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PREPARING ENVIRONMENTAL ISOTOPES DATABASES FOR DETERMINING GROUNDWATER AND SURFACE WATER RELATIONSHIPS IN IRAQ

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ABSTRACT

This study is prepared to constitute an isotopic database of Deuterium (δ^2H) and Oxygen 18 ($\delta^{18}O$) for groundwater and its relationship with the isotopic footprint for surface water The 311 samples of groundwater were collected between 2013 and 2021 and analyzed using a Liquid-Water Isotope Analyzer (LWIA). The study covered different regions of Iraq, including the Western region (Al-Anbar), Northern region (Kirkuk), Central Region (Samarra, Shirqat, Khanaqin, Baghdad, Karbala, Najaf, Diyala), and Southern region (Samawah ،Nasiriya, Diwaniyah, Basra). In addition, the 208 surface water samples were collected from different sources including (the Tigris, Euphrates, Diyala, and Shatt Al-Arab) rivers during the same period. The isotopic measurements showed a linear relationship between the two stable isotopes ($\delta^{18}O$, δ^2H) with a slope of 7.38 and an excessive deuterium reach to (-9.4597) compared with the excessive value of the domestic rain line of (14.15). It is defined according to the local meteoric water line equation (LMWL $\delta^2H = 7.7035 * \delta^{18}O + 14.158$**)**, which characterized a fingerprint of groundwater and showed the impact of the climate on it. The study showed a significant interaction between groundwater and surface water of the Tigris and Euphrates Rivers in the Southern region of Iraq, due to the aquifers in these areas being close to the surface, with depth ranges between (6 – 40 m), and high porosity that simulative of the sedimentary plain characterization. The samples of these areas calculated the highest and the lowest value for δ^2H of (12.04‰) and (-36.14‰) respectively. A similar result was found in the western regain. This region recorded the highest value of δ^2H (-4.42‰) and the lowest value (-42.2‰), the depth of the wells ranged between (2 – 22 m), which explains the relationship between the groundwater and the Euphrates River. However, the study indicated that the wells in Diyala Governorate, have depth ranges between (10 – 70 m) and were not affected by rainwater or Diyala River, with the highest and lowest value for δ2H of (4.66‰), (-38.54‰), respectively. On the other hand, the highest and lowest values of δ2H were recorded in the Khanaqin area with a value of (-13.48‰) and (-32.67‰) respectively.

INTRODUCTION

The scarcity of fresh water is one of the major threats facing humanity today. Iraq, as one of the arid to semi-arid countries, is severely affected by water shortage. Efforts must be intensified to protect the existing water resources, develop new sources of sustainable water supply, and improve the management of water resources. Groundwater is recharged by (rain,

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snow, and surface water intrusion into the soil), and recharge rates depend on the geology and weather conditions of the area, In addition to the abundance of vegetation cover on the Earth's surface. This groundwater finds its way to the surface of the earth, where it rises naturally in the form of springs or a person may dig a well to reach it. The movement of Groundwater down to recharge and then pull up again is a natural filtration process for it, which makes Groundwater under natural conditions one of the safest water sources for human use on earth, and even one of the best sources for producing agricultural crops. Hydrological studies indicate the high levels of groundwater in the sedimentary plain region, as their levels do not exceed a few meters and may reach less than one meter, while their depth increases as they move away from riverbeds (Appelo and Postma, 2004).

The application of environmental isotope techniques (both stable and radioactive) plays an important role in the assessment, management, and protection of water resources. Stable environmental isotopes (δ^2H, $\delta^{18}O$) are a powerful tool to study the sources of water bodies, allowing a better appraisal of their capacity and more rational exploitation. They also can be used in (correlation between aquifers, the interaction between surface and groundwater, sources of pollution and salinization of Groundwater, evaluate the sources and potential risk of contamination and investigation of the transport and fate of those contaminants, origin of groundwater, the efficacy of natural and artificial recharge, The exchange of water movement between lakes and adjacent groundwater aquifers, sources of recharge, and estimation of recharge (or depletion) in aquifer quantities. The change in the isotopic ratio of two isotopes of $^2H/^1H$ and oxygen of $^{18}O/^{16}O$ in water, which is known as $\delta^{18}O$, δ^2H, gives an idea of the source and quality of this water (Clarck and Fritz, 1997).

Isotopic technology plays an important role in evaluating and managing water and protecting its sources and it is an important tool for studying different types of water. The measurement of ($\delta^{18}O$, δ^2H) in different water sources is one of the possibilities for measuring different water sources, and this percentage is variable according to geographical location and time. The isotopic ratio of hydrogen and oxygen isotopes $^2H/^1H$ as well as $^{18}O/^{16}O$, which is called $\delta^{18}O$, δ^2H, is measured in relation to a reference model (2VSMOW)2 Vienna Standard Mean Ocean Water, gives an idea of the source and quality of this water (IAEA, 2007).

$$\delta = \left(\frac{R_{Sample}}{R_{Reference}} - 1\right) * 1000 \quad \text{(per mil, or ‰)}$$

There are many research studies in which the use of isotopic techniques in determining water quality and interference between ground and surface waters Using isotopic techniques to identify areas of overlap between Ground and surface waters in the Al-Shanafiya area in southern Iraq, (Ansam *et al*., 2017). studied Hydrochemical and isotopic resources Water in Haditha Dam, (Al-Paruany, 2013). studied an isotopic and geochemical study of water resources in the Samawah region, (Ajena, 2014), (Ali and Ajena, 2016). studied interaction between surface water and groundwater in north east of Diyala region (Nada *et al*., 2020).

