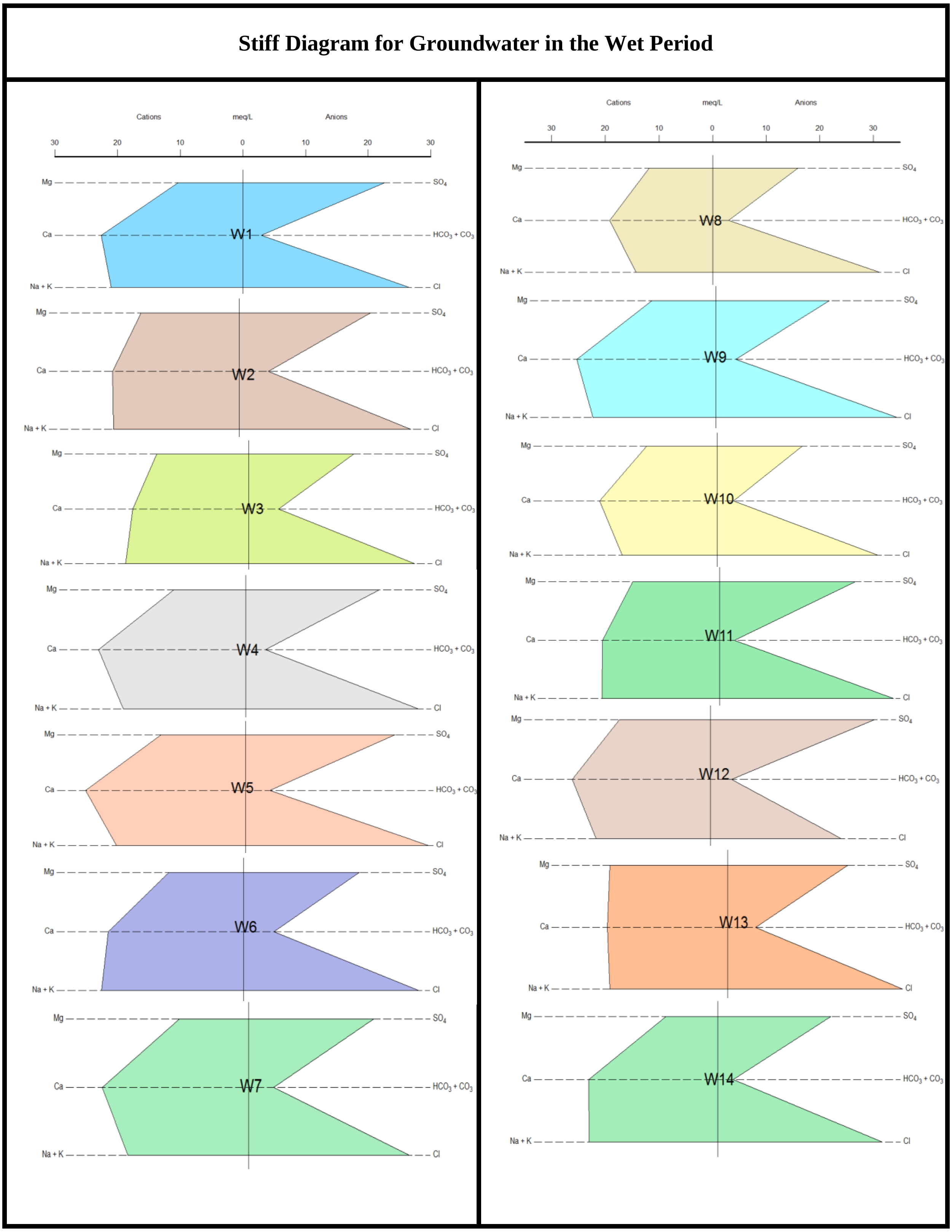


Figure 6-Stiff diagram for groundwater in the wet period.

