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Hydrochemical and Environmental Isotope of Groundwater Samples in Al-Khassa Sub-Basin, Kirkuk, Northeastern Iraq

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Abstract:

Hydrochemical study of groundwater has carried out for the Al-Khassa Sub-Basin during the October 2020 and May 2021 seasons for estimating the impacts of seasonal variation and human activity on water quality and using the isotope to determine the main source of recharge. It was found that Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Dissolved Oxygen (DO) were out of the standard indicating that the groundwater environment was reduced and difficult to recover from pollution. Physical and chemical properties that were high (Total Dissolved Solid (TDS), Total Suspended Solid (TSS), Electrical conductivity (EC), Total Hydrocarbon (THC)). Partial pollution by nitrate and phosphorous due to the use of fertilizers for these elements. The contamination by manganese, molybdenum and boron was present in allsamples of the two seasons, and partly for lead and mercury due to fertilizers, agricultural activities, the presence of animal and poultry ,ranchesbesides the poor sewage system in the basin based on a septic tank. Washing polluted agricultural soil by rain lead to polluting groundwater. From the environmental isotope analysis (δ^2H and $\delta^{18}O$), the isotopic compositions of precipitation were used to construct a local meteoric water line for the study area. The isotopic compositions of groundwater samples were situated to the left of the Global meteoric water line (GMWL), suggesting input of local rainfall that derives from weather front originating from the Mediterranean Sea. Comparing the isotope composition of groundwater and precipitation showed that the infiltrated precipitation that was the main source of recharge to the aquifer system in the study area.

Keywords: Al- Khassa Sub-Basin, Heavy metal, Stable Isotope, Meteoric water line, Groundwater pollution

النظائر الهيدروكيمائية والبيئية لعينات المياة الجوفية لحوض الخاصة الفرعي , كركوك, شمال شرق العراق

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الخلاصه

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أجريت الدراسة الهيدروكيميائية للمياه الجوفية لحوض االخاصة الفرعي خلال موسمي (تشرين الاول 2020) و (ايار 2021) لتقدير آثار التغيرات الموسمية والنشاط البشري على جودة المياه واستخدام النظائر لتحديد المصدر الرئيسي لإعادة التغذية. لقد وجد أن الاوكسجين المذاب و الطلب الاوكسجين الاحيائي والكيمائي كان خارج المعيار مما يشير إلى أن بيئة المياه الجوفية قد تاثرت ويصعب استردادها من جراء التلوث الحاصل. الخصائص الفيزيائية والكيميائية التي كانت عالية متمثل ب مجموع الاملاح المذابة والناقلية الكهربائية ومجموع الهايدروكاربونات وان هناك التلوث الجزئي والنترات والفوسفور نتيجة استخدام الأسمدة لهذه العناصر. كان التلوث بالمنغنيز والموليبديوم والبورون موجودًا في جميع عينات الموسمين ، وجزئيًا بالرصاص والزئبق بسبب الأسمدة والأنشطة الزراعية ووجود مزارع الحيوانات والدواجن ، بالإضافة إلى سوء نظام الصرف الصحي في الحوض القائم على استخدام الخزانات الحوضية التي تؤدي الى تسربها للتربة الزراعية الملوثة بسبب الامطار إلى تلوث المياه الجوفية. من تحليل النظائر البيئية. تم رسم ايجاد الخط المطري المحلي لمنطقة الدراسة وضع النظائر لعينات المياه الجوفية على يسار الخط المطري العالمي ، مما يشير إلى مدخلات هطول الأمطار المحلية المستمدة من جبهة الطقس التي نشأت من البحر الأبيض المتوسط. أظهرت مقارنة النظائر للمياه الجوفية والتساقط أن الترسيب المتسرب كان المصدر الرئيسي لإعادة تغذية نظام الخزان الجوفي في منطقة الدراسة.

1. Introduction:

Groundwater is important to the development of most arid and semiarid regions due to limited precipitation and surface water [1], with the surrounding rocks causing a variety of hydrogeochemical processes that alter groundwater chemical components. The study of the hydrogeochemical processes has been an area of interest in the past few decades, as a chemical variation of groundwater can reveal the interaction between groundwater and the environment and provide a scientific basis for water resource management[2].

An increase in water demand is occurring in many of these zones worldwide due to factors such as population, agriculture and mining growth at a time when scarce water resources are menaced by climate change [3]. Oxygen and hydrogen isotopes of water are widely used as tracers to understand hydrogeological processes like precipitation, groundwater recharge, groundwater and surface water interactions and basin hydrology[2]. A comparison of the oxygen and hydrogen isotopes of precipitation and groundwater gives a good tool to evaluate the recharge mechanism and determine the groundwater recharge sources that was important for the management of groundwater resources. Al-Khassa Sub-Basin is a part of the Al-Adhaim River Basin (Al-Khassa stream is one of the three main tributaries of Al-Adhaim River).