This study aims to use isotopic techniques ($\delta^{18}O$, δ^2H) to determine groundwater recharge sources and interference areas. The possibilities between it and the surface water (Tigris, Diyala, and Euphrates rivers), in addition to preparing an isotopic database of isotopes ($\delta^{18}O$, δ^2H) for groundwater in Iraq to enhance the role of isotopic technology in studying mutual interaction between groundwater and Surface water.

THE HYDROGEOLOGY OF IRAQ

The general direction of groundwater movement in the western part of the low folds area (to the west of the Tigris River), from the north and northwest towards the south and southeast, except for the area north of Sinjar Mountain, where the direction of flow is towards the north and west towards the Iraqi – Syrian border. As for the direction of groundwater movement in the eastern parts of the region of the low fold (east of the Tigris River), it is from the north and north-east towards the south and south-west, with a local variation in the directions of movement, due to the topographic and structural characteristics of the region, while the general direction of groundwater movement is within a range The high folds in general, towards the southwest and south, with different local directions due to the presence of multiple hydrogeological boundaries within this range, with the complexity of the structures and topography of this region (Domenico *et al*., 1998). Figure 1, showing that The direction of groundwater movement in the south of the island and the upper sedimentary plain towards the drainage areas represented by the Tigris River and the Tharthar Lake depression, the general direction of the movement of groundwater in the southern desert in general towards the east and north-east, i.e. towards the drainage area along the right (western) bank of the Euphrates River, Hammar marsh and Shatt Al-Arab. The direction of groundwater movement in the Badra-Jassan Basin in eastern central Iraq is in two main directions, from east to west in the northern regions of the basin, and from northeast to southwest in the central and southern regions of the basin (Al-Naseri *et al*., 2023) (Ali *et al*., 2015), and the direction of groundwater movement in northeastern Maysan is from the northeast to the southwest, in line with the direction of the topographic elevation (Harpy *et al*., 2022). The northern and northeastern regions represent the recharge area, while the south and southwest regions represent the drainage areas. Groundwater moves in the Karbala – Najaf region, under the influence of the surface topography and the slope of the storage layers, and the flow is radial in all directions, but the final direction of the flow is toward the east of the region (Al-Sudani, 2018), (Ali and Kadham, 2018).

(Jassem and Goff, 2006), put a map of the depths of groundwater in Iraq, Figure 2, showing that these depths increase in the Western Desert towards the west, and range from 10 meters along the banks of the Euphrates River to more than 250 meters at the Iraqi – Jordanian and Saudi borders near the river. The Euphrates River and the depths of groundwater in the Jazira area range between 10 – 20 meters, while these depths in the foothills of the hills range between 20 – 30 meters, and the depths between Baghdad and Kut range from 1 – 5 meters, while the depths are shallow in the sedimentary plain sometimes reaching less than a meter (Al-Jiburi and Al-Basrawi, 2013).

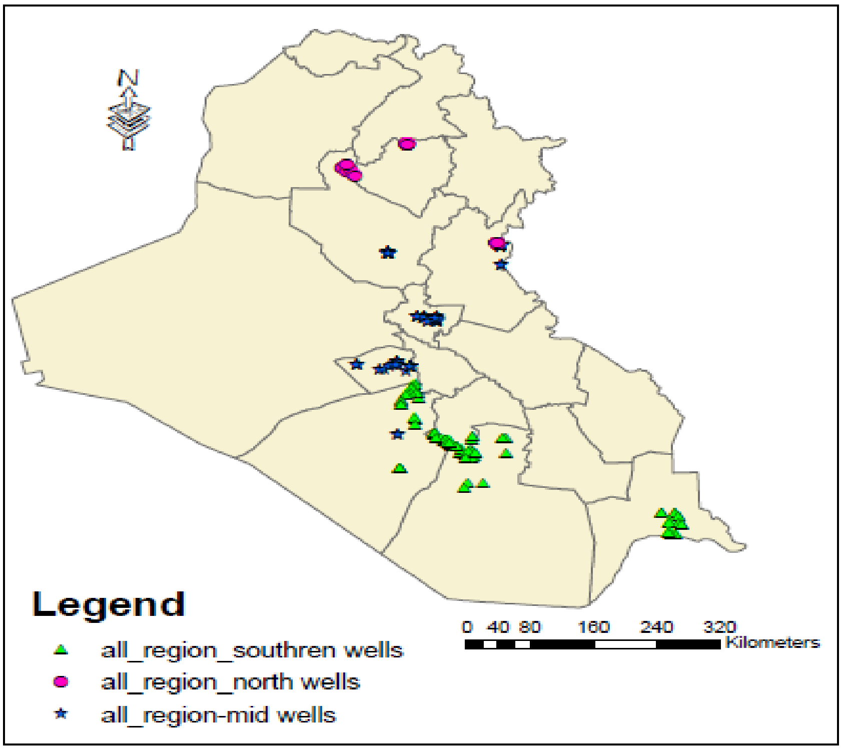

Figure 1: The region of groundwater samples in Iraq.

