

DISTRIBUTION OF ENVIRONMENTAL ISOTOPES IN THE EUPHRATES RIVER BETWEEN QAIM – FALLUJA, WESTERN IRAQ

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ABSTRACT

The environmental isotopes composition of water ($\delta^{18}O$, δ^2H and 3H) and hydrochemistry concentration were measured seasonally at eight stations along Euphrates River within the study area for two periods (January–August, 2014) to study temporal special variations of these isotopes. The results of isotopes values showed there is a little difference between the periods due to the seasonal change and the trend of distribution can be attributed to evaporation and drainage flow. Generally the river water has positive d-excess, which indicates the vapor source of the Mediterranean moisture sources in January, while a low d-excess associated with enriched isotopic values, which typically occurs during August, 2014. The Euphrates River water, is fresh (TDS < 0.39 g/L) and has slight increase in its salinity levels during the last two decades. Generally the chemical facies changes from a calcium-magnesium and bicarbonate type towards a sodium-chloride type to calcium sulfate. River salinity increases according to rock type, lake water, evaporation and human activity, and relatively higher toward downstream stations. The absence of management and a working drainage system, together with irrigation under high evaporation rates and low discharge, are the primary reasons for the continuous deterioration of water quality.

Keywords: Isotopes; Evaporation; Euphrates; Total dissolved solids; Iraq

INTRODUCTION

In general, water is the most important substance on Earth, without water there will be no life on our planet. Water is everywhere, three quarter of the Earth surface is covered with water in form of oceans, rivers, lakes, swamps and more than 70% of Earth covered by water while 0.014% is surface water. However, the declining water quality of these ecological systems threatens their sustainability and is therefore a matter

of serious concern. Rivers are waterways of strategic importance across the world, providing main water resources for domestic, industrial and agricultural purposes (Jain, 2009; Bellingham, 2012; and FAO, 2015).

Isotope data from rivers and surface waters were first collected in the 1950s and addressed primarily the variability of stable water isotopes in some large rivers such as the Mississippi and Colorado reported the first tritium values in the Mississippi River and analyzed the mixing of fallout tritium from the bomb tests in the 1950s in the river and adjacent aquifers (Clark, 1954; Dansgaard, 1954; Kaufmann, 1954; and Clark and Fritz, 1997). Isotope ratios of hydrogen and oxygen in river water are indicators for hydrological processes in the catchment (e.g. formation of base flow), for interactions between river water and ground-water, for mixing processes in a river, for travel time and the isotopic composition of hydrogen and oxygen in river water is mainly determined by the isotopic composition in precipitation water in the Drainage area (Mook, 2000; Winston, 2003; and Rank, 2005).

The relationship between the isotopic composition of precipitation (input) and newly formed groundwater and surface runoff (output) is built upon processes that differentiate between rain events on a meteorological or seasonal basis, and processes that fractionate between the different isotopic water species, primarily evaporation (Gat and Tzur, 1967). At any point along a river reach, water is ultimately derived from precipitation falling within its upstream catchment area. Depending on the size and geomorphological characteristics of the catchment, a variety of hydrological processes may affect the catchment and river water flow. The stable isotope ratios of the water molecule ($^{18}\text{O} = ^{16}\text{O}$, $^2\text{H} = ^1\text{H}$) are well-established powerful integrative recorders of key catchment processes (evaporation and transpiration, recycling, mixing) and catchment water balance, as well as tracers of river recharge sources (direct precipitation, runoff, soil water, groundwater, lakes, snow and ice) and The isotopic composition of riverine systems has proven to be a useful tool for estimating the mean residence time and storage properties of surface water. Changes in the isotopic composition of rivers may also help to better characterize the effect of snowmelt events. (Kendall and McDonnell, 1998; Gat, 2003; Henderson, 2005; Jasechko, 2013; and Kattan, 2012). Locally, many publishers have investigated the hydrology and hydrochemistry of Euphrates river (Al-Obaydi, 1983; Al-Hadithy, 2005; and

Al-Bassam, 2011). Also, Al-Paruany (2013) and Ali *et al.* (2015) have achieved an isotopic and hydrochemistry study on the same area and published their results. This study aims to apply environmental isotope methods, together with hydrochemistry, to monitoring the isotopic composition of the Euphrates River in northwest Iraq highlights the potential of stable water isotopes for tracing the influence of precipitation and other hydrological processes on runoff in tropical rivers.

Description of Euphrates River

The Euphrates River is the longest river in western Asia. with its basin lands (area= 350 000 Km²). It flows 2,700 Km through Turkey (110,000 Km²), Syria (70, 000 Km²) and Iraq (170 000 Km²). and into the Arabian Gulf through the Shatt Al-Arab. The water volume flowing from Turkey through Syria to Iraq has dropped since Turkish and Syrian dams came into operation in the 1970s, the flow into Iraq has dropped dramatically from 700 cubic meters per second (m³/s) to the current level of 260 m³/s. With an average annual discharge of 97 MCM (Al-Jubouri, 2009).