The study aims to determine the origin of shallow groundwater, construct a meteoric water line, and compare it with local and global meteoric water lines by using environmentally stable isotopes of oxygen and hydrogen and using the oxygen and hydrogen isotopes groundwater to evaluate the
Recharge mechanism and determine recharge sources in the study area.

2. Study site:

Al-Khassa Sub-Basin is located in the northeastern part of Kirkuk Province/ northeastern part of Iraq, about 21 km from the Centre of Kirkuk City. The area is located between longitudes (44° 28' 00" E - 44° 49' 00"E), and latitudes (35° 30' 00" N - 35° 43' 00" N). It covers a total area of 468 km^2 and includes about (32) villages (Figure. 1). The study area is bounded by North Chamchmal Anticline in the northeastern, Shwan Sub-Basin in the northwestern and Qara Hanger Sub-Basin in the south of the study area hydraulic characteristics of the aquifer, special distribution of the water table and groundwater movement direction of the groundwater, the hydraulic properties results of five single pumping test in the study area showed that the transmissivity (T) is ranged between (2.01 to7.5m2/day), storage coefficient

(Sc) ranged (from 6.4*10-3to7.3*10-2) and the hydraulic conductivity (K) ranged between (0.025 to 0.85 m/day)[4]. Flow it direction from of recharge waters northeast and calculated southeast head by towards there discharging areas at west [5].

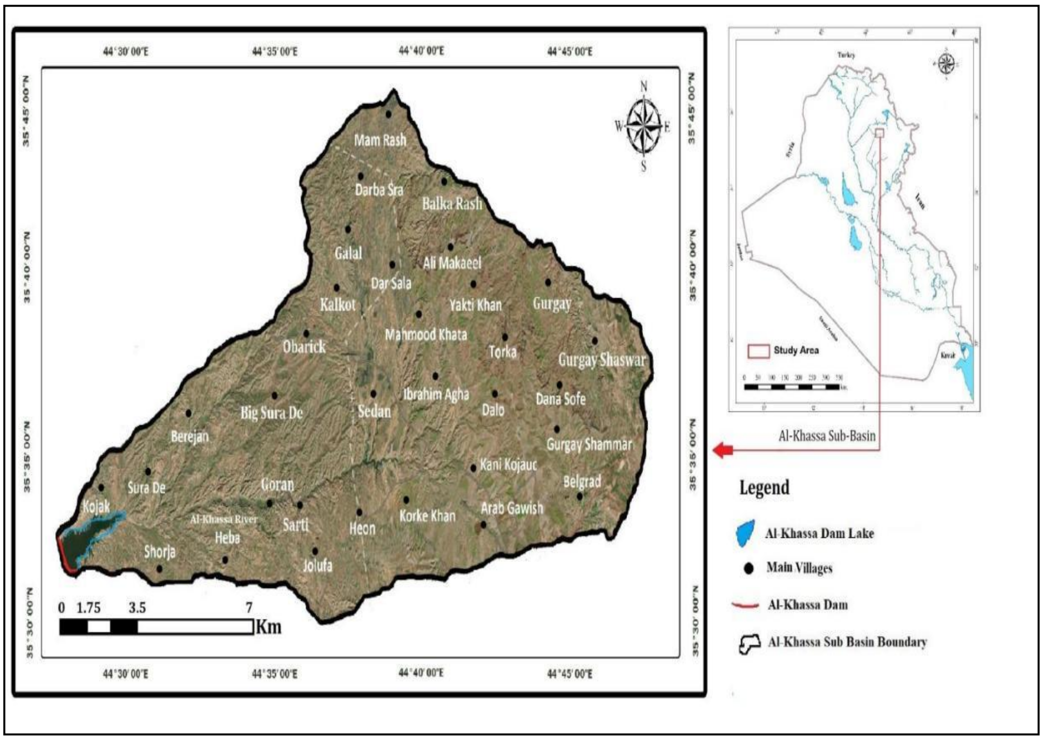

Figure 1: Location map of Al-Khassa Sub-Basin

2. Material and method :

Twenty groundwater samples had been collected from Al-Khassa Sub-Basin for each dry and wet season of 2020-2021 (Figure.2.) The purpose of the sampling was for chemical and stable isotopic analysis to assess seasonal variations. Rainwater samples were collected from the central station through a rainy period of the water year (2020 – 2021) for stable isotopic analysis and to find the local meteoric water line of the sub-basin. The physical and chemical parameters, major and minor elements, heavy metals and stable isotopes chemical analyses of water samples were performed in ALS Environmental Lab. Mississauga, Canada branch. Thermo X's inductively coupled plasma mass spectrometer, or ICP-MS, is used for heavy metal analysis. and utilized for isotope analysis (laser spectroscopy for isotope analysis).

