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Hydrochemical and Quality Assessment of Euphrates River Water Between Al-Hindiya Barrage and Nasyrah City, Iraq

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ABSTRACT

The hydrogeochemical study (major ions, heavy elements and water quality) is carried out for a section of the Euphrates River water extending between the Hindiya Barrage and Nasiriya City for a distance of 383 km. This is done by choosing eight sites for water samples (in dry and wet periods). Chemical analysis for water samples is conducted for major ions and heavy elements. To analyze the results, a hierarchical statistical analysis is used. It is found that the water samples are distributed into two main groups and three sub-groups, which indicates that there has been mixing of river water with water from another sources (drainage water and salty groundwater). Stiff diagram indicates the predominance of sodium and chlorine ions at the last site (S8). Piper plot shows a state of chemical mixing and that the water types are confined to (Ca-Cl), (Na-Cl), and (Ca-Mg-Cl) classes. Durov diagram indicates that there are chemical mixing processes for types of water as well as ion exchange processes. Through Gibbs diagram, it is found that water samples are distributed in the rock dominance and they tend to the dissolution field than to precipitation dominance. By calculating the heavy metal pollution index of some heavy metals (Pb, Co, Cu, Fe, Cd and Mn), it is found that the water is highly polluted with these heavy metals. From the Welcox and Riverside diagrams, it is found that the river's water quality is deteriorating at sites S6, S7, and S8, and that use of this water is harmful for irrigation.

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هايدروكيمياوية ونوعية مياه نهر الفرات ما بين سدة الهندية ومدينة الناصرية، العراق

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الملخص

اجريت دراسة هايدروجيوكيمياوية (الايونات الرئيسة، العناصر الثقيلة ونوعية المياه) لمياه مقطع مختار من نهر الفرات يمتد ما بين سدة الهندية ومدينة الناصرية ولمسافة (383 كم) من خلال اختيار ثمانية مواقع على طول مقطع النهر. تم اجراء التحاليل الكيمياوية للعينات المنمذجة لقياس تراكيز الايونات الرئيسة وبعض العناصر الثقيلة. من خلال تحليل نتائج تراكيز الايونات الرئيسة بواسطة التحليل الاحصائي الهرمي للمجاميع، وجد ان عينات المياه تتوزع بمجموعتين رئيستين وثلاث مجاميع فرعية، والتي اشارت الى ان هنالك عمليات مزج حصلت لمياه النهر بمياه من مصادر اخرى (مياه بزل ومياه جوفية مالحة). أشار مخطط ستيف الى سيادة أيونات الصوديوم والكلورايد وخصوصا في الموقع الثامن للنهر. اشار مخطط بايبر الى سيادة لعمليات المزج بين انواع مختلفة من المياه، وان نوع المياه هو (Na- Cl) و (Ca-Cl) و (Ca- Mg- Cl). يشير مخطط دروف الى عمليات مزج وعمليات تبادل ايوني. مخطط كبس اشار الى ان اغلب العينات تتركز في حقل سيادة التبخر. وجد من خلال حساب دليل التلوث للعناصر الثقيلة (Pb, Co, Cu, Fe, Cd و Mn) ان المياه ملوثه وفي جميع مناطق النمذجة بنسب عالية بالعناصر الثقيلة مقارنة بالمقاييس العالمية، بينما اشارت مخططات ولكس ورفر سايد الى ان المياه تتدهور سريعا وخصوصا في المحطات الثلاث الاخيرة وأن المياه غير صالحة للسقي خصوصا في المحطة الأخيرة.

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Introduction

In Iraq, surface water has played a role in the country's economy, with its various uses for drinking, agriculture, industrial purposes, fish farming and power generation etc. This water is mainly from the Tigris and Euphrates Rivers. The Euphrates River length is about 2,786 km, as it originates in Turkish territory and flows south through Syrian and Iraqi territory, where it meets the Tigris River at the city of Qurna in southern Iraq to form Shatt al-Arab River, where many dams and hydropower projects were erected, in addition to exposing the river to enormous pollution problems due to the presence of many cities on its sides (Al-Ansari et al., 2018).

The Euphrates River and its basin are the main source of water equipped for human settlements and all life aspects. As well as sediments transported by the river and for thousands of years, working to increase soil fertility, which helped the growth and development of population societies. That the water of the river at any point of it reflects all the effects whether natural, such as the river basin lithology, climate conditions or man affect (Rakotondrabe et al., 2017). Human has affected in a major impact on the water quality deterioration, which is represented by domestic and industrial waste that is daily dumped to the river (Al- Mayyahi and Al-Shammary, 2022).

The annual changes in the quantities of water feeding the river from its sources in Turkey together with the lack of rain fall and the decline of snow as a result of climate changes are dominated effects on water supply during the last two decades; another effect is the human action by dams' construction on the river course, all of these led to a quantitative and qualitative deterioration in the water (Vega et al., 1998). For these reasons, a comprehensive management is required for the sustainability of water resources (Mori and Inagaki, 2012).

This study aims to shed light on the level of pollution in the Euphrates River water, which reflects on its suitability for other purposes.