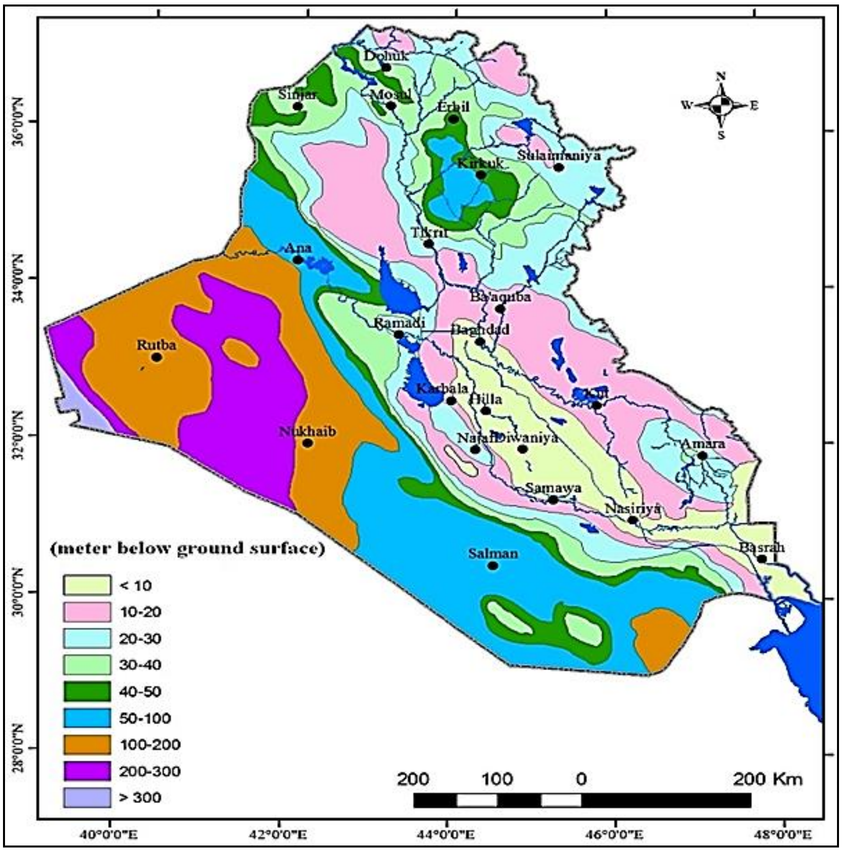

Figure 2: Depths of groundwater in different areas in Iraq.

MATERIALS AND METHODS

- **Study Area**

Iraq is located in the southwestern part of the Asian continent, between latitudes 290 and 380 North and longitudes 390 and 480 East It is distinguished by its geographical diversity and is divided into four main regions: The western plateau extends along the area west of the Euphrates River to the deserts of Syria, Jordan, and Saudi Arabia. The mountainous region starts from the south of the city of Kirkuk and extends east to Iran, and northern Turkey

The alluvial plain area southwest of Baghdad to the Gulf, which the Tigris and Euphrates rivers pass. The undulating region is a middle region between the alluvial plain and the mountainous region, starting between the Tigris River north of the city of Samarra and the Euphrates River north of the city of Hit and extending to Syria and Turkey, (Jassim and Goff, 2006).

Iraq's climate varies between temperate climates in the north, a subtropical climate in the east and southeast, and a desert continental climate in the west and southwest. Summer is characterized by dryness and extreme heat, while winter is characterized by little rain and low temperatures (Kapita, 2022).

- **Sample Collection**

Samples were taken under the instructions of the International Atomic Energy Agency (IAEA, 2007). One liter from each well for isotopic analysis of samples in addition to chemical and physical properties (pH, Ec). All bottles were marked with their coding, sampling date, and coordinates. Electrical conductivity was measured (pH, Ec) locally. As for the collected samples, they were placed in a cold box to be sent to the laboratory for measurement and analysis Stable isotopes (δ^2H and δ^{18}O) were measured. The samples of groundwater were collected between the years 2013 – 2021, which included the northern region of Iraq (Kirkuk) with (60) samples, the central region (Baghdad, Karbala, Najaf, Diyala, Khanaqin, Samarra, and Sharqat), with (124) samples, The western region (Al-Anbar) governorate with (13) samples, and the southern region (Samawah, Nasiriyah, Diwaniyah, and Basra) with (114) samples. The samples of Surface Water were collected between the years 2013 – 2021 (Tigris, Diyala, Euphrates rivers, and Shatt Al-Arab) (154, 33, 9, and 12) respectively.

- **Measurement**

The concentration of stable isotopes (δ^{18}O, δ^2H) was measured using a Liquid-Water Isotope Analyzer (LWIA) from (Los Gatos Research) model DLT100 in the Laboratory of Environmental Isotopes in The Ministry of Science and Technology. The standard solutions used in the calibration of the device Three local solutions (Internal Standards) Table 1. Available in the environmental isotope's laboratories in the Department of Environment and Water, relative to the international standards solutions in Table 2, which were calibrated in 1-8-2015 at the International Atomic Energy Agency IAEA.

Table 1: Content of the stable isotopes (δ^{18}O, δ^2H) for local standard solutions.

Standard Known Values	δ^2H (‰)	δ^{18}O (‰)
St 1 (FAO southern Iraq representing the stable isotope-rich concentration)	-11.43	-2.70
St 2 (north represents a low concentration of stable isotopes)	-61.7	-10.87
(Represents a sample with an average concentration) control St 3 Tigris	-37.5	-6.54

Table 2: Content of the stable isotopes (δ ^{18}O, δ ^{2}H) for international standard solutions.

