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Study of the Water Quality in the Tigris River Using Isotopic and Hydrochemical Techniques in South-Eastern Iraq

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Abstract

Isotopes and Hydrochemical analysis in groundwater were attempted in the study area of Maysan Governorate, located in southern Iraq to learn more about water quality conditions and geochemical evolution. The study also relied on the analysis of water samples for data on the main ions (Cations and Anions), as the water of the Tigris River was dominated by ions (Ca^{+2}, Mg^{+2}, Cl^{-} and SO_4^{2-}), and the water quality was classified according to the Piper alkaline classification of the calcium chloride type. Through the relationship between δ^2H and $\delta^{18}O$, there is a convergence for all areas except near the Amara Dam, where the results showed a slight depletion in the values of stable isotopes. The Umm al-Jari Canal (One of the canals that flows into the Tigris River) water system had a different isotopic fingerprint from the fingerprint of the water of the Tigris River. The rates of radioactive isotope Radon-222 (^{222}Rn) concentrations for samples from the study area ranged between (0.149 - 0.329) Bq/L and were within the normal permissible limits for radon concentration in water. The sodium absorption rate was between 12-11, which is within good water, and river water in the study area can be used for irrigation purposes. Measurement of four heavy elements, including Cadmium (Cd^{+2}) Zinc (Zn^{+2}) Copper (Cu^{+2}), and Lead (Pb^{+1}), were carried out for water samples in the study area, and all concentrations were within the permissible limits, except for the cadmium element, which was higher than the permissible limit, for drinking purposes and according to the Iraqi standard (IQS).

Keywords: *Kut , Maysan, Tigris River, Deuterium, Oxygen-18, Radon-222*

1. Introduction

The scarcity of freshwater is one of the greatest threats facing humanity today. It is not only limited to the scarcity of water supplies but also extends to the deterioration of water quality. The efficiency of wastewater treatment plants, discharging into rivers, is not high, resulting in a substantial of pollution to surface water (Al-kubaisi et al., 2020). Understanding the hydro-chemical properties of groundwater and how they evolve during water circulation processes is required to effectively protect and utilize valuable water resources and predict changes in surface water environments (Al-paruany et al., 2013).

Isotope hydrology has become a widely used technique for rational management of the global water crisis (Heydarizad et al., 2021). The isotopic composition of oxygen and hydrogen in natural water (precipitation, groundwater, and surface water) provides important information to study the origin of water as a function of geohydrological and meteorological factors such as the source of water vapor and climate change, processes involved in groundwater (water residence and travel times in aquifer systems, interrelationships between surface and groundwater, sources of pollution and salinization of groundwater, and the exchange of water movement between lakes and adjacent groundwater aquifers (Hamdan. et al., 2016).

In nature, two stable isotopes of hydrogen (^1H, protium and ^2H, deuterium) and three stable isotopes of oxygen (^{16}O, ^{17}O, ^{18}O). 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 abundance of the isotopes ^2H and ^{18}O in ocean waters is close as follows: $^2H/^1H = (155.95 \pm 0.08) \times 10^{-6}$, $^{18}O/^{16}O = (2005.20 \pm 0.45) \times 10^{-6}$ (Gat et al., 1996). These values are close to the average isotopic composition of ocean water given by Craig. The heavy isotope content of water samples is usually expressed in delta (δ) values defined as the relative deviation from the adopted standard representing the mean isotopic composition of the global ocean:

$$[\delta \text{‰}] = \left(\frac{R(sample)}{R(References)} - 1\right) * 1000 \tag{1}$$