The stable isotopes composition of surface water (Euphrates River)

For more than four decades, stable and radioisotopes have been used to study hydrological systems and have been particularly useful in understanding the surface water system [15] . The results of the analysis of the environmental isotopes (δ18O and δ^2H) in surface water samples collected from the Euphrates River are expressed in δ notation as (per ml). Evaporation processes in surface water largely affect the isotope compositions in a river system. The results of the environmental isotopes of Euphrates River are shown in (Table-2).

Table 2-Stable isotopes data (**δ ‰**) and Ec values of Euphrates River

Samples No.	δ^2H	$\delta^{18}O$	EC(µs/cm)	d-excess
R1	-38.21	-5.32	1465	4.35
R2	-33.71	-5.06	1437	6.77
R3	-34.81	-4.98	1453	5.03
R4	-36.78	-4.84	1402	1.94
R5	-36.60	-4.75	1446	1.4
R6	-36.96	-5.13	1471	4.08

The δ^2H value of Euphrates river was between -38.21‰ and -33.71‰, with a mean of -36.17‰. The $\delta^{18}O$ value ranged between -5.32‰ and -4.75‰, with a mean of -5.01‰. In Figure-7, the sample points of surface water are plotted close to each other, which suggests similar sources [16].

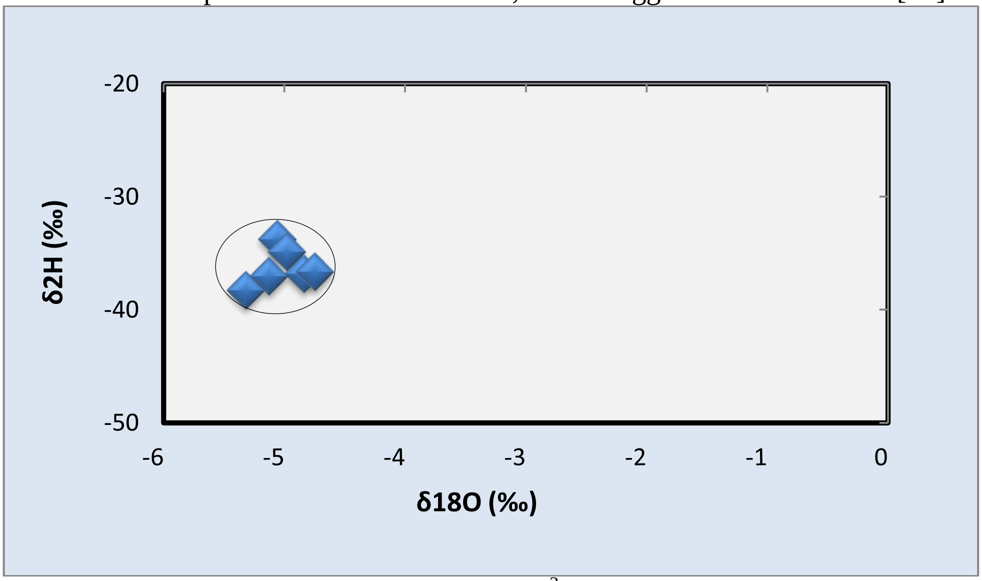


Figure7-The relationship between δ18O and δ^2H values in the surface water samples.

The stable isotopes composition of groundwater

The application of isotopes in hydrology is based on the general concept of tracing. The majority of the applications of isotopes in atmospheric precipitation use the difference of isotopes in the input into the hydrological system [17]. The results of environmental isotopes of the groundwater are shown in Table-3.