Geology plays an important role in water quality of Euphrates River; in Iraq Euphrates River passes through many formations such as (Baba, Ana, Euphrates, Fatha and Quaternary deposits. All these formations effects the quality of the water (Jassim and Goff, 2006). The topography of the river basin in Iraq generally is simple, with the presence of a number of small hills near its banks. The elevation of the Euphrates River in Iraq is of about 170 m above sea level (a.s.l.) at Al-Qaim town, and 80 m at Al-Basra city. The depth of Euphrates water is ranging between 3 – 11 m.

Climatically, the Euphrates River Basin in Iraq ranges from arid to semi-arid and the mean monthly rainfall decreases and ranging during the rainy season (October to May) from 20 to 60 mm in Qaim town and 10 – 23 mm in Al-falluja town. The mean annual value of relative air humidity varies between 56% (Qaim) and 47% and declines to less than 44% (Falluja), while the temperature and evaporation are highest in July and August.

MATERIALS AND METHODS

Sampling Strategy

The study area from Qaim to Falluja which has length of about 380 Km. Eight samples were taken in the study area during two periods of high flow (January 2014)

and of low flow (August, 2014). Water samples were collected from sites distributed along the Euphrates River course in Iraq. The first sampling site was selected in Al-Qaim, close to the Syrian – Iraq border, while the last sampling site was selected in the Falluja area (Fig. 1). The name of stations and their locations are listed in Table (1). Unfortunately, water samples were generally collected in three rinsed plastic bottles, and immediately after returning back from the field, all samples were preserved in a refrigerated room ($T \approx$ below $5\text{ }^{\circ}\text{C}$) until the time of analysis. A small bottle of 50 mL was filled for the determination of stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). A second bottle with a volume of one liter was collected for tritium measurement.

samples for hydrochemistry analysis are collected from same sites, 500 mL bottle was filled for the determination of major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4 and HCO_3). Air and water temperature, pH and electric conductivity were measured in situ using a thermometer (accurate to nearest $0.1\text{ }^{\circ}\text{C}$), pH-meter (model WTW), and conductivity meter (model WTW 303) respectively.

All data of geology, Topography, industrial uses, drainage water system are observed in order to help for interpretation.

Analytical Methods

Stable isotope analyses were carried out at Water Authority Laboratories/ Jordan. The methodology as it is described in (IAEA, 1983). Tritium samples were measured using liquid scintillation direct counting in the Sandia laboratory (after electrolysis). The results are expressed in TU, measurement accuracy for $\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium are ± 0.1 , $\pm 1.0\text{‰}$ versus VSMOW, and ± 1 TU, respectively. The chemical analyses were carried out in the Environment and Water Directorate/ Ministry of Science and Technology. Air and water temperature, pH and electric conductivity were measured in the field using a thermometer, pH meter (model WTW) and Ec. meter (model WTW305). Total dissolved solids (TDS) were estimated. Cations, Anions in water are measured using ion chromatograph technique procedure to determine the ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4 and HCO_3).