Where R Sample and R Reference standard for the isotope ratio(R) are the atom ratio ($^2H/^1H$ and $^{18}O/^{16}O$) in the sample and the reference material (standard), respectively. The isotopic concentration or abundance ratios are generally referred to as those of a specifically chosen standard. The internationally accepted standard for reporting the hydrogen and oxygen isotopic ratios of water is Vienna Standard Mean Ocean Water, V-SMOW, positive δ values indicate that the water sample is enriched in its isotopic concentration, while negative values refer to depleted water samples. (Gat et al., 1970). ^2H and ^{18}O isotopic compositions of meteoric waters (precipitation, atmospheric water vapor) are strongly correlated. If δ^2H is plotted versus $\delta^{18}O$, the data cluster along a straight line will be as follows:

$$\delta^2H = 8\delta^{18}O + 10 \tag{2}$$

Radon-222 (^{222}Rn) is a naturally occurring radioactive

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gas, originating from the decay of Radium-226, a decay product of Uranium-238(^{238}U) found in rocks and soils. The most prevalent radioactive isotope of radon in the environment is Rn-222 (^{222}Rn), which has a relatively short half-life of 3.8 days. While there are two other naturally occurring isotopes, Rn-220 (Thoron) and Rn-219 (Actinon), their short half-lives (5.66 and 3.92 minutes respectively) make them negligible in comparison. Consequently, the concentration of Radon-222 (^{222}Rn) in groundwater can be significantly higher than its rate in surface water (Al-Harahsheh et al., 2020).

Isotopic techniques are utilized in various research studies to evaluate water quality and identify points of interaction between groundwater and surface water. Kamal (2015) Isotopic study of water resources in a semi-arid region, Western Iraq. Environmental Earth Sciences. Hussien (2021) used stable isotopes and Hydrochemical analysis of water samples to study the interaction between the water resources of the Euphrates River and groundwater in a limited area in the western plateau of Iraq. Al-paruany (2013) studied Hydrochemical and isotopic resources water between Hadith Dam and Al-Baghdadi Dam.

This research aims to assess the water quality of the Tigris River specifically examining the extent of environmental pollution’s impact on the Tigris River’s water, to protect water resources, and predict environmental changes in surface water using isotopic technologies, supported by hydro chemical analyses and heavy metal measurements. This is intended to support hydrological studies and formulate sound water policies.

2. The Study Area Location and Description

The study area is located in the cities of Kut and Amara in southern Iraq and the center of Maysan Governorate, about 320 kilometers to the southeast of the capital, Baghdad. It is on the banks of the Tigris River and about 50 kilometers from the Iranian-Iraqi border and a few kilometers from the marshes area, within the following coordinates (45^{0}47’10.7” – 47^{0}35’52.3”) E (31^{0}51’2.2”– 32^{0}64’35.4”) N. The climate of the region is subject to the climate conditions of arid and semi-arid regions, which are characterized by cold winters with little rain and hot, dry summers. The Tigris River forms the backbone of irrigation operations in the Amarah Governorate by penetrating it from its far north. Up to its southern borders, a number of canals that originate from Iranian territory flow into the Tigris River, including the Jabab Canal, which is located in the east of Kut and belongs to the Sheikh Saad District, extending from the Iranian border in the east to the Tigris River in the west. Other canals are the Umm al-Jari Canal (Figure 1) (Jummah et al., 2020).