Table 3-Stable isotopes data (**δ ‰**) and Ec values of the groundwater for the dry period

Samples No.	δ^2H	$\delta^{18}O$	EC(µs/cm)	d-excess
W1	-32.72	-4.16	5682	0.56
W2	-36.87	-4.92	2547	2.49
W3	-37.26	-4.95	2871	2.34
W4	-42.25	-6.15	5768	6.95
W5	-40.20	-5.37	3885	2.76
W6	-35.88	-5.11	1597	5
W7	-27.34	-3.80	7294	3.06
W8	-23.10	-2.35	5438	-4.3
W9	-37.38	-5.02	4031	2.78
W10	-34.77	-4.52	5586	1.39
W11	-31.10	-3.79	7301	-0.78
W12	-20.78	-1.60	7543	-7.98
W13	-30.64	-3.91	4271	0.64
W14	-33.78	-4.78	3883	4.46

The δ^2H value of the groundwater in the study area was between -42.25‰ and -20.78‰, with a mean of -33.14‰. The δ^{18}O value ranged between -6.15‰ and -1.60‰, with a mean of -4.31‰. It appears that water of the groundwater lie on the same regression line as that of rainwater (source of feeding). However, they have underwent different degrees of evaporation, due to their difference in depth, their influence by evaporation within infiltration, as well as resident time effects, in this case [4], but the recharge is less than that observed in the direction of the wells W8 and W12 (Figure-8).

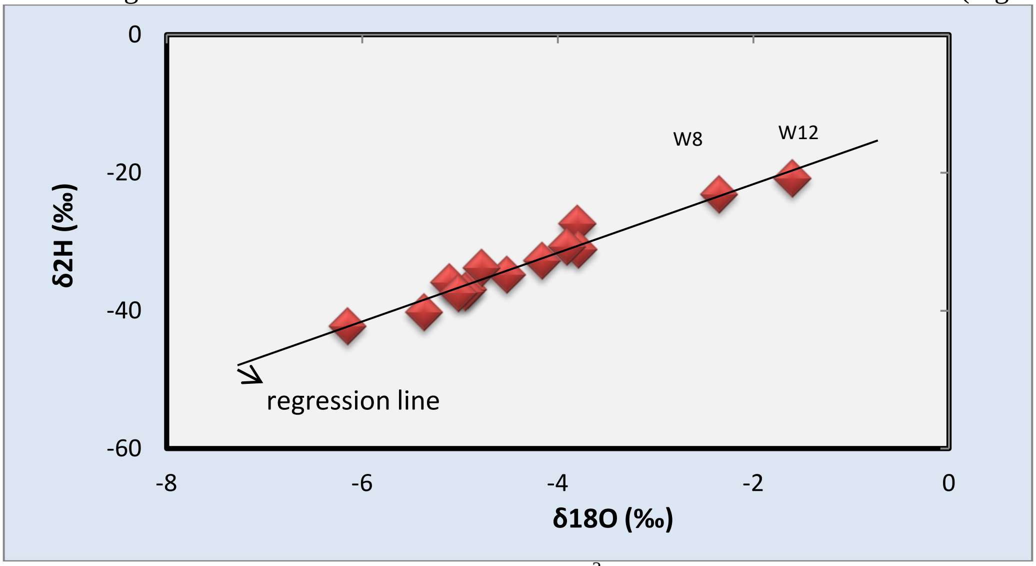


Figure 8-The relationship between δ18O and δ^2H in the groundwater samples.

It appears that water of the surface and groundwater lie on the same regression line, which indicates the same source of rainwater r(source of feeding). to the results also demonstrate the effect of water recharge from Euphrates River to groundwater in the study area (Figure-9).