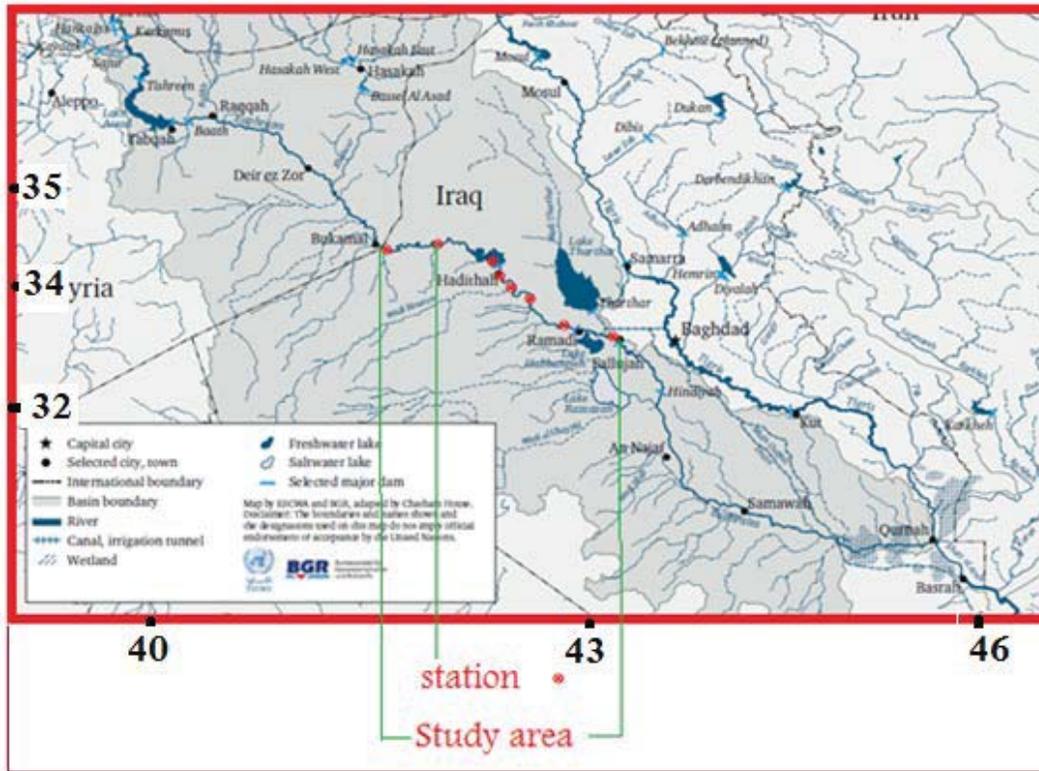


Fig. 1: Map area showing sampling locations

Table 1: Name of sampling location and their coordinates

Name of samples site	East latitude	North longitude	Elevation from sea level (m)
<i>Qaim Station</i>	41° 07'	34° 21'	170
<i>Ana Station</i>	41° 88'	34° 37'	153
<i>Haditha Lake Station</i>	42° 20'	34° 10'	137
<i>Haditha Station</i>	42° 23'	34° 07'	93
<i>Baghdadi Station</i>	42° 33'	33° 55'	75
<i>Heet Station</i>	42 48 62.7	33 39 49	65
<i>Rammadi Station</i>	43 18 47.1	33 26 28.6	50
<i>Falluja Station</i>	43 36 16.4	33 22 07	46

RESULTS AND DISCUSSION

Seasonal and temporal variations in the values of physicochemical parameters and total ion concentration at different sampling sites along Euphrates River (Qaim, Ana, Haditha lake, Haditha, Baghdadi, Heet, Rammadi and Falluja) for the Euphrates River are shown in Tables (2 and 3).

Table 2: Total ions concentration and physiochemical parameter in Euphrates River, August, 2014

Parameters	Sampling sites								
	Unit	Qaim	Ana	H.Lake	Haditha	Baghdadi	Heet	Ramadi	Falluja
T	C	26	25	22	21	22	22	23	23
PH	-	7.3	7.3	7.7	7.6	7.6	8.2	8.4	8.3
Ec	µs/cm	747	725	1061	810	937	1200	1267	1287
TDS	ppm	418	508	849	601	704	755	823	832
Na	ppm	90	95	153	110	117	109	120	82
Ca	ppm	72	73	110	104	100	87	120	66
Mg	ppm	14	16	18	16	15	23	25	27
K	ppm	1.9	2	2	2.1	3.1	1.2	2.5	1.9
Cl	ppm	110	112	181	90	153	261	246	215
SO ₄	ppm	66	90	196	105	192	210	210	310
HCO ₃	ppm	65	120	189	174	124	55	78	130
CO ₃	ppm	0.2	0.2	0.7	0.0	0.0	0.5	0.0	0.0

Table 3: Ions concentrations and physicochemical parameters in water; wet season January, 2014

Parameters	Sampling sites								
	Unit	Qaim	Ana	H.Lake	Haditha	Baghdadi	Heet	Ramadi	Falluja
T	C	20	20	17.3	20	21	21	22	22
PH	-	7.2	7.5	7.5	7.6	7.5	8.3	7.8	7.9
Ec	µs/cm	740	719	1040	799	922	1145	1247	1255
TDS	ppm	396.6	496	819	576	671	718	737	802
Na	ppm	82	80	148	100	109	99	86	77
Ca	ppm	68	69	106	98	90	77	100	62
Mg	ppm	10	11	14	12	10	20	22	24
K	ppm	1.4	1.7	1.8	2	2	1	2.3	1.6
Cl	ppm	100	102	179	80	140	245	230	204
SO ₄	ppm	50	78	170	89	177	198	197	283
HCO ₃	ppm	58	100	176	168	115	50	70	120
CO ₃	ppm	0.2	0.2	0.7	0.0	0.0	0.5	0.0	0.0

The highest pH values were recorded during August (8.4) in Fallujastation and the lowest values were recorded during January (7.2) in Qaim station. The pH was showed slightly alkaline trend. Generally pH of water would have been influenced by geological of catchments area and buffering capacity of water and industrial pollutant. (Al-Jubouri, 2009). The temperature of air and water values were ranged between 21 – 26 °C and 17.3 – 0 °C, respectively, in August and January 2014 for air temperature 50 °C in August, and 8 °C in January 2014 for water temperature. The present study was showed obvious change in air and water temperature during the seasons. this variation was occurred because the seasonal and geographical change and the difference in time of sampling.

The electric conductivity values were ranged from 747 $\mu\text{S}\cdot\text{cm}^{-1}$ recorded at Qaim station, to 1289 $\mu\text{S}\cdot\text{cm}^{-1}$ at Falluja station in August 2014. And ranged from 740 $\mu\text{S}\cdot\text{cm}^{-1}$ recorded at Qaim station, to 1255 $\mu\text{S}\cdot\text{cm}^{-1}$ at Falluja station in January 2014.

The results of electric conductivity were showed lowest values during January and, while highest values were recorded during August, there was a significant difference recorded among study sites. Euphrates River's water was significantly different among sampling sites and in the two seasons, however the higher in flow season than dry seasons. Higher values of low flow season are possibly due to evaporation process which could also increase the concentration of TDS (major ions) (Hem, 1992).

Total Dissolved Solids (TDS) further indicate the salinity behavior of river water. TDS content of the river water was in the range of 418 – 831 mg L^{-1} ; 396 – 819 mg L^{-1} in August, January periods respectively. TDS in water system lead to increase the Ec, Salinity, Cation, Anion level in water. It is considered to be a good indicator for the presence of some dissolved solid substance in water such as the Na, Ca and Mg, SO_4 , HCO_3 .Cl.