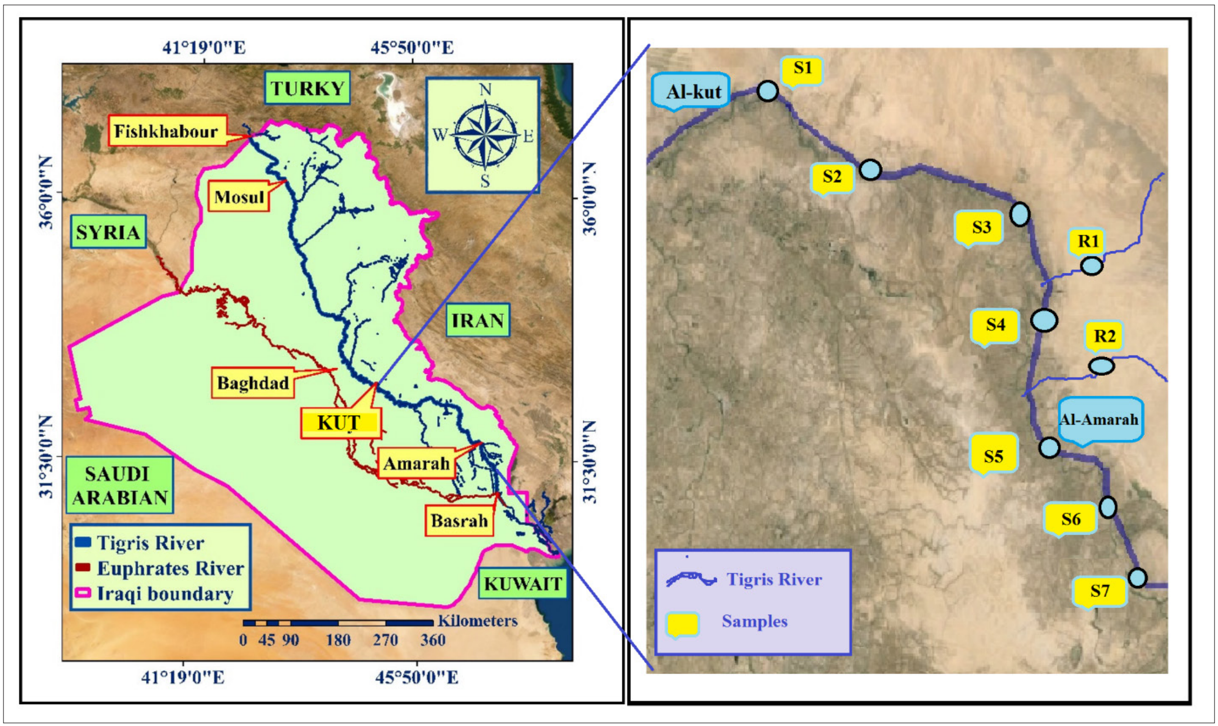

Figure 1. Location map of the study area showing the Surface water sampling sites

3. Materials and Methods

Eighteen water samples were collected from different locations along the Tigris River, during the months of March (Wet seasons) (9 samples) and August (Dry season) (9 samples) in 2022, including that of the Al-Kut Dam (S1), After the Al-Kut Dam (S2), Sheikh Saad area (S3), Ali Al-Gharbi area (S4), Ali Al-Sharqi area (S5), and the Al-Amara Dam (S6) after Al-Amara Dam (S7) (Table 1). Additionally, two samples were taken from the canals that flow into the Tigris River, namely the Jabba Canal (R1) and the Umm Al-Geri Canal (R2). Water temperature, electrical conductivity, hydrogen number, and total dissolved solids were measured directly in the field and the coordinates of each sampling site were recorded using a Global Positioning System (GPS). The chemical analyses and analysed for isotopic of samples were carried in the laboratory of water research Centre/ Ministry Science and Technology using Liquid-Water Isotope Analyser (LWIA) was used for determining ^{18}O,

^{2}H, and Use the Durridge Company RAD7 radon detector, which is designed to measure radon gas in water with high accuracy and a wide range of concentrations (Durridge Radon ,2013). The samples for hydrochemical measurement by ion chromatography.

Table 1. Locations of the Study Area.

No.	Stations	Symbol	Latitude	Longitude
1	Al-Kut Dam	S1	32^{0}64’35.4”N	45^{0}47’10.7”E
2	After Al-Kut Dam	S2	32^{0}59’24.3”N	45^{0}69’49.5”E
3	Al- Sheikh Saad	S3	32^{0}34’12.1”N	46^{0}16’07.4”E
4	Ali Al-Gharbi	S4	32^{0}28’14.6”N	46^{0}31’07.4”E
5	Ali Al-Sharqi	S5	32^{0}07’19.0”N	46^{0}44’44.7”E
6	Al-Amara Dam	S6	31^{0}51’2.2”N	47^{0}08’29.3”E
7	after Al-Amara Dam	S7	31^{0}54’55.6”N	47^{0}35’52.3”E
8	Al- Jabba Canal	R1	32^{0}39’28.7”N	46^{0} 22’54.3”E
9	Umm Al-Geri Canal	R2	32^{0}27’54.1”N	46^{0}41’15.3”E