Standard Known Values	δ2H (‰)	δ18O (‰)
VSMOW2	0	0
SLAP2	-427.5	-55.5
GISP	-189.8	-24.85

RESULTS AND DISCUSSION

Distribution of groundwater with global metric water line (GMWL) and local (LMWL). The isotope techniques were adopted to monitor water resources globally. A linear relationship was established between δ^{2}H and δ^{18}O values in meteoric water (δ^{2}H = 8 δ^{18}O + 10), and this regression line is referred to as the Global Meteoric Water Line (GMWL) (Craig, 1961). The first study on the isotopic composition of atmospheric waters in the Mediterranean region was established by Gat and Carmi (1970). Recently, several regional efforts have brought out local meteoric water lines (LMWL: δ^{2}H = 7.66 δ^{18}O + 14.19). (Al-Naseri *et al.*, 2022) for a few countries in the region. Further, few isotopic studies on the precipitation in different regions of Iraq have derived linear regression lines and they are used to describe the association of the rainwater to the groundwater for different places in the country. Stable isotope measurements (δ^{18}O, δ^{2}H) for (311) samples of groundwater samples during (2013 – 2021) (Figure 3). The linear relationship between stable isotopes (δ^{18}O, δ^{2}H) with a slope of 3.87 intersects with the slope of the equation of the local rain line for Iraq, and the excess of deuterium -9.4597, which is less than the surplus of local deuterium (14.158), which makes it different in the climate of Iraq, which is characterized by hot, dry, high humidity and low rainfall, the nature of groundwater. in Iraq, Figure 3.

$$\delta^2H = 7.66\ \delta^{18}O + 14.19 \text{ ....(1)}$$

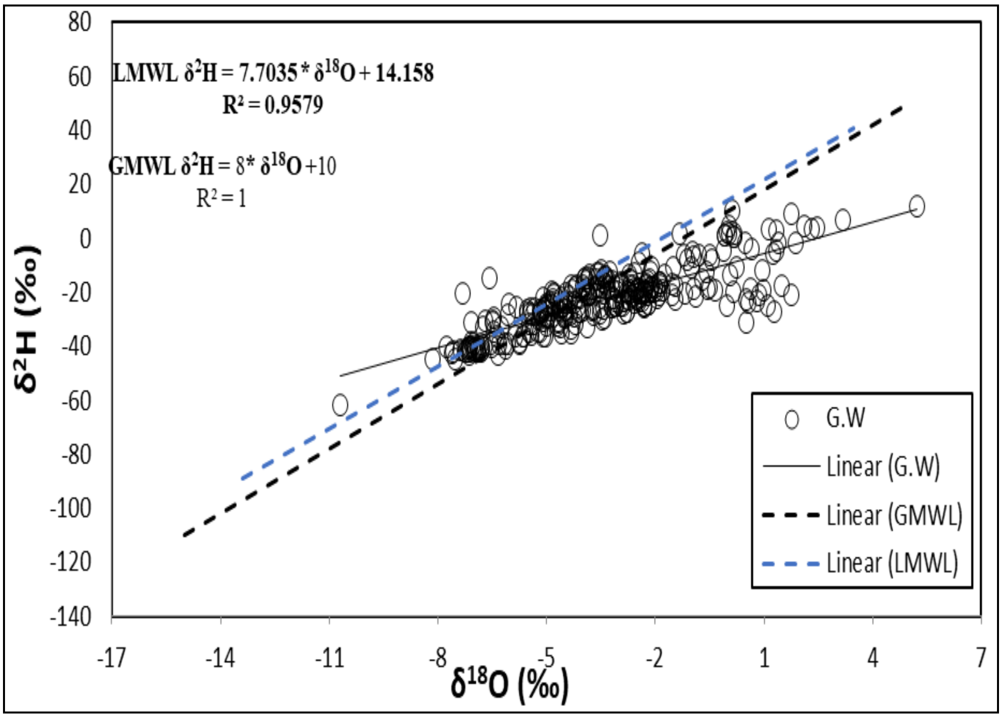

Figure 3: Environmental isotopes **δ**^{2}H, **δ**^{18}O plot of groundwater samples for the period of 2013 – 2021.

- **Isotopic Measurements of Groundwater and Surface Water in the Southern Region**

Table 3 shwing that the values of deuterium isotope for Groundwater in the southern region of Iraq (Samawah, Diwaniyah, and Basra) for the period from 2013 to 2021 showed a clear variation in their values, where the highest value of deuterium was (12.04‰) and the lowest value (-36.14‰) and the annual rate of concentration of deuterium values for the surface water. Table 4 shwing that the tigris River has the highest value of deuterium (-32.46‰) and the lowest is (-43.36‰), and the Euphrates has the highest value of deuterium (-21.47‰) and the lowest value (-45.22‰). The Euphrates are due to the geological nature of the sedimentary plain area, as the water-bearing reservoirs are porous, and most of the wells range in depth between (6 – 40 m), and they are not deep wells Figure 4.

Table 3: The lower and upper limits of the concentration of stable isotopes ($\delta^{18}O$, $\delta^{2}H$), d-excess, pH, Ec, and TDS in groundwater/ Iraq.