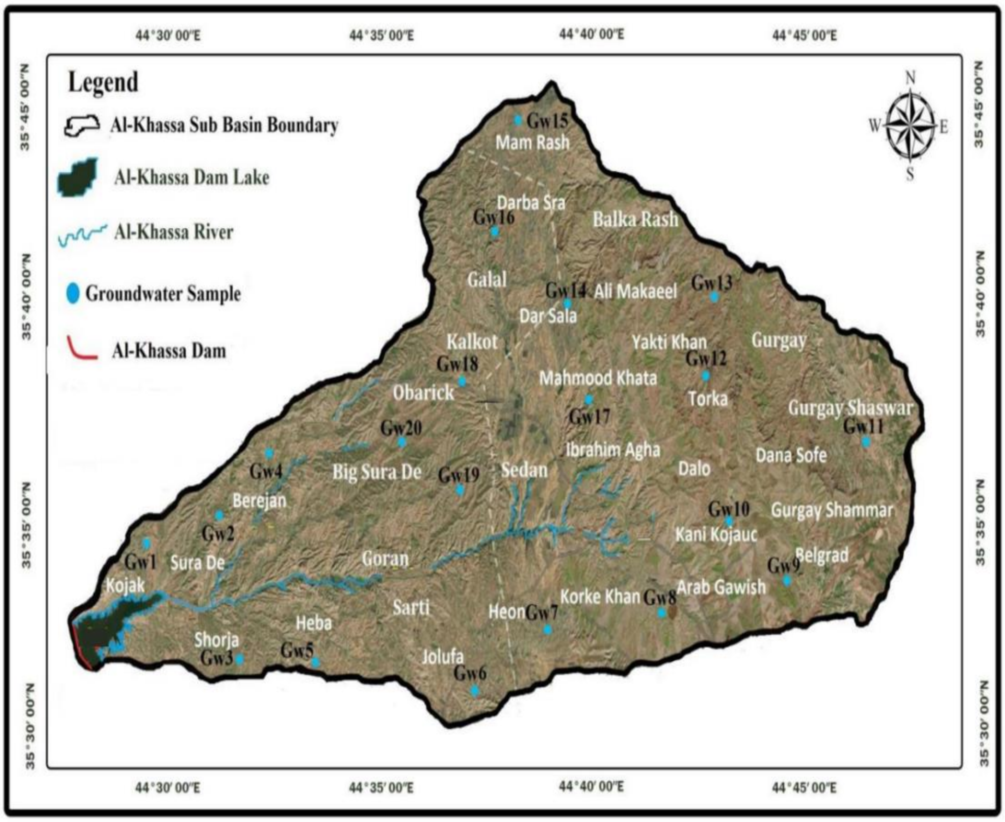

Figure 2: Location of groundwater samples.

4. Physical and chemical and biological parameters:

Total suspended solids (TSS) concentration values ranged from 201ppm to 531 ppm with a mean of 370 ppm, and from 263ppm to 576 ppm with a mean 402 .7 ppm for dry and wet seasons respectively both seasons were within the standard [6]. Dissolved oxygen (DO) ranged from 1.6 ppm to 7 ppm with mean7.5 ppm and 2.5 ppm to 7.8 ppm with a mean of 5.2 ppm for dry and wet season respectively all was considered unacceptable according to EPA standard[7]. Biological oxygen demand (BOD) during the dry season ranged from 4.7 ppm to 9.4 ppm with a mean of 6.8 ppm, and 4.4 ppm to 9.4 ppm with a mean of 6.7 ppm (Table.1), values for the two seasons were above the standards and more than allowable limits. Chemical oxygen demand (COD) ranged from 89 ppm to 298 ppm with a mean of 155.5 ppm and from 79.6 ppm to 284 ppm with a mean of 159.3 ppm for dry and wet seasons respectively. All the COD concentration results of the two seasons were out of the acceptable limit. The total hydrocarbon of groundwater samples ranged from 28 ppm to 49 ppm with a mean of 37.9 ppm and from 30 ppm to 50 ppm with a mean of 41 ppm for the dry and wet seasons, respectively. THC concentrations in the surface water are less than those in the groundwater. All the THC were out of standard concentration results are out of acceptable limit [8]all groundwater samples were out of standard. Redox(ORP) was within the standard for both seasons. The main source of Total Dissolved Solid (TDS) in water is rocks, soils, precipitation, wind and household wastes of human and livestock[9]. The TDS concentration of the groundwater during the dry season ranges from 763.6 ppm to 1206 ppm with a mean of 1008 ppm and from 808 ppm to 1239.2 ppm with a mean of 1055 ppm, for the wet season (Table .1). Potential of Hydrogen (pH) of groundwater samples of dry season varied between 7 - 8.2 with a mean of 7.5 and 7.2 to 8.4 with a mean of 7.65 for Al-Khassa Sub-Basin samples respectively (Table.1). pH for all groundwater samples of groundwater in both wet and dry seasons was within acceptable limits for both Iraqi standards[6] and WHO [10]. Electrical Conductivity (EC) for groundwater samples ranged from 381-1098 µs/cm with a mean of 655 µs/cm, and from 456 µs/cm to 1013 µs/cm with a mean of 740.8 µs/cm, for dry and wet seasons respectively (Table.1). The EC shows similar behaviour with TDS for both seasons there was a strong correlation between them. Most EC results for the two seasons were above the acceptable limits[6]which are 500µs/cm except (Gw18, Gw19) in the wet season.