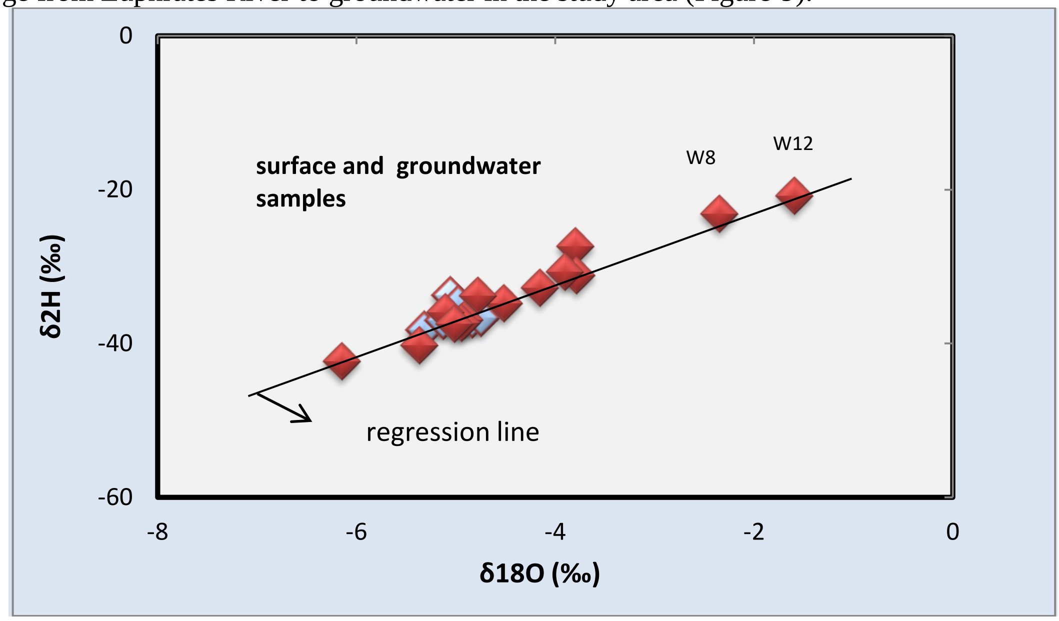


Figure 9-The relationship between groundwater samples and the Euphrates river.

Deuterium Excess (d)

The excess deuterium is a standard character of air mass source. Dansgaard (1964) [18] first proposed using the d value to describe excess deuterium in global precipitation. The d value was set for slope 8 and determined for any sample of precipitation as follows:

$$d = \delta 2H - 8 * \delta 18O \qquad ....1$$

The d-excess value is an index showing the effect of evaporation on the physical-chemical properties of water. If water evaporates, the d-excess decreases [19]. Figure- 10 shows that water from

Euphrates River and groundwater have nearly similar values of d-excess, which is affected by rain water in the regional scale (Figure-10).

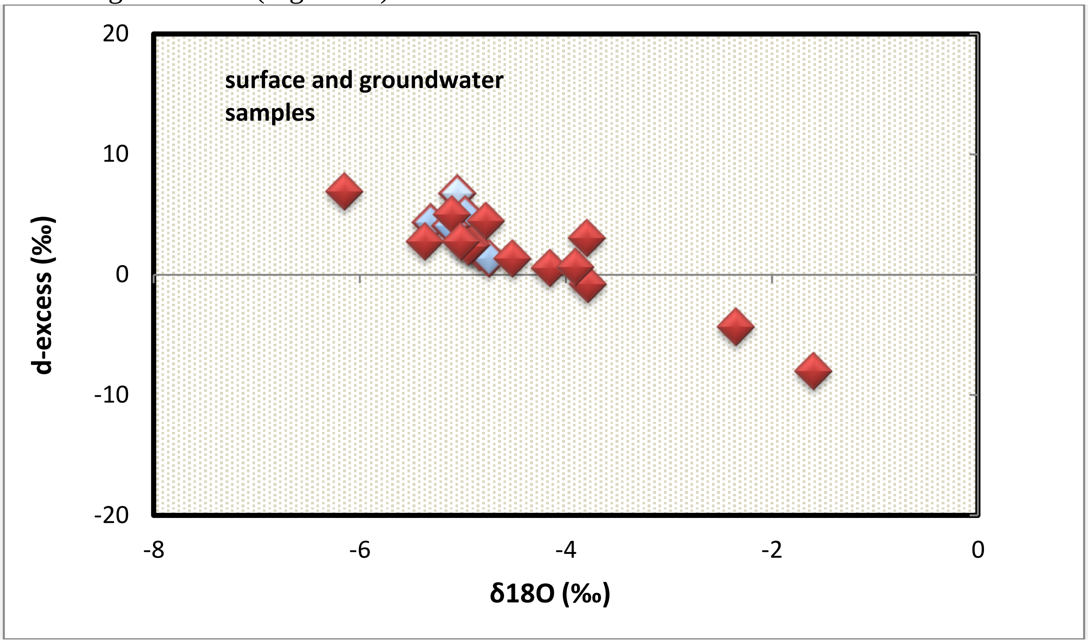


Figure 10-The relationship between δ18O D-excess of the water resources in the study area.