4. Results and Discussion

4.1 Physico-chemical Properties of Water

Surface water contains different types of salts in different proportions and concentrations depending on the source and movement of this water. The results show that (Table 2) pH levels for both wet (March) and dry (August) seasons ranged from 6.81 to 7.79, and these values did not exceed the permissible limits (6.5-8.5) for drinking and irrigation purposes, as specified by WHO (2017). The Total Dissolved Solids (TDS) rates are varied, with a range of 574.16 ppm at the front of the Kut Dam (S1), while there was a significant increase in the after Amara Dam (S7), reaching 914.77 mg/L during the dry season (August). The reason for this result is attributed to its susceptibility to the leaching process from agricultural lands, as well as the inadequate drainage of water from Iranian territories and its exposure to evaporation due to high temperatures in dry season. However, all values in both seasons remained within the allowable limits of ppm (500-1000) mg/L as per WHO (2017) standards (Djoudi et al., 2023).

Table 2. Physico-chemical properties, Temperature (T) and Humidity (R.H) of samples in the study region.

Sample	Wet season		Dry season		Month	Av.T. (°C)	R.H. (%)
	pH	TDS	pH	TDS			
S1	7.23	471.37	6.81	574.16	Feb.	21.5	35.4
S2	7.21	533.37	7.2	581.77	March	26	28.2
S3	7.35	591.57	6.88	687.8	April	35.7	27
S4	7.1	689.7	6.93	711.44	May	39.82	15
S5	7.1	748.12	7.23	761.94	June	47.18	16.6
S6	7.5	793.2	7.31	851.26	July	49.33	12.9
S7	7.71	864.47	7.32	914.77	Aug.	53.17	17.9
R1	6.78	8186.91	6.78	8196	Sep.	43.33	15.2
R2	6.83	1093.85	6.83	1011	Oct.	37.86	22.5
WHO (2017)	6.5 -8.5	500-1000	6.5 -8.5	500-1000	Nov.	29.50	25.7

4.2 Cationic and Anionic Concentrations

The concentrations of cations (Calcium, Magnesium, Sodium, and Potassium) and anions (Chlorides, Sulphates, and Bicarbonates) in the water of the Tigris River in the study area were within the permissible limits internationally and locally, respectively (WHO, 2017) (Table 3). The results of chemical tests for the Canal Umm Jari (R1) water sample showed a noticeable increase, as the total values of dissolved salts reached (8168) mg/L. The reason is that it is affected by the drainage process by agricultural lands, in addition to the lack of water drainage from Iranian lands and its exposure to the evaporation process due to high temperatures. The presence of nitrate ions in water is evidence of pollution from the leakage of sewage, in addition to the second source of nitrates being nitrogen fertilizers. Nitrate values in all water samples of the Tigris River ranged from (48-65) mg/l, where we notice a relative increase of the permissible values, which are 45 mg/L (El-Naqa et al., 2021).

The reason is attributed to human activities resulting from agricultural activities, as the study area was agricultural in nature. According to the Piper Diagram, all samples in the water of the Tigris River in the study area indicate earth alkaline water with a higher percentage of alkali and prevailing sulphate and chloride, (SO_4^{2-} - Cl^- and Ca^{2+} - Mg^{2+}) (permanent hardness); (noncarbonated hardness exceeds 50 %) calcium chloride type. Figure (2) (Piper et al.,1944).

Table 3. Major Cation and Anion Concentrations Samples Water for Wet and Dry Seasons.