Table 1: Physicochemical and biological data of the groundwater during dry and wet seasons in the study area.

Parameter	**Unit**	**Min.**	**Max.**	**Mean**	**Min.**	**Max.**	**Mean**	**(IQS, 2009)**	**(WHO, 2017)**	**(EPA,2018)**
		Dry season			Wet season					
TSS	ppm	201	531	370	236	358	316.4	700*		
DO	ppm	1.6	7	7.5	2.5	7.8	5.2			8.5
H_2S	ppm	1	3.9	2.06	0.459	3.8	1.9			
pH		7	8.2	7.5	7.2	8.48	7.6		6.5-8.5	
EC	µs/cm	381	1098	655	456	1013	740.8	250		
TDS	ppm	763.6	1206	1008	808	1239.2	1055	1000		
TH	ppm	804.1	1172	1002	778	1139	994.4			
BOD	ppm	4.75	9.4	6.8	4.41	9.4	6.7		4	5
COD	ppm	89	298	155.5	79.6	284	159.3		10	25
OPR	mV	115	289	184.5	236	389	316.4	300-500**		
THC	ppm	28	49	37.9	30	50	41	30***		

* According to [11]**According to [12]****According to [8]

5. Major and minor Ions:

Calcium (Ca^{2+}) concentration in the groundwater samples during the dry season ranged from 13.8 ppm - 55 ppm with an average of 27.5 ppm while for the wet season ranged from 14.6 ppm -9 ppm with a mean of 10.9 ppm (Table.2).

Concentrations of calcium ions in the groundwater were less than [6],[10] and [11] standards.

Magnesium (Mg^{2+}) concentrations in the groundwater were less than [6],[10] and [11] standards.concentration in the groundwater samples during the dry season ranged from 9 ppm - 17 ppm with an average of 12.3 ppm while for the wet season ranged from 9ppm -20 ppm with a mean of 12.8 ppm (Table.2).

Na^+ concentration varies from 4.13 ppm - 19 ppm with a mean of 13.5 ppm and 1.09 ppm-17.6 ppm with a mean of 13.9 ppm of groundwater samples during dry and wet seasons respectively. The Potassium K^+ concentration in groundwater samples varied between 0.08 ppm and 0.94 ppm during the dry season and between 0.1 ppm and 0.8 ppm during the wet season (Table .2). Presence of potassium may be due to the use of Iraqi fertilizer (NPK) and Muriate of Potash Mop the concentration values of potassium ion in the groundwater were within the limits may be due to extensive use of Iraqi phosphate fertilizer (NPK) contains 19 % K_2O [13].

Bicarbonate HCO_3^- concentration in groundwater samples ranged between 100 ppm and 174 ppm during the dry season and between 96 ppm and 185ppm during the wet season (Table.2). The mean concentration of Cl^- in the groundwater samples was 1.6 ppm and 7.9 ppm with mean 4.41 ppm and ranged between 1.4 ppm and 7.4ppm with mean 33 ppm that's all were with the standard.

The concentration of SO_4^{2-} for groundwater samples varied between 22 ppm to 42 ppm, with a mean of 29.05 ppm and for wet season varies between 10 ppm and 19.6 ppm with a mean of 14.9 ppm SO_4^{2-} concentration value of both seasons was within the standard of [6],[10] and [11] standard.

The concentration of NO_3^- for groundwater samples varies between 14.52 ppm to18.2 ppm with a mean of 15.7 ppm and between 14.2 ppm to 19.8ppm with a mean of 16.4 ppm during dry and wet seasons respectively as shown in (Table .2), all was higher than the standard[6],[10] and [11]Phosphate (PO_4^{3-}) ranged from 1.77 ppm to13.5 ppm with a mean of 6.4 ppm in the dry season and the wet season ranged from 3 ppm to 16.5 ppm with a mean of 8.2 ppm, all were above the standard of[10]. The main sources of phosphate were because municipal and industrial waste, stormwater, soil erosion, and an increase of using of fertilizers (NPK)besides other factors such as human and animal waste from a proper septic system in the area [14]. Agricultural activities may increase soluble reactive phosphorous (SRP) levels. Particulate phosphorous include P incorporated into mineral structures, adsorbed onto clays, and incorporated into organic matter.

