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Determination of Chemicals and its Isotopic Composition in Tigris River, Iraq

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Stable isotope ($\delta^{18}O$, δD) values were determined along with the chemical compositions at 10 different locations along the Tigris river between Baghdad-Ammara cities of Iraq. The physico-chemical parameters and isotopic data were measured. The sampling site represents 34 % of total Tigris river in the republic of Iraq. The systematically increased in values of stable isotope as move from the downstream of the river and the most significantly appears at Kut lake. This increase occurs as a result of several factors, *viz*. (a) evaporation occurs low water level in the river and its tributaries, and (b) return flow water to the river from irrigation water in groundwater systems. The change in ion distribution and in the isotopic values related directly with the outcome from the groundwater and sewage station's water.

Keywords: Isotope, Tigris river, Physico-chemical parameters, Iraq.

INTRODUCTION

Freshwater resources from rivers are the most important for economic, social and political development [1]. Studying the stable isotopes ($\delta^{18}O$, δD) participate as unmistakably to our comprehension of the water cycle and related diverse hydrological processes [2-8]. Baghdad, capital of Iraq, that is the biggest second biggest city in the Arabic world with a population of 7.5 million and its the main supply of drinking water comes from Tigris river [9].

The river originates within the Taurus Mountains of eastern Turkey, total length of the river is 1850 kilometer. The river flows for about 400 kilometers through Turkey before entering in Iraq, the total length of Tigris river within Iraqi territory is 1418 km. It irrigates land area is 473,103 km^2 shared it with Turkey, Syria and Iraq. About 58 basins are located in Iraq and no major tributary joined the Tigris river [10,11]. The typical yearly flow discharge of Tigris river is 672 m^3/s) once it enters Iraq and in southern cities of Iraq, it provides a daily flow rate (1140 m^3/s) to Kut and Amara cities. The main river tributaries are supplied with a quantity of 786 m^3/s of water and a few minor channels from of Iran carrying 222 m^3/s directly into the southern marsh space [12].

During last few years, several features are controlled on morphology of Tigris basin such as erosion, island, channel bank lining and dumping of debris due to local war and has been classified as unstable river [13]. The water flows of Tigris and Euphrates rivers entering to Iraq have been diminished dramatically because water impounding is created while few of them are still being created on these rivers from the adjoining countries, Turkey, Iran and Syria [12].

On the other hand, flow of Tigris river at Baghdad city has been decreased and the problem become more critical due to the recent dry climatic period in Iraq during 2000-2010. The average discharge of 544 m^3/s is less than half of the mean daily flow of 1140 m^3/s prior to 2005 and well below the flood discharges of 4480, 3050 and 1315 m^3/s recorded in 1971, 1988 and 2005, respectively.

However, the reduction in the levels of Tigris river in recent years propelled due to dig wells for irrigation and other purposes. Water quality index was analyzed to estimate the raw and treated drinking water from Tigris river within Baghdad [14], by using this trajectory, Tigris river water doesn't fall on the category of excellent level and unsuitable condition of Tigris river is totally different between Baghdad and Amara cities because of the variety of formations and human activities.

Water quality is determined by comparing the physical and chemical properties of the samples of water in accordance to international institutions specialized in water quality [15,16]. The objective of this study is to analyze the chemical constituents and the isotopic values ($\delta^{18}O$, δD) of Tigris river, which will be accustomed to facilitate the water supply and determination of geographic sources.

EXPERIMENTAL

Study area: The study area (320 km) was chosen along Tigris river and it lies on latitudes between (44º37′48 to 47º63′) and longitudes (33º28′28 to 31º53′) with elevation (7 to 30 m). The river passes through many cities and villages carrying effluents from domestis, industries and agricultural wastewaters. Geology, the study area is covered by miocene-quaternary formation with gypsum, limestone and shall [17,18]. The distance between Baghdad and Ammara cities is about 200 miles (320 km). There is a barrage, meanders, the island and the channel of Al-Garraf. During the flood times, Tigris river carries as much as 1.5 million tons of eroded materials (sand, clay and silt). Climatic features are extreme heat of summer with temperature exceeding of 49 ºC, humidity in most areas is as low as 15 %, dust storm and wind dust consists of particles of clay, silt and rain water can be usually does not exceed 80-120 mm.