Sample	Ca^{+2} mg/L		Mg^{+2} mg/L		Na^{+} mg/L		K^{+} mg/L		Cl^{-1} mg/L		So_4^{-2} mg/L		Co_3^{-2} mg/L		Hco_3^{-1} mg/L		No_3^{-1} mg/L	
Season	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*
S1	56	70	30	40	60	73	1.3	1.9	112	120	160	207	4.96	8.54	22.11	23.7	25	30
S2	62	71	38	38	68	76	1.5	1.9	128	132	178	200	5.7	8.7	24.17	24.1	28	30
S3	65	75	43	31	78	79	1.9	2.3	140	148	190	257	6.5	10.5	29.17	32.0	38	53
S4	77	79	51	33	92	97	2.1	2.3	164	174	218	233	7.1	13.14	36.50	40.0	42	40
S5	80	85	58	36	102	112	2.1	2.7	175	180	240	250	9.24	13.24	36.78	43.0	45	40
S6	85	91	62	43	112	118	1.8	2.8	195	218	243	273	9.46	15.46	42.94	48.0	42	42
S7	93	98	70	48	119	127	2.3	2.9	215	230	257	277	11	17.7	49.17	52.0	48	65
R1	743	768	520	540	1003	1023	25	27	2018	2034	3015	3043	144	154	400	429	318	325
R2	116	125	60	67	134	154	2.5	3.4	287	301	366	387	16.2	18	45.11	50.4	67	72
WHO	75-200		50-150		200		12		250-400		250-400				300-500		45	

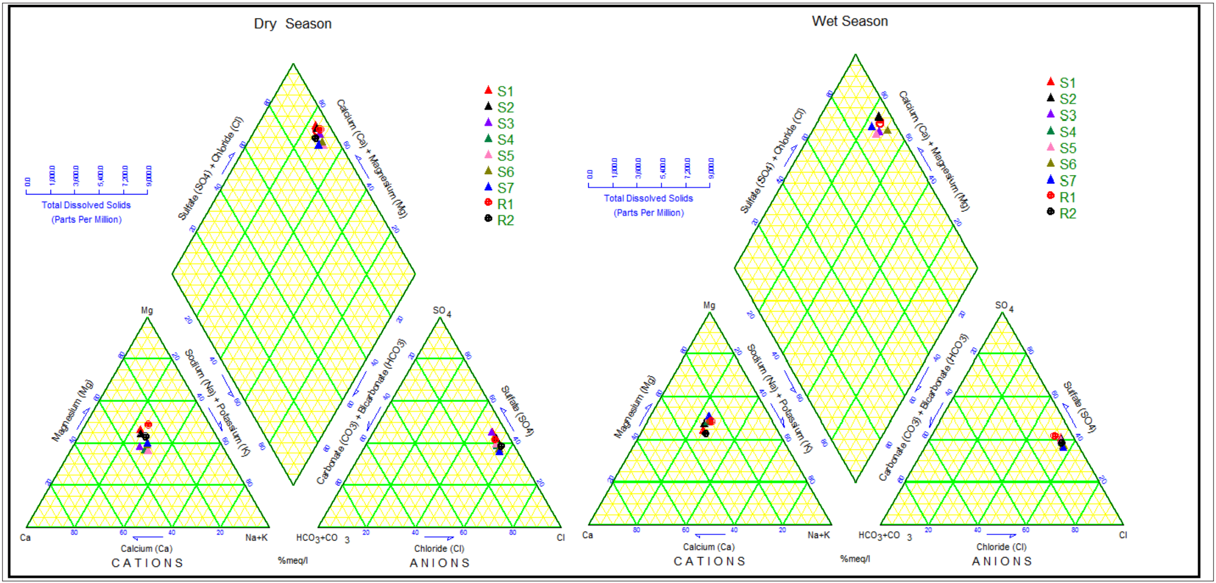

Figure 2. Type of water according Piper diagram

4.3 Heavy Element Concentrations

Pollution with heavy metals primarily resulting from human activities poses a serious health problem due to their cumulative nature, even at low concentrations. Additionally, they are non-degradable and have a severe impact on living organisms. Measurements were conducted for four trace elements Cadmium (Cd), Zinc (Zn), Copper (Cu), and Lead (Pb) in water samples from the study area or both wet and dry seasons. The average values of concentrations of Zinc (Zn) range between (0.75 mg/L - 0.94 mg/L), falling within the Iraqi standard specifications for drinking water in 2009, which set a maximum limit of 3 mg/L. Average values of concentrations of Lead (Pb) and Nickel (Ni) range between (0.008 - 0.005), within the permissible limits of (0.02, 0.01) mg/L respectively.