Study area

The study area extends between Hindiya Barrage (32°43'42.04"N, 44°16'4.74"E) and Nasiriyah City (31°1'54.14"N, 46°16'20.69"E). The studied section of the Euphrates River extends for a distance of 383 km (Fig. 1). The river is the main source of water for all uses, serving an area of about 6470 km2. The whole Euphrates River is controlled by an advanced set of dams and regulators, which in turn are working on distributing water and upgrading it to all lands within the Euphrates River basin. The temperature ranges between 17- 44.7° C, rainfall amounts are between 0 - 48.44 mm, while evaporation rates are very high and range from 80.57 - 452.74 mm (Iraq Meteorological Organization, 2016).

Geology

The Euphrates River runs in the study area through the Mesopotamian plain that occupies the central part of Iraq as a large low basin covered by a thick layer of Quaternary sediments of the Tigris and Euphrates Rivers and their tributaries. The Euphrates River forms the boundary between the Mesopotamian plain and the southern Iraqi desert. The river runs parallel to the Euphrates-Abu Jir fault zone between Najaf and Samawa, but after Samawa City, the river tends to flow through the Mesopotamian (Sabah, 2011). This segment is characterized by the presence of lakes, marshes and aeolian sediments, which are usually unconsolidated less soft granules than the underlying formation (Saad and Goff, 2006).

The river flows between the cities of Al-Shinafiyah and Samawah, passing through Quaternary salt deposits from the Holocene period. This salt, which is derived from the dissolution of deep rocks of Rus Formation by groundwater rising upward via the faults fractures that spread in the area (Abu-Gir faults system), where spring groundwater flows towards the Euphrates River (Jassim and Al-Badri, 2018).

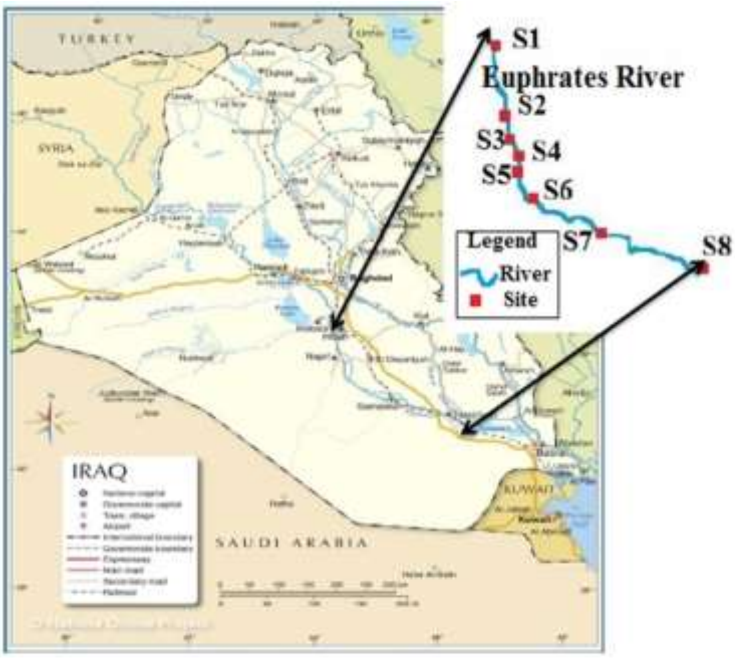

Fig. 1. The study area.

Materials, Methods and samples analysis

Samples collection

In this study, the concentration of major ions ($Na1+$, $K+$, $Ca2+$, $Mg2+$, $Cl-$, $SO2-4$, $NO-3$ and $HCO-3$) and heavy metal in water are studied along a selected section of Euphrates River extending between Al- Hindiya Barrage through the cities of Kifl, Kofah, Abu-Skher, Mishkhab, Shanafiyia, Samawa and Nasiriyah. A GPS device (GARMIN, GPS62st) is used to determine the locations of the selected water samples sites along the river. The acidity (pH), conductivity (EC), and total dissolved ions (TDS) are measured in sites using the Hana device. Water samples were collected during the year (2022) from eight sites along the selected section of the river, specifically during the months of July and December of the dry and wet periods respectively for hydrochemical analysis. For this purpose, polyethylene bottles were used for sampling, that were sterilized using diluted hydrochloric acid (10%), then washed with distilled water and then washed with river water before sampling (Nollet, 2007). All these samples were filtered by 0.45 milipore filter. For the purpose of determining the concentrations of heavy elements, 1 ml of nitric acid is added. All samples were kept at a temperature of 4°C until they were sent to the General Commission of groundwater laboratories for major element analysis for the ions ($Na1+$, $K+$, $Ca2+$, $Mg2+$, $Cl-$, $SO2-4$, $NO-3$ and $HCO-3$), while for heavy metals (Pb, Co, Cu, Fe, Cd and Mn) are analyzed using a Shimazu Atomic Absorption Spectrometer at the laboratories of the College of Science, Al-Qadisiyah University.

To perform the water quality analysis and temporal-spatial hydrochemical variations of wet and dry periods, various types of techniques have been applied such as (IBMSPSS Statics v.22, AqQA, Diagram softwares, Piper Plot, Dorov Plot, Stiff Diagram and Gibbs Diagram).