Temporal and special evolutions in major ions (Na^+ , K, Mg, Ca^{2+} , HCO_3Cl and SO_4) and TDS concentrations (Figs. 2 and 3) are identical, with rather small fluctuations in the upstream stations and more pronounced variations at downstream stations, The variation in concentration may be due to the input from groundwater salinization, plant fertilizers, pesticides and other pollutants, high irrigation rates under arid conditions.

The behavior and distribution of ions along the Euphrates river may be affected by water hydrology, domestic discharge and many biological, chemical and geological operations in aquatic system. The water chemistry of the Euphrates river is generally characterized by three type of water in both periods of study area:

1. Calcium-carbonate type at stations (Qaim, Ana and Hadith lake).
2. Sodium-chloride type at stations (Haditha Baghdadi).
3. Calcium-sulphate type at (Heet, Ramadi and Faluujja).

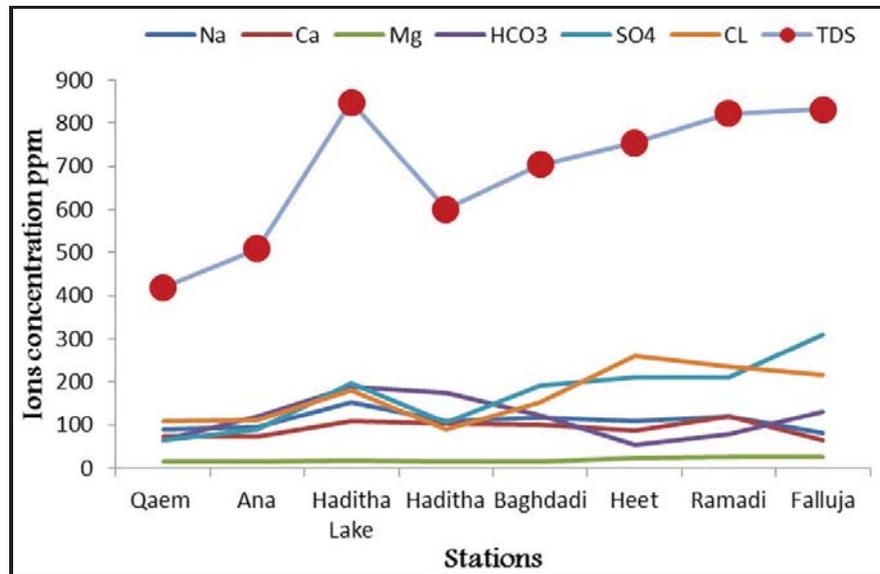


Fig. 2: Temporal and special evolutions in major ions (Na^+ , K , Mg , Ca^{2+} , HCO_3 , Cl and SO_4) and TDS concentrations in August, 2014

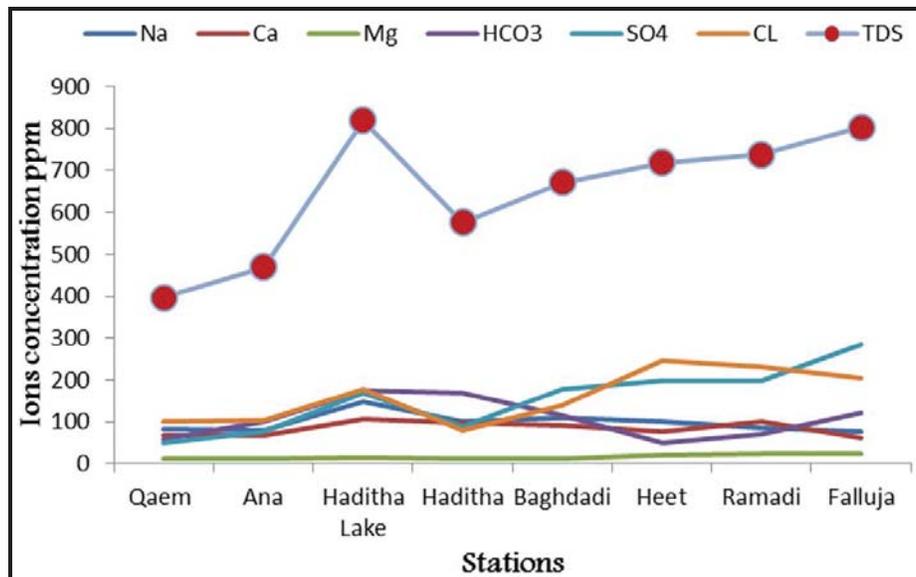


Fig. 3: Temporal and special evolutions in major ions (Na^+ , K , Mg , Ca^{2+} , HCO_3 , Cl and SO_4) and TDS concentrations in January, 2014

The change in water type of Euphrates River water can be related mainly from the dissolution of halite, limestone, gypsum within Euphrates in ad River addition of effects by Sewage industrial, natural sources of contamination. When, comparison our results of chemical parameter with many pervious study, some significant differences arise, which continually change of Euphrates water type with time.