Sampling: The sampling strategies were performed in the month of February 2018. Ten different sites are chosen along the river near cities and all sites are named listed in Table-1. The samples of river water were collected in two bottles for chemicals and stable isotopes determinations. The physico-chemical parameters *viz*., temperature, pH, electrical conductivity, total dissolved solids, cations, anions, nitrate, *etc*. were estimated. The isotopic analyses were performed by LWIA at the laboratory of isotopes in Ministry of Science and Technology of Iraq. The measurement accuracy is < 0.2 for both $\delta^{18}O$ and δD.

RESULTS AND DISCUSSION

Spatial variation in the values of physico-chemical parameters in different locations of sampling sites of Tigris river are shown in Table-2. There is a little spatial fluctuation of water temperature as shown in the study area due to the homogenity in Tigris river water. The pH range was found to be 7.3 to 8.2 and these values showed that in some sites the water is alkaline in nature, however these values are within the range [19]. The electrical conductivity (EC) values were ranged from 916 to 2250 µs/cm. However, total dissolved solid (TDS) values (494-1323 ppm) are fluctuated at different sites.

In this study, the maximum value is < 1000 ppm which was recorded as the lowest value in site TR1. The fluctuation of electrical conductivity and TDS at study area are possibly due to many factors such as storm water runoff that brings from farms. Increased value of TDS was observed at site TR10 due to the presence of various pollutants in river which may be due to the different anthropogenic activities, groundwater salinization, plant fertilizers, pesticides and/or high irrigation activities. The results of cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (SO_4^{2-}, Cl^-, HCO_3^- and CO_3^{2-}) are found to be in a wide range, (Fig. 1). The variation in cations and anions values in the study may be due to multiple sources like sewage discharge, agriculture activities and industrial wastes), in addition to

TABLE-1
NAME OF SAMPLING LOCATION AND THEIR COORDINATES

Name of samples site	Symbol	East latitude	North longitude	Elevation from sea level (m)
Baghdad (East)	TR1	44° 37'48	33° 28'28	30
Baghdad (Karada Marime)	TR2	44° 35'	33° 26'	30
Baghdad (Jaderia)	TR3	44° 23	33° 22'	29
Madain	TR4	44° 53'	33° 57'	22
Suawryah	TR5	44° 93'	33° 85'	20
Aziziyha	TR6	45 03 38.7	33 39 49	17
Kut Dam	TR7	45 04 88.1	33 24 4.6	13
After Dam	TR8	46 01 46	32 38 16	12
Shwacha	TR9	42° 23'	42° 23'	11
Ammara	TR10	47° 63'	31° 53'	7

TABLE-2
TOTAL IONS CONCENTRATION AND PHYSIO-CHEMICAL PARAMETER IN TIGRIS RIVER (FEBRUARY, 2018)

Parameters	Unit	Sampling sites									
		TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	TR9	TR10
T	°C	19	19	20	20	20	20	20	21	19	19
pH	–	8	8.1	7.9	7.7	7.5	7.3	8	8.2	7.9	8
EC	µs/cm	916	932	945	1090	1249	1389	1290	1543	1120	2550
TDS	ppm	494	580	648	738	803	990	857	1065	720	1323
Na^+	ppm	65	77	80	73	65	88	37	92	117	330
Ca^{2+}	ppm	60	65	73	142	145	148	167	142	88	80
Mg^{2+}	ppm	17	23	31	5	42	55	48	52	24	26
K^+	ppm	4	5	8	9	12	14	1	13	15	41
Cl^-	ppm	70	93	98	134	170	155	122	220	160	534
SO_4^{2-}	ppm	150	169	190	189	220	340	220	350	260	248
HCO_3^-	ppm	120	137	155	179	145	183	260	190	63	63
CO_3^{2-}	ppm	8	11	13	8	4	7	2	6	1	1

geological process (dissolution and/or ion exchange). The total cation and total anion in the Tigris river water samples show a wide range, varies from 7.22 to 21.79 meq (TZ+) and 7.34 to 21.5 meq (TZ-), respectively.