The Use of Isotopic Techniques to Determine the Origin of Groundwater Salinity

Salinization in brackish or highly saline water can be detected by plotting the relation between ^{18}O and chloride content. The enrichment of a stable isotope due to evaporation, or the increase of salinity due to leaching and/ or dissolution, or the mixture of the two cases, could be defined [20]. These processes are clearly noted in Figure-11.

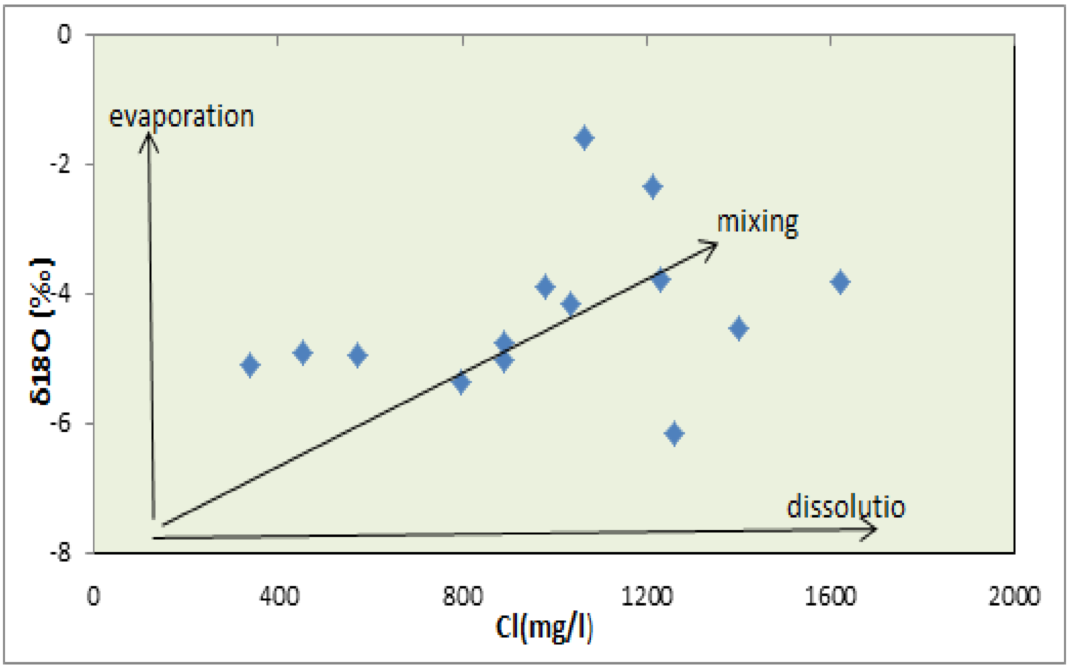


Figure 11-The relationship between δ18 O and Cl^- (meq/l) in groundwater samples.

Stable isotopes and local meteoric water line

The relationship between $\delta^{18}O$ and δD for Euphrates River and groundwater in the study area (Figure-12) shows that these waters fall below the GMWL, $\delta 2H=8\ \delta^{18}O+10$, given by Craig (1961) [21]. While the LMWL (Table-4) followed a linear regression: δD= 7.59 δ18O+12.04. Most waters in this area lie below or immediately to the lower right of the LMWL. The isotopic composition of rainwater in Iraq is located between the Global Meteoric Water Line and the Eastern Mediterranean Meteoric Water Line, which indicates that the precipitation is generally resulting from the mixing between the Mediterranean and Atlantic Ocean air masses[22]. Figure- 12 shows that all samples controlled by the influence of the local climate factors, such as secondary evaporation (evaporation within the rain event) and seasonal variations.