Table 2: Major and minor ions in the groundwater samples during the dry season and wet seasons in ppm.

			Dry season			Wet season				
Parameters	units	Min	Max	Mean	Min	Max	Mean	IQS,2009	WHO,2017	EPA,2018
Ca^{++}	ppm	13.8	55	27.5	14.6	39	28.1	150	100	200
Mg^{++}	ppm	9	17	12.3	9	20	12.8	100	125	200
Na^+	ppm	4.13	19	13.5	10.9	17.6	13.9	200	200	200
K^+	ppm	0.08	0.94	0.30	0.1	0.8	0.38	-----	12	15
Cl^-	ppm	1.6	7.9	4.41	1.4	7.4	3.3	350	250	250
HCO_3^-	ppm	100	174	145.03	96	185	128.8	-----	-----	-----
SO_4^-	ppm	22	42	29.05	10	19.6	14.9	400	250	200
PO_4^-	ppm	1.77	13.5	6.4	3	16.5	8.2	----	0.4	-----
NO_3^-	ppm	14.52	18.2	15.7	14.2	19.8	16.4	50	50	10

6. Trace elements and heavy metals in groundwater:

Arsenic (As) polluted sample was (Gw5, Gw10, Gw17, Gw19, and Gw20) for the dry and wet season because the presence of arsenic was due to fertilizer and pesticide (Table.3). Mercury (Hg) all samples were polluted for dry and wet season mercury was found in high concentration in an agricultural area in Al-Khassa Sub Basin was due to using of agricultural chemical as fungicide, mildewcide or pesticide. Lead (Pb) was acceptable in both seasons except (Gw8, Gw14, Gw17, and Gw20) in wet season two. Boron (B) all was unacceptable except (Gw11, Gw13) in the dry season and (Gw9, Gw11) in the wet season because of the use of fertilizer and herbicides and wastewater used for irrigation [9]. Manganese (Mn) and molybdenum (Mo) concentration value were out of the standard all was polluted because many fertilizer formulations with molybdenum and manganese [15]. Each of the following elements(Cr, Cu, Zn, Al, Co, Fe, Ni,V) was within the accepted limit, and this is something to be expected, given that these elements are abundant in industrial and urban areas, and this is far from the nature of the basin as it is a village basin

Table 3: Trace element concentration value of groundwater samples.

Groundwater Samples									
Elements	**Dry season**			**Wet season**			****IQS, 2009**	***WHO ,2017**	**(EPA, 2018)**
	Min.	**Max.**	**Mean**	**Min.**	**Max.**	**Mean**			
	µg/l								
As	4.8	19.8	10.8	5	21.3	11.8	10	10	10
Cr	0.31	0.96	0.6	0.31	2	0.8	50	5	10
Cu	0.985	2.1	1.5	1.02	2.1	1.5	1000	2000	1300
Hg	1.2	2.66	2.01	2.9	6.7	4.6	1	2	2
Pb	3.4	9.89	6.1	4.5	11	7.9	10	10	15
Zn	12.9	46.2	30.7	13.6	63.5	35.1	300	3000	5000
Al	13.9	34	22.8	18.7	52	31.4	100	50-200	------
B	398	736	482.5	421	789	562.8	500	500	500
Co	0.12	0.398	0.2	0.23	0.74	0.4	------	50	------
Fe	12	77	38.3	22	86.5	48.7	300	300	300
Mn	100.65	278	176.2	109.3	321	208.9	100	50	50
Mo	53.8	87.5	73.5	74.2	168.9	95.0	------	70	------
Ni	1.25	3.4	2.2	1.23	3.98	2.7	20	70	70
V	84.6	158	104.8	96.6	187	134.9	------	1000	1000

7. Environmental stable isotope values of Groundwater

The $\delta^{18}O$ and $\delta^{2}H$ values in groundwater samples during the dry period range from -4.96 ‰ to --3.7 ‰ with a mean of -4.3195 ‰ and from -29.74 ‰ to -21 ‰ with a mean of -25.7645 ‰ respectively, while in dry period ranged from -4.8 ‰ to -3.4 ‰ with a mean -4.2725 ‰ and from -29.4 ‰ to -22.01‰ with a mean-25.335‰ respectively (Table.4).