Region		No.	Depth	Oxygen-18	Deuterium	d-excess	pH	Ec ms/cm	TDS mg/L	zone
Baghdad	Max	124	12	-4.35	-26.68	18.32	8.28	6.55	2947.5	Central Region 2016 – 2021
	Mina		1	-7.62	-45.03	0	6.8	0.97	436.5	
Diyala	Max		70	2.47	4.66	24.00	8.53	16.39	11473	
	Mina		10	-6.03	-38.54	-15.86	6.53	0.993	311	
Karbala	Max		30	1.88	1.95	28.99	8.65	8.5	5100	
	Mina		10	-3.51	-31.13	-37.56	6	2.17	976.5	
Najaf	Max		10	-2.12	-19.20	2.22	7.3	3.56	2600	
	Mina		8	-2.79	-20.1	-2.24	7.21	3.45	2500	
Khanaqin	Max		13	-3.83	-13.48	25.31	7.50	3.20	1300	
	Mina		11	-7.07	-32.67	12.78	6.70	0.30	113	
Samarra	Max	60	8	-2.69	-17.39	16.69	8.45	11.32	4590	Northern Region 2017 – 2020
	Mina			-7.17	-42.85	4.13	7.47	2.00	1080	
AL-Sharkatt	Max		15	-3.08	-18.14	18.18	7.90	7.50	4500	
	Mina		9	-7.26	-42.20	6.50	6.00	2.00	850	
Kirkuk	Max		14	-3.72	-18.43	21.99	8.30	0.65	396	
	Mina		12	-6.50	-34.53	9.81	7.00	0.31	180	
Samawa	Max	114	30	5.21	12.04	38.40	8.71	82.90	78680	Southern Region 2013 – 2021
	Mina		8	-7.32	-35.40	-29.64	6.75	3.47	2600	
Diwaniyah	Max		30	-0.50	-18.40	9.50	8.06	53.60	34304	
	Mina		6	-5.62	-36.14	-14.40	7.00	2.40	1080	
Basra	Max		40	3.17	10.16	13.37	8.00	16.07	11115	
	Mina		10	-5.09	-30.69	-18.74	0.00	1.34	1080	
Anbar	Max	13	22	-0.10	-4.42	23.08	8.37	12.52	5634	Western Region 2017 – 2018
	Mina		2	-8.16	-42.20	-3.62	7.34	2.60	1170	

Table 4: The lower and upper limits of the concentration of stable isotopes ($\delta^{18}O$, $\delta^{2}H$), d-excess, pH, Ec, and TDS in river water/ Iraq.

Region		No.	Depth	Oxygen-18	Deuterium	d-excess	pH	Ec ms/cm	TDS mg/L	Sal	period
Tigris	Max	154	-	-5.62	-32.46	-	8.80	3.00	1355	7.00	2011 – 2021
	Mina		-	-7.24	-43.36	-	6.78	0.44	0	-0.01	
Euphrates	Max	33	-	-4.14	-28.40	-	8.50	4.80	2160	2.60	2013 – 2018
	Mina		-	-5.56	-38.76	-	6.90	0.76	318	0.10	
Diyala	Max	9	-	-4.74	-26.34	-	7.92	2.50	1055	1.20	2018 – 2019
	Mina		-	-5.04	-27.13	-	6.76	0.39	204	0.00	
Shatt Al-Arab	Max	12	-	-0.48	-4.14	-	7.28	60.20	28725	40.20	2020 – 2021
	Mina		-	-2.88	-13.43	-	6.69	3.63	1488	1.80	

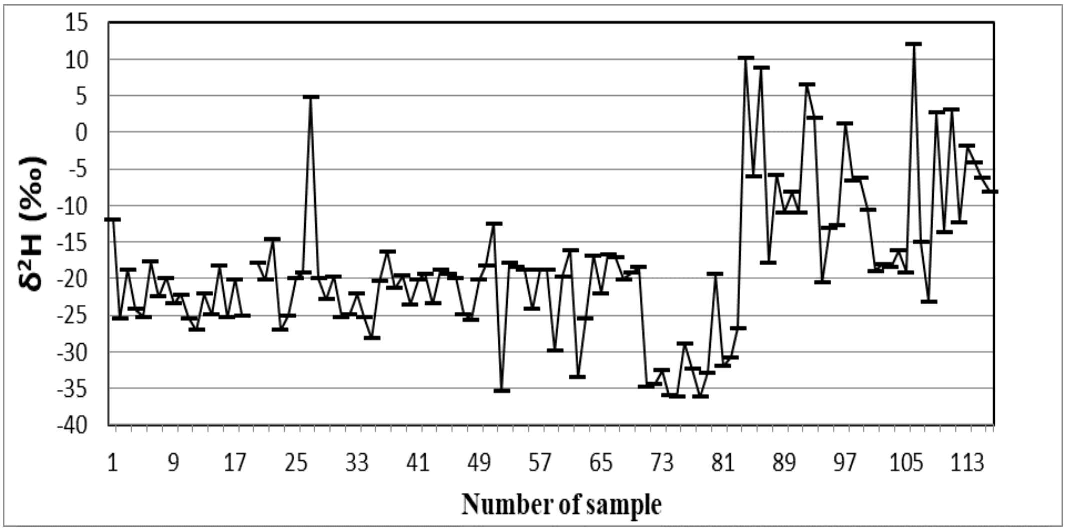

Figure 4: represents the values of δ ^{2}H wells in the southern region of Iraq Samawah, Diwaniyah, and Basra for the period from 2013 to 2021.