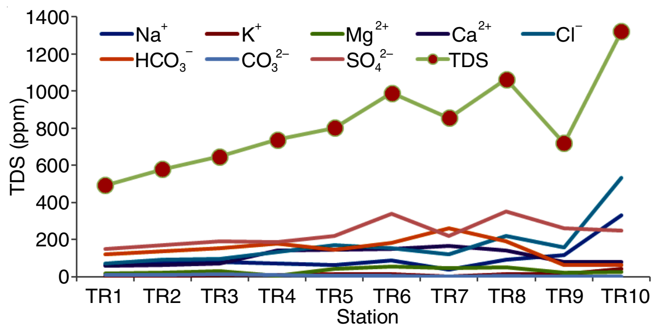

Fig. 1. Special evolutions in major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^- and SO_4^{2-}) and TDS concentrations in February, 2018

The order of cation and anion present in river was found to be as Na, SO_4^{2-} at TR1, TR2 and TR3 sites; Ca^{2+}, SO_4^{2-} at TR4, TR5, TR6, TR7 and TR8 sites; and Na^+, SO_4^{2-} at TR9 and TR10 sites. The high values of Ca^{2+} and SO_4^{2-} were recorded in most of the sites, which may be due to direct discharge of sewage and agriculture activities in the river. While the primary sources for high TDS values resulted from agricultural waters and residential runoff, soil contamination and discharge from industrial or waste sluge.

According to Todd and Mays [20] classification based on total dissolved solid (TDS), Tigris river having fresh water in TR1, TR2, TR3, TR4, TR5, TR6, TR7 and TR9 sites, while being a Brackish in site TR8 and TR10. Finally, the change in water type of Tigris river water can be related by mainly from the industrial and natural sources of contamination. In addition, it is found that human activities in the surroundings of Tigris river study area are relatively high.

Isotopic analysis: Water samples which contained the isotopic compositions ($\delta^{18}O$, δD) in collected Tigris river samples taken from the ten stations are shown in Table-3, along with the other characteristic parameters. The spatial distribution of $\delta^{18}O$ and δD in Tigris river is low in Baghdad city but have high values in Ammara city.

Clear spatial variation was found in $\delta^{18}O$ value and measurements of $\delta^{18}O$ and δD values of water samples, showed $\delta^{18}O$ values between -7.2 and -2.8 % and the δD between -45.9 and -22 %. The $\delta^{18}O$ of river water decreased from Baghdad to Ammara during the month of February, 2018, which may be due to the flow of fresh water because of melting of snow. In the classified water samples, first group contains heavy isotopes, collected from river water in the region between Baghdad and Azizia, second collection was more enriched in heavy isotopes and involved in water specimens which collected between Kut to Ammara except the sites TR7 and TR9. Moreover, during the investigations, it was found that most of the water sample undergone evaporation. It appears that ^2H and ^{18}O isotopes are more enriched along the river course, which may be due to the evaporation process, which lead to an increase in the concentration of heavy isotopes in river water samples, as collected from Shwacha site, and also this high level may be caused by a difference in the rate of rainfall during the winter as compared to other sites. Due to evaporation, we found that the isotopic components in river water, which are regulated by Kut lake and more positive than unregulated water in neighbouring sites. Due to evaporation of the surface water along the course of river, most of the values of δ^2H-$\delta^{18}O$ are located near close to Global Meteoric Water Line ($\delta^2H = 8 \times \delta^{18}O + 10$) as shown in Fig. 2.

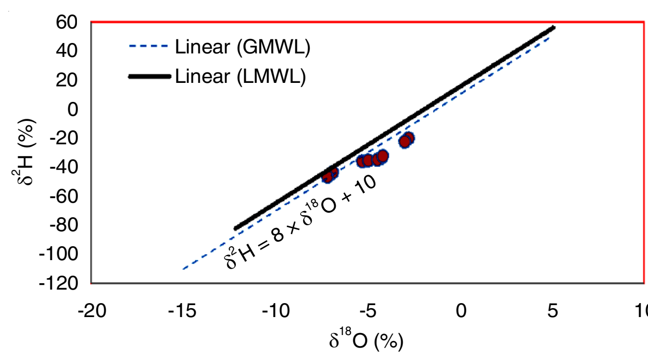

Fig. 2. δ^2H *vs.* $\delta^{18}O$, GMWL, LMWL in the study area (February, 2018)

Water sample points are generally distributed between two evaporation lines, with two different slopes (4.37 and 9.5), The difference observed in the slope values indicate a different mechanism of evaporation (Fig. 3). The values of $\delta^{18}O$ and d-excess obtained from the Tigris river waters, Clear spatial variation was found in δ of O, H value, with d-excess in February, 2018. The $\delta^{18}O$ of river water samples decreased downstream with different conditions (inflow, discharge).