On the other hand, the average concentrations of cadmium (Cd) range between 0.06 mg/L and 0.078 mg/L, which are elevated at all sites compared to the Iraqi standard specifications, setting a maximum limit of 0.003 mg/L. The increase in cadmium levels in water samples can be attributed to the reduced level of the Tigris River, coupled with waste from factories and sewage water flowing into it. Industrial facilities frequently discharge cadmium-laden waste into water bodies, resulting in its accumulation. Additionally, cadmium from fertilizers and pesticides used in agriculture can enter water sources through runoff from farmland.

4.4 The Sodium Absorption Rate (SAR)

The Sodium Adsorption Ratio (SAR) is a measure used in hydrology and soil science to evaluate the suitability of water for irrigation purposes. It indicates the relative concentration of sodium ions to other (such as calcium and magnesium) in the water

$$\boldsymbol{SAR} = \frac{\boldsymbol{Na}}{\sqrt{\frac{\boldsymbol{Ca+Mg}}{\boldsymbol{2}}}} \qquad (3)$$

where SARfor Na^{+}, Ca^{2+} and Mg^{2+} concentrations of ions in mill equivalents per liter (meq/L) units is examined.

Reassessing the hydrochemical characteristics of irrigation water is paramount in evaluating soil leaching issues. The detrimental impacts of elevated Sodium Adsorption Ratio (SAR) levels include salt accumulation on soil surfaces, impeding water penetration to plant roots. Certain agricultural crops exhibit high sensitivity to SAR values, rendering the use of water with high sodium concentrations in irrigation impractical. Hence, SAR values for irrigation purposes are categorized accordingly; SAR < 10 is deemed excellent for irrigation, while SAR ranging from 10 to 18 is classified as good (APHA, 2012).

The results of (SAR) were counted for Al-Kut Dam (S1), After the Al-Kut Dam (S2), Sheikh Saad area (S3), Ali Al-Gharbi area(S4), Ali Al-Sharqi area(S5), Al-Amara Dam (S6), after Al-Amara Dam (S7) and the Umm Al-Geri Canal (R2) ranged from (1.6-2.7) for both dry and wet seasons. However, the results of (SAR) Jabba Canal (R1) were (6.7-6.9). All SAR values within the study area fell within the excellent range for irrigation water quality. However, the SAR value of the (R1) sample showed a slight elevation, which can be attributed to its higher sodium content.

4.5 Isotopic Deuterium (δ^2H) and Oxygen-18 ($\delta^{18}O$)

Table 4 shows the results of isotopic analyses for the stations studied on the Tigris River and some of the systems that flow into it. The δ^2H isotope measurements for the Tigris River water in the study area during the wet season (March) were (-37.36 to -40.7) ‰, and for $\delta^{18}O$, they were (-7.87 to -6.59) ‰. These values were consistent across all areas, except in the vicinity of the Amara Dam (S6) that has more elevated concentrations. The variation in stable isotope values suggests the influence of evaporation and low discharge. Notably, there was a distinct contrast in the stable isotope results for the Tigris River between the dry and wet seasons, with values ranging from (-39.95 to -33.09) ‰ for δ^2H and (-5.55 to -7.78) ‰ for $\delta^{18}O$ during the dry season. This difference reflects the impact of higher summer temperatures and water evaporation, leading to reduced water levels in the Tigris River due to decreased discharge. The water from the Umm Jiri Canal (R1) exhibited different isotopic signatures compared to the Tigris River, with values of (-17.9 to -3.98) ‰ for δ^2H and $\delta^{18}O$, respectively. On the other hand, the isotopic concentrations of δ^2H and $\delta^{18}O$ in the water samples were measured at (R2) (35.63, -6.49) ‰, respectively. Notably, the isotopic composition of (R2) closely resembles that of the Tigris River, indicating a significant similarity between the water samples from the Tigris River and those from (R2), in contrast to the values observed in the water sample (R1).

Table 4. Isotopes data (δ2H, δ18O, d-excess) of samples in the study region.