River water $\delta^{18}\text{O}$ and d-excess at Euphrates River

Stable isotopic compositions of river water samples were measured at Water Authority/ Jordan. The analytical error can be assumed to be on the order of $\delta 0.2\%$ for $\delta^{18}\text{O}$ and $\delta 2.0\%$ for $\delta^2\text{H}$. Nevertheless, all stable isotope measurements are expressed as δ value relative isotope-ratio differences. The results of isotopic composition of water samples collected from the study area during the period January – August 2014, together with the deuterium excess values ($d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$) and tritium Values are reported in Table 4.

Table 4: Mean, Isotopic values, d-excess and tritium in the studied area for both periods, 2014

Station	Coordinates		Elevation	$\delta^{18}\text{O}$			$\delta^2\text{H}$			d-excess		Tritium TU
	Latitude	Longitude		August	January	Mean	August	January	Mean	Aug.	Janu.	
Qaim	41° 07'	34° 21'	170	-6.1	-6.6	-6.3	-40.4	-42.2	-41.6	8.4	10.6	6.6
Ana	41° 88'	34° 37'	153	-6.2	-6.53	-6.36	-40.8	-43	-41.4	8.8	9.24	6.8
Haditha. L	42° 20'	34° 10'	137	-7.1	-7.53	-7.36	-46	-49.6	-48.8	10.8	10.64	7
Haditha	42° 23'	34° 07'	93	-6.18	-6.5	-6.49	-40.2	-42.8	-38.8	9.24	9.2	6.5
Baghdadi	42° 33'	33° 55'	75	-6.26	-6.45	-6.37	-41.02	-43.8	-41.6	9.06	7.8	6.4
Heet	42 48 62.7	33 39 49	65	-6	-6.25	-5.79	-39.5	-41.9	-40.6	8.5	8.1	6.2
Ramadi	43 18 47.1	33 26 28.6	50	-5.7	-6.1	-5.4	-38.2	-40.29	-38.9	7.4	8.51	5.9
Falluja	43 36 16.4	33 22 07	46	-5.4	-5.89	-5.09	-37	-39.5	-38.6	6.2	7.62	5.6

The depleted values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are found at Haditha reservoir, with values of -7.53 to -7.2% and -48 to -49.6% on January and August, 2014, respectively. Similarly, the other stations are also depleted in heavy isotopes. The δ oxygen-18 and δ deuterium values show a wide range of variation from -6.3 to -5.5% and from -39.2 to -42.2% in January, 2014, respectively. While the δ oxygen-18 and δ deuterium values range from -6.3 to -5.0% and from -38 to -41% in August, 2014, respectively, as shown in Figures (4 and 5). The $\delta^{18}\text{O}$ record exhibits three significant changes along the river. The first is at the Qaim; the second is caused by inflow from the Haditha reservoir with their higher ^{18}O content; the third significant change in stable isotope ratios in the region of the Ramadi. This variation in both seasons can be attributed to the mixing with water inflow and evaporation. The decrease in $\delta^{18}\text{O}$ in fall and January is quite an interesting phenomenon. A relatively rapid decrease during the period of January suggests a change in the source of runoff water.

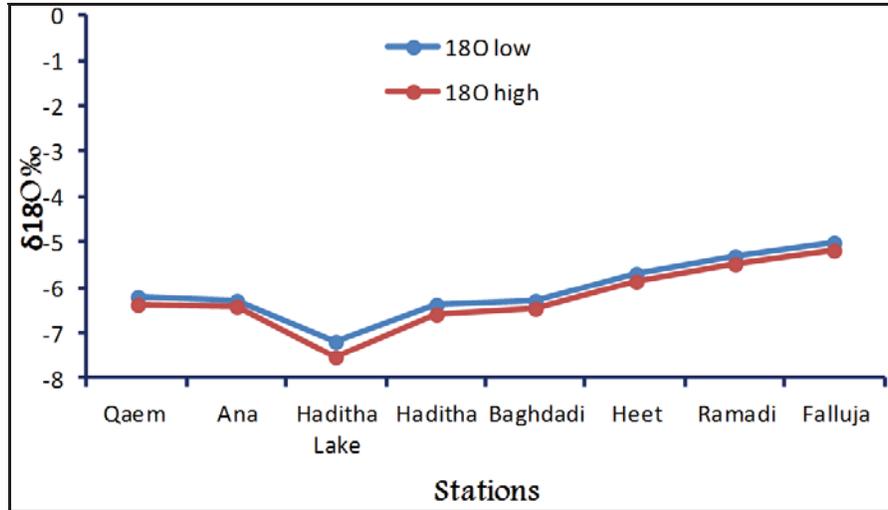


Fig. 4: variation of $\delta^{18}\text{O}\text{‰}$ at studied station in both Periods (January-August, 2014)