While the deuterium excess values ranged from 2.3‰ to 17.4‰ with an average of 9.48‰ during the dry season. The deuterium excess values ranged from 0.5‰ to 15.59‰ with an average of 9.165‰ during the wet season. There is a slight seasonal variation of isotope content in groundwater, where the highest values for $\delta^{18}O$ and $\delta^{2}H$ were recorded in the wet season and the lowest values in the dry season. The variation in the isotopic composition of groundwater in the study area is caused by water mixing during groundwater recharge, in addition to the effect of evaporation during the trajectory of waters from the atmosphere to aquifers and the variation of stable isotope content in rainwater. Dissolution and re-precipitation of minerals, silicate weathering and direct exchange between water and mineral crystal lattice allow isotopic enrichment of $\delta^{18}O$ in groundwater [16]. The relation between $\delta^{18}O$ and δD in groundwater showed that the samples for both seasons are lies between EMWL and GMWL close to the local meteoric water line (LMWL) (Figure.3),(Figure.4) indicating that the groundwater recharge is mainly from precipitation origin, whether from direct infiltration through the soil and unsaturated zone or discrete infiltration during the flow of Al-Khassa river during the wet period. The deviation of the isotopic composition of groundwater (GWWL) from (LMWL), indicates the effect of evaporation and water mixing. By comparing (GWWL) within dry and wet seasons, there is a small difference between both seasons (Figure.3 and Figure.4).

Table 4 : Isotopic composition and D-excess of groundwater sample.

Groundwater	**Dry Season**	**Wet Season**	**Dry Season**	**Wet Season**

	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	D-EXCESS	D-EXCESS
Gw1	-4.12	-22.9	-3.9	-22.4	10.06	8.8
Gw2	-4.8	-21	-4.6	-22.5	17.4	14.3
Gw3	-4.6	-23.9	-4.2	-23.67	12.9	9.93
Gw4	-3.9	-22.4	-3.7	-22.2	8.8	7.4
Gw5	-4.1	-23.75	-4.8	-23.5	9.05	14.9
Gw6	-4.6	-24.87	-4.4	-22.4	11.93	12.8
Gw7	-4.21	-22.9	-4.6	-22.4	10.78	14.4
Gw8	-4.1	-22.89	-4.7	-22.01	9.91	15.59
Gw9	-4.1	-28.77	-4.8	-28.45	4.03	9.95
Gw10	-4.89	-28.67	-4.7	-28.4	10.45	9.2
Gw11	-4.01	-29.74	-3.4	-29.4	2.34	2.2
Gw12	-4.06	-29.4	-3.7	-29.1	3.08	0.5
Gw13	-4.1	-26.5	-4.4	-26.07	6.3	9.13
Gw14	-4.2	-26.7	-4.2	-26.1	6.9	7.5
Gw15	-4.96	-28.5	-4.7	-28.4	11.18	9.2
Gw16	-4.76	-27.9	-4.35	-27.1	10.18	7.7
Gw17	-3.98	-26	-3.8	-26.3	5.84	4.1
Gw18	-4.8	-26.2	-4.7	-26	12.2	11.6
Gw19	-4.4	-26.3	-4.1	-25.3	8.9	7.5
Gw20	-3.7	-26	-3.7	-25	3.6	4.6

8. Isotopic Compositions of Precipitation

determining and comparing the isotopic composition of precipitation with differing water sources is required in stable isotope studies. Oxygen and hydrogen isotope composition in precipitation differs from its initial phase in oceanic water as a result of the distillation process (rainout effect). Fractionation of isotopic during the evaporation of ocean water and intensification of water in clouds leads to a depletion of ^{18}O and ^{2}H. Consequently, negative values of ^{18}O and ^{2}H in fresh waters compared to ocean waters. The depletion of Oxygen and hydrogen isotopes in precipitation is in general more negative with increasing distance from the equator (latitude effect), from coastal regions (continental effect) and increasing elevation (altitude effect) [17]. The intense rain events lead to a strong depletion of ^{18}O and ^{2}H (amount effect) [18]. Generally, the values of $\delta^{18}O$ are more positive in the summer and more negative in the winter and decrease with an increase the altitude because of seasonal temperature variations[19]. The equation is modified to include the isotopes of the primary vapor and precipitation along the trajectory (Eq.1)[20]:

$$\delta^{18}O_{w(f)} = \delta^{18}O_{v(f=1)} + \delta^{18}O_{w-v}(1 + \ln f) \ldots\ldots \text{ Eq.1}$$

$\delta^{18}O_{w(f)}$ isotopic value of the residual fraction, f

$\delta^{18}O_{v(f=1)}$ isotope value for the initial water vapor

$\delta^{18}O_{w-}$ enrichment factor for equilibrium water-vapor exchange at the prevailing in-cloud temperature, at 25°C, $\delta^{18}O_{w-v}$ is 9.3 ‰.

Table.5: Show the isotopic composition of rainwater.