Sample	Wet season			Dry season		
	δ^2H‰	$\delta^{18}O$‰	d-excess	δ^2H‰	$\delta^{18}O$‰	d-excess
S1	-40.7	-7.2	18.5	-39.95	-7.2	17.65
S2	-40.5	-7.78	18.4	-39.89	-7.78	17.55
S3	-40.7	-7.75	18.1	-39.88	-7.75	16.52
S4	-40.35	-7.53	17.4	-37.05	-7.53	16.34
S5	-39.35	-7.43	17	-36.38	-6.67	15.41
S6	-37.88	-6.92	16.7	-33.09	-5.55	12.93
S7	-37.36	-6.59	15.4	-33.67	-5.65	11.54
R1	-17.9	-3.98	13.9	-16.9	-3.78	12.9
R2	-35.63	-6.49	16.3	-31.63	-5.49	15.3
*VSOMW2	0	0		0	0	
*SLAP2	-427.5	-55.5		-427.5	-427.5	
*GISP	-189.8	-24.85		-189.8	-189.8	

VSOMW2, SLAP2, GISP: Standard Solution

Figure 3 depicts the distribution of water samples from the Tigris River in the study area and compares it with the Global Meteoric Water Line (GMWL), which serves as a reference line for identifying water sources and understanding the physical processes influencing isotopic compositions in meteoric waters. Additionally, the Local Meteoric Water Line (LMWL) is represented (Al-Paruany et al., 2020), consisting of isotopic values derived from a mixture of local water samples, particularly from rainfall (rain and snow) (Kattan,1997). This line acts as a reference to determine water sources based on regional factors such as variations in rainfall, temperature changes, evaporation, and fractionation processes. These factors collectively influence the relationship between deuterium and oxygen-18 isotopes, causing deviations from the global rainfall line at the local level. The equations used to establish these two lines as follows:

$\delta 2H = 7.66\ \delta^{18}O + 14.19$ (4) LMWL (Al-Naseri et al.,2022)

$\delta 2H = 8\ \delta^{18}O + 10$ (5) GMWL (Craig, 1961)

It is observed from Figure 3 that all water samples are within the boundaries of both the local and global rainfall lines. This indicates that the source of water feeding into the Tigris River is closely tied to rainfall and snowfall. The variations in the distribution of water samples can be attributed to differences in the extent of evaporation.

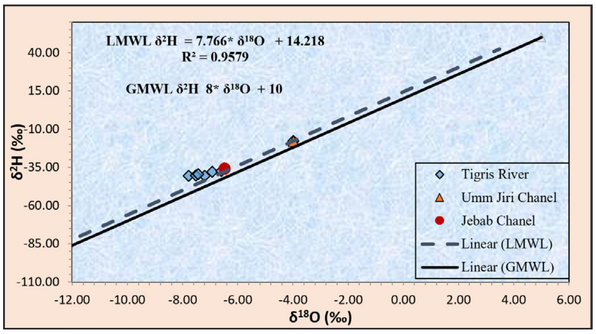

Figure 3. Stable isotopes (δ ^{8}O and δ^2H) with GMWL and LMWL

The deuterium excess (d-excess) serves as an indicator revealing the impact of evaporation on the chemical and physical characteristics of water. It is calculated using the following equation:

$$d = \delta^2H - 8\delta^{18}O \quad (6)$$ (Craig, 1961)

Figure 4 illustrates the correlation between excess deuterium and the total dissolved salts (TDS) content in water samples within the study area. As the evaporation process intensifies, there is an increase in TDS values, resulting in a reduction in deuterium excess values. This decrease in deuterium excess is particularly notable in the Tigris River water samples near the Amara Dam area compared to other regions. This phenomenon is attributed to the heightened exposure of water to substantial evaporation, leading to an elevation in dissolved salts concentration (TDS) (Falih et al., 2023).

Distinct differences are evident between the wet and dry seasons, with noticeable divergence in results. This discrepancy underscores the concurrence of elevated electrical conductivity (EC) and TDS levels, indicative of the effects of evaporation during the summer season characterized by high temperatures (53°C) in August and minimal rainfall during the wet season.