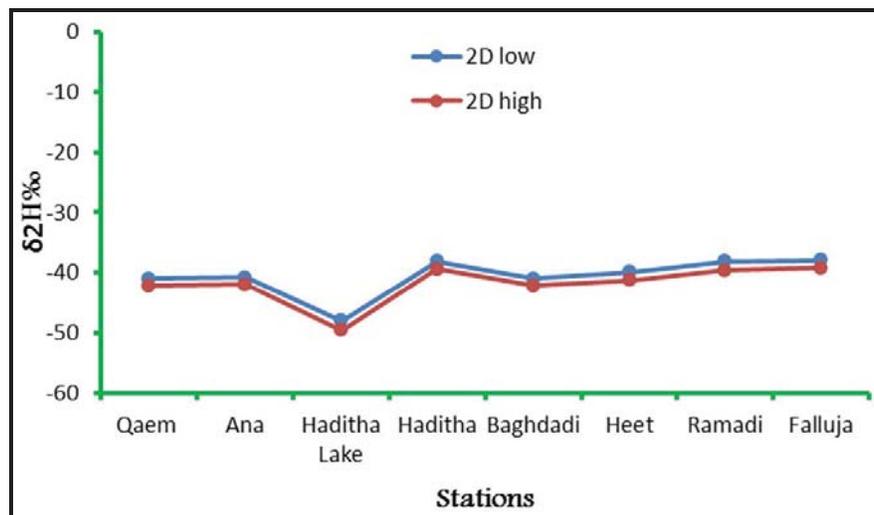


Fig. 5: variation of $\delta^2\text{H}\text{‰}$ at studied station in both Periods (January-August, 2014)

Mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were -6.49‰ and -5.09‰ and from -38.6‰ and -48.8‰ , respectively. The large amplitude of isotopic variations in Euphrates River clearly indicates the complexity of its source as well as the climatic and topography characteristics of the region, which affect the composition of local rain. The $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ plot of all samples collected from all rivers are scattered all along the GMWL, while the Haditha reservoir is more depleted in ^{18}O and ^2H . Some samples are below the GMWL, indicating an evaporation effect. Sometimes, the river has very low flow and the river water seems to have undergone evaporation.

The $\delta^2\text{H} - \delta^{18}\text{O}$ diagram (Fig. 6) shows that most of the values lie close to the Global Meteoric Water Line ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$), Water sample points are generally distributed between two evaporation lines, with two different slopes (2.5 and 3.7). The difference observed in the slope values could indicate a different mechanism of evaporation.

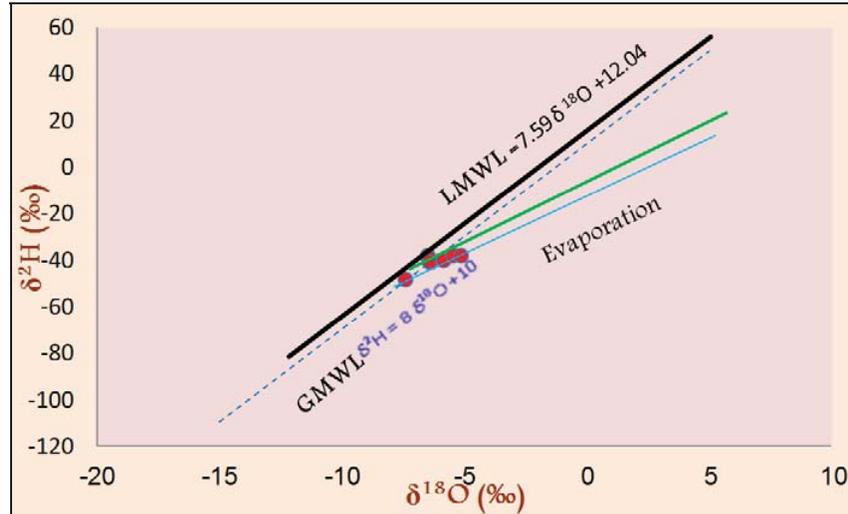


Fig. 6: mean values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with GWML, LWML at study area

There are three possibilities for variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$:

- The contribution of precipitation.
- depleted due to evaporation;
- The contribution of base flow in river discharge.

$\delta^{18}\text{O}$ of River water and d-excess obtained at Euphrates are shown in Figure (7). Clear seasonal variation was found in the δ of O, H value, with a minimum value (-7.2 to -5.0‰) in August and a maximum value (-7.53 to -5.5‰) in January. The $\delta^{18}\text{O}$ of river watersamples decreases downstream with different conditions (inflow, discharge). The spatial distribution of the stable isotope values, together with the deuterium excess values in the study area, clearly shows a gradual depletion of the stable isotope composition towards the upstream of Euphrates river course. These patterns coincide completely with the distribution patterns of E.C., TDS and major ion concentrations, indicating hence the effects of the mixing and evaporation processes.

The d-excess values were found to be relatively high in north part of Euphrates River (Figs. 7 and 8). Compare with that lower latitude toward south study area. The

observed higher d-excess values in the upstream could be effect by Mediterranean air mass.