- **Isotopic Measurements of Ggroundwater for the Central Region**

The values of isotope deuterium for wells in the central region of Iraq (Baghdad, Karbala, Najaf, and Diyala) for the period from 2016 to 2021 showed fluctuation in their values, especially those whose depth ranges between (1 – 30 m), which not deep wells, which reflects the impact of these wells with rainwater. And the water of the Tigris and Euphrates rivers, where the highest value of deuterium was (1.95‰) and the lowest value was (-45.03‰). When compared with the annual rate of deuterium concentration of the Tigris and Euphrates rivers for the period (2013 – 2021) it ranged from (-43.36‰) to (-32.46.‰) for the Tigris River and from (-38.76‰) to (-28.40‰) for the Euphrates River. Except for some other wells in Diyala Governorate, the highest value of deuterium was (4.66‰) and the lowest value (-38.54‰), and their depths ranged between (10 – 70 m). There was no clear effect of rainwater and Diyala River water when compared with the annual average of Deuterium for the Diyala River, in which the values of deuterium range from(-27.13‰ to -26.34‰) Table 3, Table 4, Figure 5.

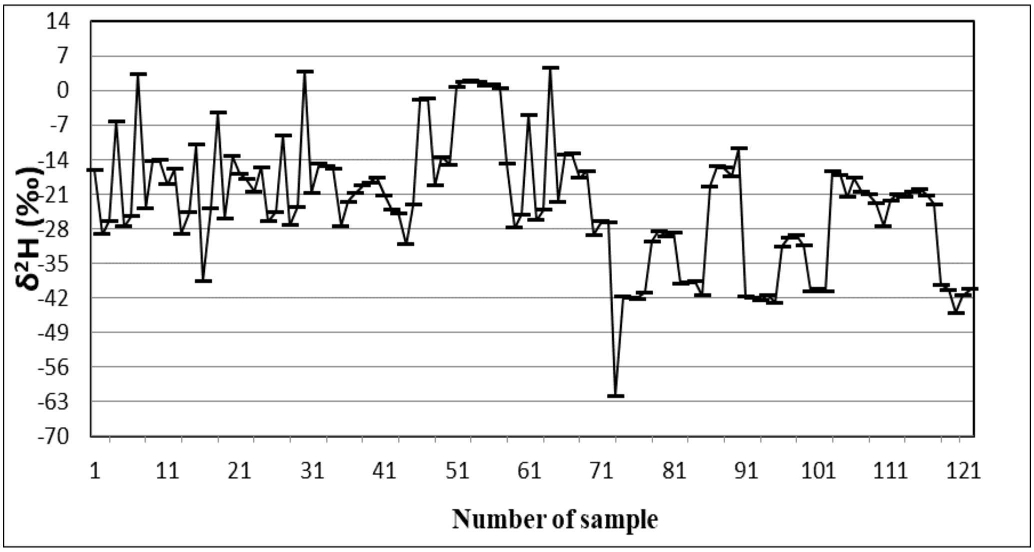

Figure 5: represents the fluctuation of the values of ^{2}H in the wells of the central region (Baghdad, Diyala, Karbala, and Najaf) for the period from 2013 to 2021.

- **Isotopic Measurements of Groundwater for the Western Region**

Table 3 Showed the values of deuterium isotope for groundwater wells in the western region, of Anbar for the period from (2017 – 2021) conspicuous fluctuation in their values that reflect the impact of groundwater on rainwater and surface water representing the Euphrates River, where the highest deuterium value is (-4.42‰) and the lowest value (-42.2‰) and the average annual concentration of deuterium in the Euphrates River, which ranged from (-38.76‰) to (-28.40‰) and most of the wells' depth ranges between (2 – 22 m) and not deep wells Table 4 and Figure 6.

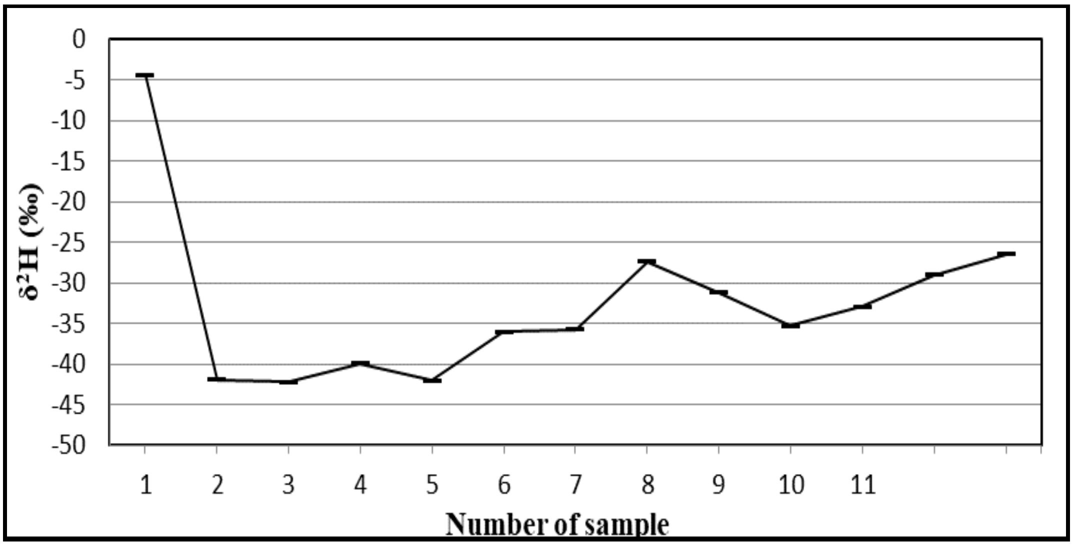

Figure 6: Fluctuation in the values of isotope deuterium in wells in the western region, Anbar from (2017 – 2021).