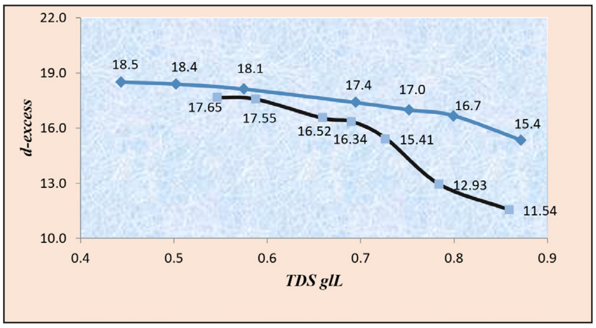

Figure 4. Relationship of deuterium excess and (TDS) for water samples in the study area

4.6 Radon -222(^{222}R)

The radioactive isotope of Radon (^{222}Rn) is one of the important environmental isotopes. It is used as an important tracer in hydrological studies due to its physical properties (it is in the form of a gas) and its short half-life (3.8 d) (Al-Paruany et al., 2021), Radon gas, once released from rocks and soil, can migrate to groundwater, surface water, and the air. The radon isotope is also considered a good indicator for identifying the interaction between groundwater and surface water. It can decide whether radon levels are below 0.4 Bq/L in surface water supplies, while they can reach around 20 Bq/L in groundwater, depending on the geological characteristics of the region and the quality of the groundwater (Mohammed et al.,2023). Concentration average of the Radon (^{222}Rn) of samples from the study area were measured and ranged between (0.149 - 0.329) Bq/L and were within the normal permissible limits for Radon concentration in water, according to the US Environmental Protection Agency (EPA), which is 11 Bq/L. (Figure 4). There is a low variation in Radon concentration between all the stations in the study area. This indicates that all locations are similar in the type of soil, sediments, and same conditions in the climate elements in these regions.

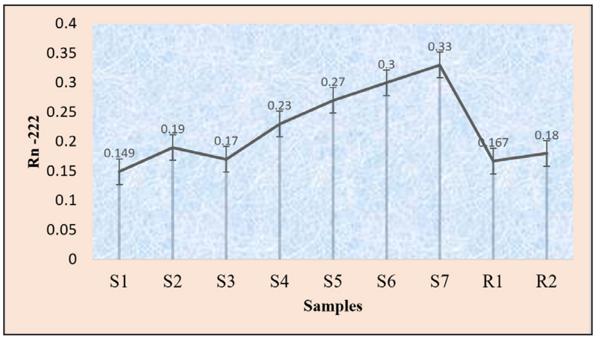

Figure 5. Radon-222 (^{222}Rn) concentrations for samples water in the study area.

5. Conclusion

The results for the stable isotopes of deuterium (^{2}H) and oxygen-18 (^{18}O) were similar for all study areas except near the Amara Dam, where the results showed depletion in the values of the stable isotopes, and the rates of stable isotope results for the waters of the Tigris River for the dry season were lower than they are in the wet season. This reflects the effect of high temperatures in the summer, the influence of the water by the evaporation process, and low river water levels of the Tigris due to lack of drainage. The water of the Umm Jiri regulator had a different isotopic fingerprint from the water of the Tigris River, while the isotopic fingerprint of the water of the Tigris River was, according to Nazim Al-Jabab, close to the waters of the Tigris River. This indicates the presence of mixing and its influence with the waters of the Tigris River. The results of the Radon-222 (^{222}Rn) isotope concentrations were within the normal limits allowed for the concentration of Radon in water, according to the US Environmental Protection Agency (EPA), which is 11 Bq/L. This indicates the low variation in Radon concentration between all the stations in the study area. This also indicates that all locations are similar in the type of soil, sediments and same conditions in the climate elements in these regions. The type (Ca^{+2} - Mg^{+2} - Cl^- - SO_4^{-2}) and the water quality is calcium chloride, which reflects the geology of the rocks of the area through which the water flows. All SAR values in study area fell within the excellent range for irrigation water quality.

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