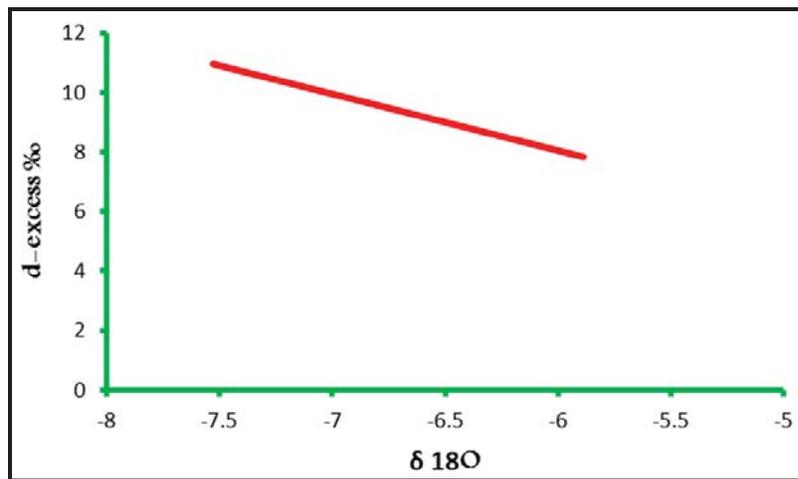


Fig. 7: d-excess v $\delta^{18}\text{O}$ at studied area in January, 2014

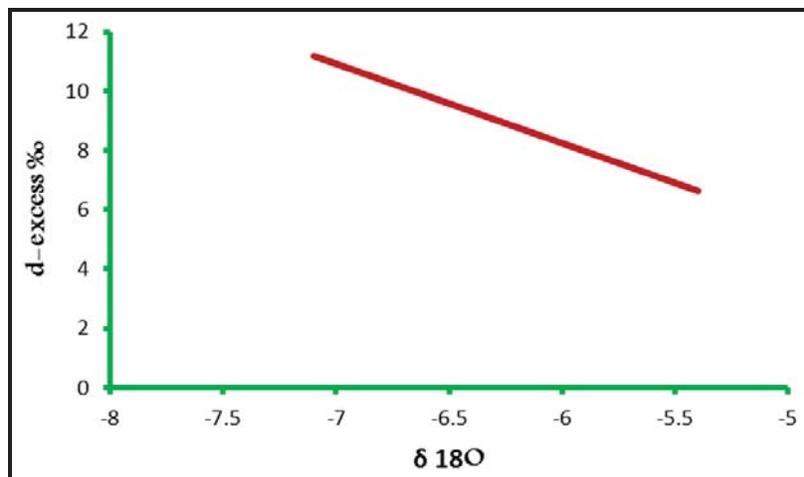


Fig. 8: d-excess v $\delta^{18}\text{O}$ at studied area in August, 2014

The waters of the majority of the sampled site, including those of the Haditha lake, which show more depleted isotopic compositions ($-7.2\text{‰} < \delta^{18}\text{O} < -7.53\text{‰}$ and $-49.6\text{‰} < \delta^2\text{H} < -48.0\text{‰}$), together with higher deuterium excess values ($10.6\text{‰} < \delta < 10.8\text{‰}$), comparable with those of other stations. Generally these waters have low d-excess, which indicates that the moisture source indicates a dominance of Mediterranean moisture sources in January, while a low d-excess associated with enriched isotopic values, which typically occurs during August.

The relationships between $\delta^{18}\text{O}$ compositions and SO_4^{2-} , and between $\delta^{18}\text{O}$ and TDS values, are illustrated in Figures (9 and 10). These plots suggest the existence that dissolution processes is controlled for the increasing salinity in the study area:

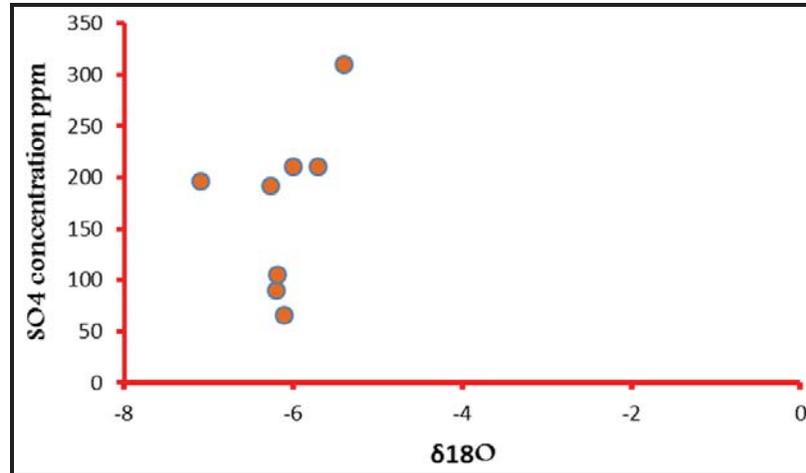


Fig. 9: $\delta^{18}\text{O}$ compositions and SO_4^{2-} , the relationship in August, 2014

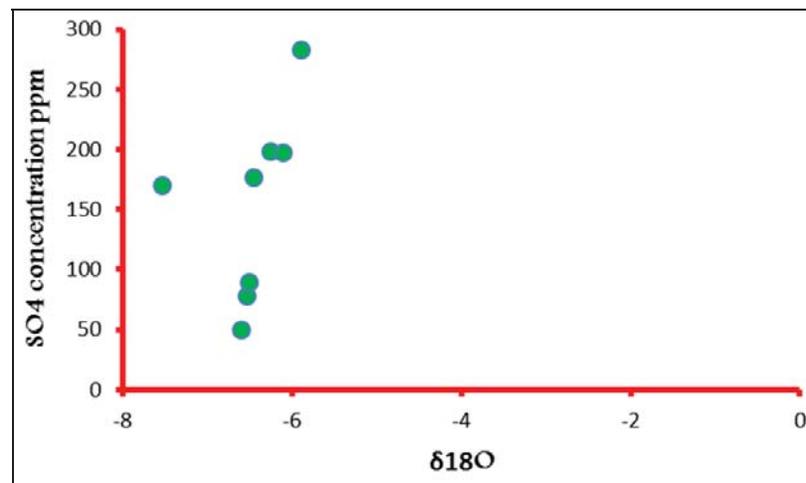


Fig. 10: $\delta^{18}\text{O}$ compositions and SO_4^{2-} , the relationship in January, 2014