Month	Isotope	R1	D-EXCESS(R1)

November	$\delta^{18}O$	-4.7	20.8
	$\delta^{2}H$	-16.8	
December	$\delta^{18}O$	-4.2	14.7
	$\delta^{2}H$	-18.9	
January	$\delta^{18}O$	-4.42	16.26
	$\delta^{2}H$	-19.1	
February	$\delta^{18}O$	-4.43	17.34
	$\delta^{2}H$	-18.1	
March	$\delta^{18}O$	-3.65	12.85
	$\delta^{2}H$	-16.35	
April	$\delta^{18}O$	-3.76	14.58
	$\delta^{2}H$	-15.5	

The correlation between $\delta\,^{18}O$ and $\delta\,^{2}H$ in precipitation on a global scale showed a linear correlation. This relationship is called the global meteoric water line (GMWL). [17] defined this relation by the following equation [21]:

$\delta\,^{2}H = 8\ \delta\,^{18}O + 10$‰……Eq.2

The global meteoric line is a combination of many local meteoric water lines, where any given region will have a distinctive Local Meteoric Water Line (LMWL) with a slightly different slope and intercept [22]. In general, LMWL provides information about vapor origin and the isotopic composition of precipitation at a specific location where it can be compared with other water sources to determine their origin [23].
To compare the isotopic composition of precipitation in the study area with Global Meteoric Water Line (GMWL), the Local Meteoric Water Line (LMWL) was drawn depending on the correlation between $\delta^{18}O$ and $\delta^{2}H$ in monthly precipitation (Figures 3 and 4), and the following correlation was obtained:

$\delta^{2}H = 7.55 \times \delta^{18}O + 13.68$…..Eq.3

The correlation coefficient between $\delta^{18}O$ and $\delta^{2}H$ of precipitation is (0.98), indicating a strong relationship between them and this may reflect less impact of fractionation processes in rainwater samples. Both the slope and the intercept of LMWL are different than for the GMWL due to variations in climatic and geographic parameters. LMWL was having an intercept value of (13.68), which is much higher than that of the GMWL of 10 due to the influence of different air masses. Generally, the deviations from the (GMWL) can be attributed to the local processes effect, like rainwater evaporation and seasonal transport changes rather than different fractionation processes (Gat, 1996)[24]. Some degree of evaporation already occurs during raindrops fall to the ground beneath the cloud base [25]. On the other hand, the East Mediterranean Water Line (EMWL) (Eq. 4) defined by [26] and Iraq Meteoric Water Line (IMWL) (Eq.3) which is defined by [27] have been plotted along with LMWL and GMWL (Figure 5.6). Clearly, the precipitation samples and local water line located between EMWL and GMWL, reflecting that the source of local rains can be attributed to EMWL.

$\delta^{2}H = 8 \times \delta^{18}O + 22$ …..Eq.4
$\delta^{2}H = 7.57 \times \delta^{18}O + 11.976$…….Eq.5

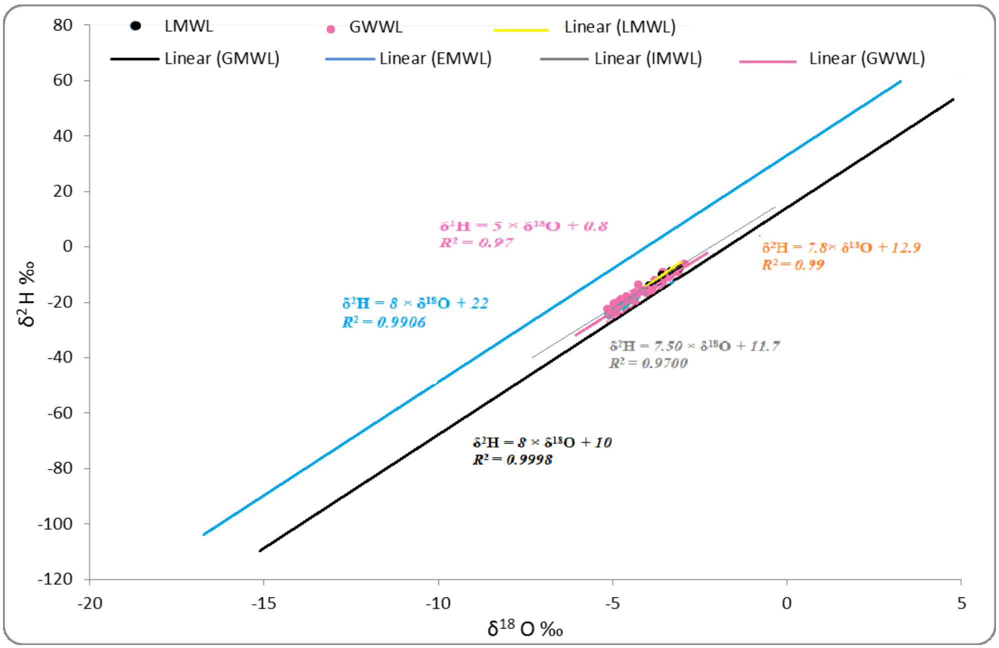

Figure 3: The plot of ^{18}O and ^{2}H of groundwater samples during the dry season versus GMWL, EMWL and LMWL.