Showed the values of deuterium isotopes in the groundwater of the wells of the northern region (Samarra, Sharqat, and Kirkuk) the northern region (2017 – 2020) conspicuous fluctuated similarly to the central and southern regions where the lowest value (-42.85‰) and the highest value (-17.39‰), as a result of the effect of groundwater with The waters of the Tigris and Euphrates rivers and rain as a result of the geological nature of the area, which is a middle area between the sedimentary plain and the adjacent area, starting between the Tigris River north of the city of Samarra and the Euphrates River north of the city of Hit to reach Syria and Turkey, and most of the wells are not deep (8 – 15 m) Figure 7.

While the deuterium isotope values in the groundwater of the Khanaqin region for 2019 were higher compared to the central, southern, and western regions where they were the lowest value (-32.67‰) and the highest value (-13.48‰), due to the geological nature of the Khanaqin region being rocky and non-porous, the effect of Rainwater and the water of the nearby rivers have little to no groundwater in that area Figure 8.

showed there is a good relationship between stable isotopes and electrical conductivity values (Ec mS/cm) for (311) samples of groundwater for the period (2013 – 2021) including the central region (Baghdad, Karbala, Najaf, and Diyala), whose values ranged from 0.97 mS/cm to 16.39 mS/cm, and the northern region (Samarra, Sharqat, and Kirkuk) has values ranging from 0.30 mS/cm to 11.32 mS/cm, and the western region (Al-Anbar) ranges from 2.60 mS/cm to 12.52 mS/cm, while the southern region (Samawah, Diwaniyah, and Basra) its values were high, the highest value was in Samawah 82.9 mS/cm and Diwaniyah 53.6 mS/cm, which reflects the nature of the underground reservoirs located within the geological formations (Dammam Formation) which are dominated by layers of gypsum and anhydrides. As for Basra, it had the highest value of 16.07 mS/cm due to the relative impact of the Basra groundwater on the waters of the Arabian Gulf, Table 3 and Figure 9.

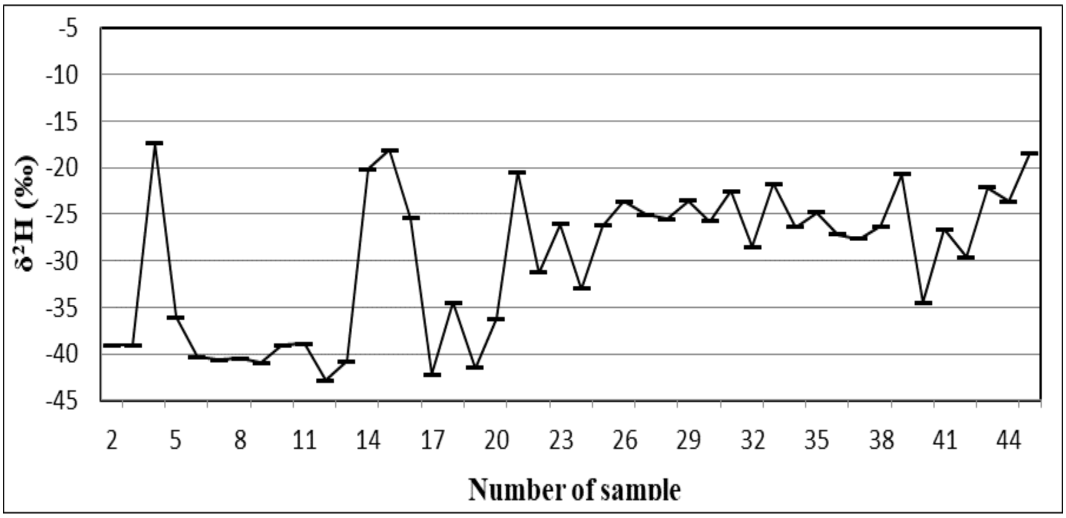

Figure 7: Fluctuation isotope values in wells (Samarra, Shirqat, and Kirkuk) 2017 – 2020.