The results of these investigations lead to the conclusion that the relatively big variations of deuterium excess in Euphrates basin precipitation. Deuterium excess is probably no reliable tool to trace the origin of air masses and moisture coming from far away. For this purpose to distinguish between Atlantic and Mediterranean origin.

In the current study, the effects of Haditha lake in the monitoring area, it is clear in both chemical and isotopic values relative to those other stations, This could be caused by an evaporation effect due to high temperatures.

Tritium content in the Euphrates River

The tritium values of water samples collected from the Euphrates River at different stations along its course during the period January – 2014 are given in Table 2. The data shows that the tritium content of Euphrates River water varies within a very small range (5.6 – 7 TU). Figure (11) illustrates the spatial variations of tritium content at eight different stations along the course of the Euphrates River at January 2014. The tritium content of Euphrates River water is apparently higher than that of actual rainfall in Iraq (below 5 – 6 TU) during 2013 (Al-Paruany, 2013). The cause of high tritium content in Euphrates River water compared to that of actual rainfall is mostly the storing of river water in divers dams in both Turkey, Syria and Iraq. lower than that of Syria (7.6) (Kattan, 2012). It seems that the tritium content of the river water reflects the effect of residence time in the different lakes, mainly Al-Assad Lake, Haditha Reservoir, where mean residence time is close to ≈ 250 and ≈ 201 days respectively.

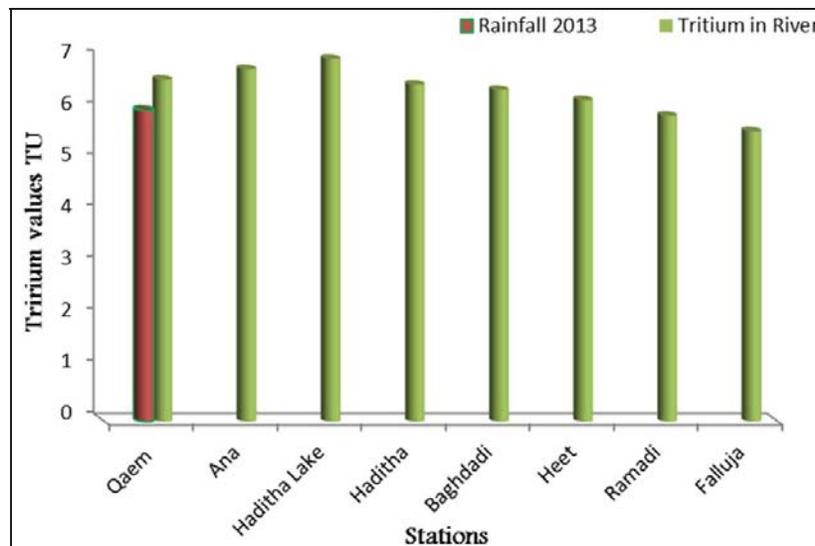


Fig. 11: illustrates the spatial variations of tritium content at eight different stations along the course of the Euphrates River at January, 2014 with rainfall actual values, 2013

CONCLUSIONS

The combination of both hydrochemical and isotopic investigations of surface and lake in the down-stream valley of the Euphrates led to general conclusions, that can be learned from this study, as the following:

1. The Euphrates river water is rather fresh ($418 < \text{TDS} < 831 \text{ mg/L}$), and its TDS content had slightly increased within the last two decades, most probably as a result of seepage of saline water in the Euphrates river. The chemistry of the Euphrates river water was of a calcium-sodium and sulphate, bicarbonate and -chloride type, and it differs largely from that of local groundwater, which were more saline and The trend of studied hydrochemical formula can be represented as Ca-HCO₃ at upstream . Na-Cl at middle, and in downstream is Ca-SO₄.
2. Seasonal variations in concentrations of salinity refer to decrease of these concentrations in wet season, while increase in dry season. And deterioration the water quality of Euphrates River was increase towards the downstream of Falluga city because of pollutants discharge to the river.
3. The relationships between stable isotopes and major ions suggest the existence of one processes for the increasing salinity (dissolution).
4. The presence of high tritium content in groundwater confirms that groundwater resources in this zone are of recent age and annually renewable.
5. Concentrations of stable isotopes generally increase downstream, The tritium content of Euphrates River within Iraq, lower than that of Syria (7.6), changed slightly to around 7 TU.6 multifactors effect to the isotopes values such as residence time in reservoir, irrigation drainage , and evaporation rate.

This paper makes a number of recommendations based on short- and long-term goals.

Given the security situation in Syria and Iraq, the severing of relations between Turkey and Syria, with Continuous monitoring of quality water and insure the environmental strategies need to be improves to protect and enhance the water quality in Euphrates River.

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