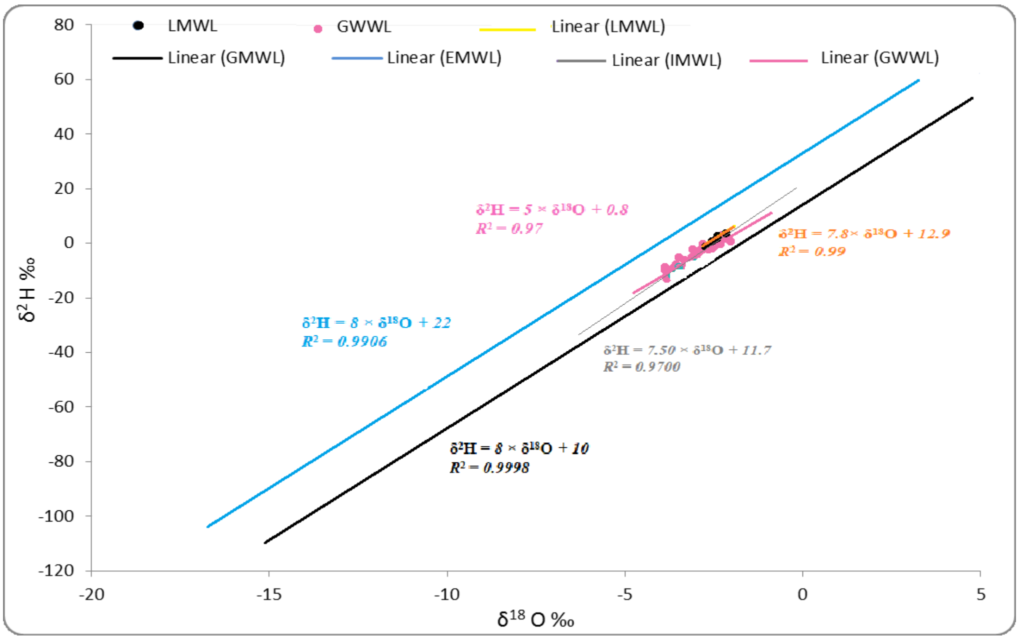

Figure 4: Plot of ^{18}O and ^{2}H of groundwater at wet season versus GMWL, EMWL and LMWL,

9. Results and discussions:

1-Physical and chemical properties reveal that was found that the properties BOD, COD, and DO were out of the standard indicating that the groundwater environment is reduced and difficult to recover from pollution and physical and chemical properties that were high than the standard (TDS, TSS, EC, THC).

2- Partial pollution of sulfate, nitrate and phosphorous due to the use of fertilizers.

3-T he contamination of manganese, molybdenum and boron was present in all models of the two seasons, and partly for lead and mercury due to fertilizers, agricultural activities, the presence of animal and poultry ranches, and theabsence of sewage system in the basin based on septic tank^{i} soil washing due to rain for polluted agricultural soils, which led to the pollution reaching the deep groundwater.

4-The results of stable isotope analysis of rainfall, and groundwater of the study area showed:
5- High values of δ^{18}O and δ^{2}H in rainwater were observed in the months of March and April, whereas low values were recorded in the months of December, January and February. Based on the correlation between δ^{18}O and δ^{2}H in monthly rainwater, the Local Meteoric Water Line (LMWL) and lies between EMWL and GMWL gives the following correlation:

$$\delta^{2}H = 7.8 \times \delta^{18} O + 12.9$$

6- Isotopic composition of rainwater showed a positive relation between air temperature and evaporation with enrichment of δ ^{18}O and δ^{2}H in precipitation of the study area, while δ ^{18}O and δ^{2}H were depleted with
increasing relative humidity and rainfall amount.
7- Deuterium excess contents in precipitation of the study area ranged from 12.85 ‰ to 20.8‰ highest was in November lowest was in March deuterium excess values were located between EMWL and GMWL, indicating that the origin of water vapor can be attributed to the Mediterranean sea.
8-The relation between δ^{18}O and δ^{2}H in groundwater showed that the water samples for both seasons are lies between EMWL and GMWL close to the local meteoric water line (LMWL).

The deviation from (LMWL) is due to the effect of evaporation and water mixing. The isotopic composition of groundwater for both seasons wet and dry showed a slight seasonal variation, where the highest values for δ^{18}O and δ^{2}H were recorded in the wet period and the lowest in the dry period. The deuterium excess values mean value ranged from 9.48 ‰ to 9.16 ‰ for the wet and dry season the high values of d- excess indicates that the water has suffered much more evaporation during the travelling stages.

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