Table 4-Results of previous studies for local meteoric water line

Reference	LMWL value
Al-Paruany, 2013 [6]	$\delta D = 7.53\ \delta^{18}O + 11.97$
Ali et al., 2015 [7]	$\delta D = 7.573\delta^{18}O + 13.82$
Ali & Ajeena 2016 [8]	$\delta D = 7.59\delta^{18}O + 12.04$
Al-Khafagi, 2018 [4]	$\delta D = 8.23\ \delta\ ^{18}O‰ + 15.53$

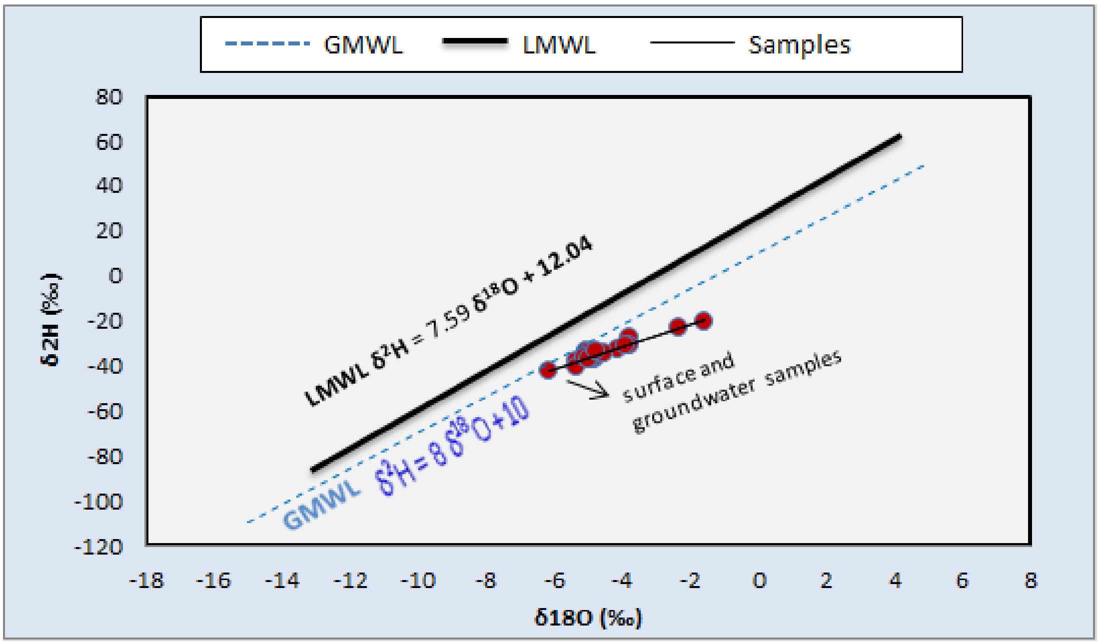


Figure 12 Ezekwe **-**The values of ^{18}O, ^{2}H, GMWL, and LMWL in the study area.

Conclusions

The interaction between surface and groundwater is complex and varies depending on climate, landform, and geology. The hydrochemistry analysis indicates that calcium ion is a predominant cation and Chloride is a predominant anion for surface water samples, whereas calcium and sodium ions are predominant cations and chloride is a predominant anion for groundwater samples. This may reflect the fact of the presence of limestone rocks and halite minerals, which are considered as the main sources for these ions. The hydrochemistry results also indicated a high similarity in the chemical composition between surface and groundwater samples, implying a hydraulic connection between them. An obvious relationship exists between the $\delta^{18}O$ and δD values of Euphrates river and groundwater; it appears that water of the surface and groundwater lie on the same regression line, indicating the same source of rainwater (source of feeding), in addition to the effect of water recharge from Euphrates River to groundwater in the study area. All the samples in the study area refer to a stronger influence by GMWL as compared to that by LMWL. Also, the water is controlled by influences of local climate factors, such as secondary evaporation (evaporation within the rain event) and seasonal variations.

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