Values of d-excess (*d*) below 10 indicate an evaporation process. The smallest d values were seen toward Ammara, while the highest δ^2H values observed in Baghdad sites. In addition, the d-value was found to be decreased in Kut lake and its values less than 10, which explains the evaporation and thus affecting the river quality of Kut lake.

TABLE-3
STABLE ISOTOPIC VALUES, DEUTERIUM EXCESS (d), WATER TEMPERATURE, pH, EC AND CHLORIDE CONCENTRATION IN THE STUDIED AREA

Parameters	Unit	Sampling sites									
		TR1	TR2	TR3	TR4	TR5	TR6	TR7	TR8	TR9	TR10
T	°C	19	19	20	20	20	20	20	21	19	19
EC	µs/cm	916	932	945	1090	1249	1389	1290	1543	1120	2550
Cl	ppm	70	93	98	134	170	155	122	220	160	534
$\delta^{18}O$	%	-7.1	-6.9	-7.2	-5.3	-5	-4.3	-2.8	-4.5	-4.2	-3
δD	%	-45	-45.5	-45.9	-35.5	-35	-33	-20	-34.5	-32	-22
d-excess	%	11.8	11.7	11.7	6.9	5	1.4	2.4	1.5	1.6	2

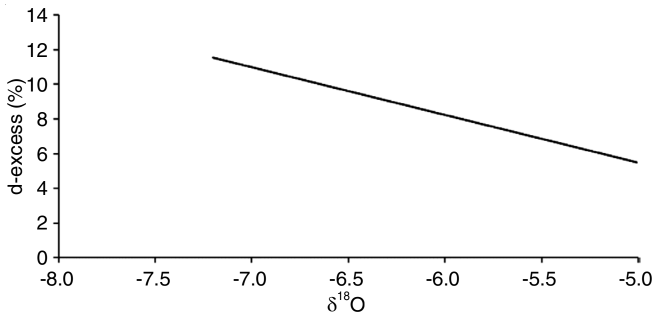

Fig. 3. d-excess *vs.* $\delta^{18}O$ in the study area (February, 2018)

Isotopes was also used to study the origin of salinity and chloride concentration of water. During the study period, the values were found more variations in Cl^- concentration at 10 stations situated along the Tigris river course, evaporation process and anthropogenic are controlled to chloride concentration in the study area (Fig. 4). Similarly, the same trend can be use to investigate the source of salinity. The variations of isotopic behaviour of tributaries are due to the geographical and hydrometeorological parameters, like altitude of drainage areas, spatial and temporal precipitation distribution, sources of air moisture, residence times of ground or evaporation processes, *etc*. By comparing the values of stable isotopes found in Tigris river with Euphrates river, the range of stable isotopes ($\delta^{18}O$) in Tigris river is relatively small which ranged -6.6 to -6.3 % in Euphrates river [21].

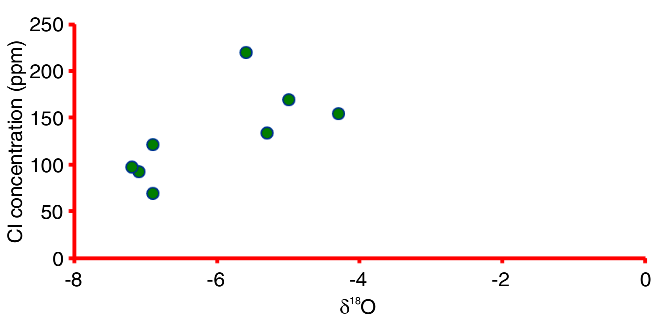

Fig. 4. Chloride concentration *vs.* $\delta^{18}O$ in the study area (February, 2018)

Conclusions

The results of isotopes and chemicals distribution in Tigris river flowing between Baghdad and Ammara cities as follows:

• There is a huge difference in isotopic data and chemical composition between the studied sites along Tigris river.

• The oxygen-10 showed a steady increase in the downstream direction.

• Distribution of isotopic values in the north sector (Baghdad city to Aziziyah) more depleted than in the south sector (Ammara city). The adverse trend shows in the chemical compositions also.

• The differences in isotopic values in Tigris river between Baghdad and Ammara city could be attributed to water interaction from wades mixing (Shwacha valley) with groundwater. The effect of runoff valleys is a quite clear in the enrichment of both isotopic and chemical composition in Tigris river as compared to previous years.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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