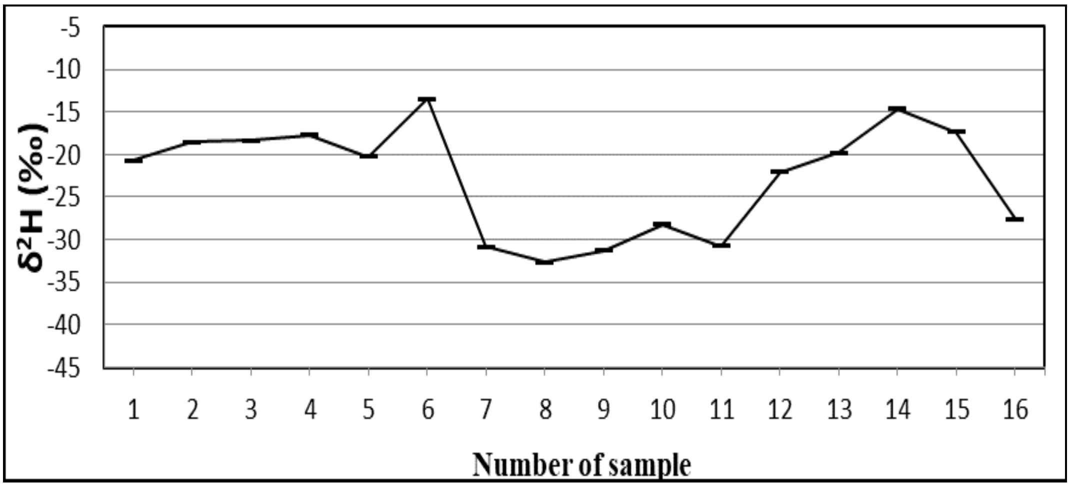

Figure 8: Fluctuation of the values of isotope deuterium in the wells of the Khanaqin region.

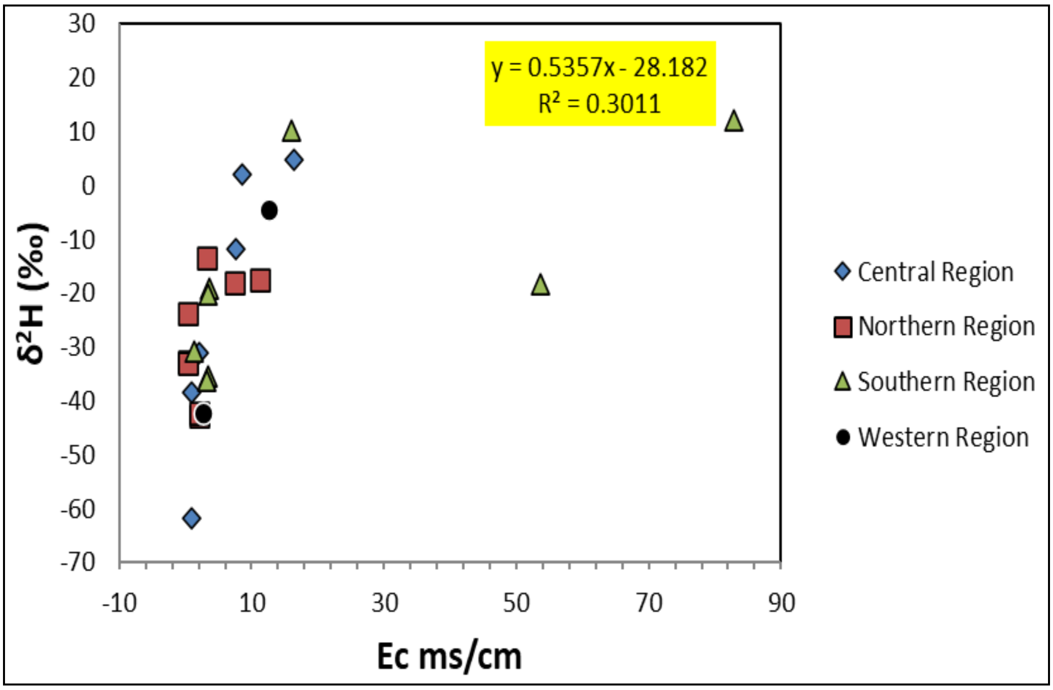

Figure 9: Relationship between stable isotopes (^{18}O,^{2}H) and electrical conductivity values of groundwater for the period from 2013 to 2021.

CONCLUSION

- The linear relationship between deuterium and oxygen-18 for samples groundwater ($\delta^2H = 3.87 * \delta^{18}O - 9.4597$) showed a decrease in the value of excess deuterium compared to its value in the Local meteoric water line $\delta^2H = 7.66\ \delta\ ^{18}O + 14.19$ Because of the nature of Iraq's climate, which is characterized by hot dry summers, low temperatures, high humidity, and less rainfall in winter have a clear impact on the nature of groundwater.
- The interaction of groundwater in the southern region of (Samawa, and Basra) with surface water representing the Tigris and Euphrates rivers due to the geological nature of the sedimentary plain area in Mesopotamia.
- There is a clear relationship between the depth of water in the wells and the isotopic value of that water, as some wells whose depth ranges between (1 – 30 m), especially in Baghdad and Karbala, are affected by the waters of the Tigris and Euphrates rivers, while some other wells in Diyala governorate whose depth ranges between (40 – 70 m) do not appear affected by and Diyala River water.
- The impact of groundwater in Anbar Governorate for the period (2017 – 2021) by surface water representing the Euphrates River, and most of the wells range in depth between (2 – 22 m) and are not deep.
- The increase in the concentration of stable isotopes in the Khanaqin region compared to the central, southern, and western regions, is due to the geological nature of the Khanaqin region being rocky and non-porous, so the effect of rivers is small on groundwater.
- Some wells in (Samarra, Shirqat, and Kirkuk), which are not deep wells ranging in depth (8 – 15 m), by the waters of the Tigris and Euphrates Rivers due to the geological nature of the area, which is a middle area between the sedimentary plain and the mountainous area.

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CONFLICTS OF INTEREST

The authors have declared no conflict of interest. The work described here has not been submitted elsewhere for publication, in whole or in part, and all the authors listed have approved the manuscript that is enclosed.

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