Statistical hierarchical cluster analysis

Statistical hierarchical cluster technique analysis is used to identify the similarity between groups together (Varol et al., 2013). It is used to identify similarities between water samples constituents according to the variable locations depending on the chemical composition of the river water's samples. The chemical factors that have been chosen for cluster hierarchical analysis are ($Ca2+$, $Mg2+$, $K+$, $Na+$, $HCO- 3$, $SO2-4$, $Cl1-$ and TDS).

Gibb's plot

Data are represented on a Gibbs Diagram (Gibbs, 1970) in terms of the equivalent ratio of the ions ($Na+/Na++Ca2+$) and ($Cl-/Cl-+HCO-3$) with TDS. This scheme is widely used to evaluate the hydrochemical process. The samples are distributed between the phases of precipitation, erosion of rocks and their dissolution, evaporation and crystallization.

Heavy metal pollution index (HPI)

It is an important indicator for assessing pollution in water bodies. This indicator is formulated on the basis of weighted mathematical quality (Prasad and Sangita, 2008; Sing and Rakesh, 2016). The values of weights (wi) range between (0 and 1) for each element whose concentration is measured in the water samples, where the total value of the critical pollution index is 100 (WHO, 2011). This classification is based on the proportional importance of each element for individual quality considerations and is defined as being inversely proportional to the recommended standards (Si) for each parameter (Rakotondrabe et al., 2017). The index calculation process includes the following mathematical operations. The first is represented by calculating the weighted value (Wi) of each variable using the following equation:

$$Wi = k / Si \text{ .... } (1)$$

Note that k is a constant while Si represents the permissible standard limits for each element according to WHO (2011) and Bhardwaj et al. (2017). Second, the quality ratio (Qi) is calculated for each heavy element according to the following formula:

$$Qi = 100 \times Vi/Si \;........... (2)$$

Where Qi is a sub-index for every single variable, Vi is the value of the actual concentration of the variable in the water sample in (mg/l) and Si is the standard permissible value for each variable (Mohan et al., 1996).

The concentration of each pollutant is converted to HPI according to the following formula:

$$HPI = \sum_{i=1}^{n} W\mathrm{i}\, Qi \,/\, \sum_{i=0}^{n} W\mathrm{i} \;.......... (3)$$

Water quality for irrigation purposes

The validity of the water for irrigation purposes requires calculation of Sodium Absorption Ratio (SAR) and Sodium Percentage (% Na) using the Wilcox and Riverside plots. The calculation of Na% is related to the relative percentage of cations concentrations in the water. The ion concentrations are calculated in meq/l by the following equation:

$$Na\% = Na^{+} + K^{+} / Ca^{2+} + Mg^{2+} + K^{+} \;............. (4)$$

SAR is calculated by the ratio of the concentrations of sodium, calcium and magnesium ions according to the following equation in meq/l:

$$SAR = Na^{+} / [(Ca^{2+} + Mg^{2+})/2]^{0.5} \;………. (5)$$

There is a relationship between SAR concentrations in irrigation water and the absorbance of sodium ions (Wilcox, 1948). The presence of high concentrations of ions in the water has a direct effect on the plant and its productivity, as it works to break down the physicochemical properties of the soil (Wilcox, 1948; US Salinity Laboratory Staff, 1954).

Results and Discussion

Hierarchical analysis

Hierarchical analysis of surface water chemistry component is performed based on the concentrations of the major ions in the Euphrates River of two periods (dry and wet) (Tables 1 and 2). As a result of the analyses, dendritic patterns, each consists of two important groups and sub group distributed along the selected section of the river (Figs. 2 and 3). The first subgroup (A) includes the sites (S3, S4 and S5) during the dry season, as well as the same sites included during the wet season, where these sites occupy the central part of the chosen river section. The second subgroup (B) includes sites S1 and S2 for both seasons, and these sites occupy the upstream of the river section, while the third subgroup (C) includes the sites (S6, S7 and S8), where these sites occupy the downstream of the river from the chosen section.

It is noted in Figures (2 and 3) that the sixth site are placed with a sub group because during summer period, large quantities of drain water were discharged into the river at this site through the Nagarat Abu-Hajaar drain project, this project collects drainage water for all agricultural rice lands surrounding the river during the summer season, while during the wet season, it was found that this site (S6) falls within a subgroup with the (S7), and there is no big difference in their chemical concentration. However, it is found that (S8) is isolated in an individual subgroup during the wet season as a result of the pollution of the river water through its passage, which surrounds the river.

Table 1: Concentration of major ions (Dry period).

Station	site	pH	EC	TDS	Na^{2+}	K^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}
Hindiya	S1	8.20	1640	820	67	4.7	128	49	234	181	2.5	147
Kifel	S2	8.00	1820	910	69	4	123	49	211	300	2	144
Kufa	S3	8.10	2510	1255	165	6.8	160	60	220	485	2.6	149
Abu Skheer	S4	8.00	2690	1345	180	5	141	90	257	492	2.9	170
Mishkhab	S5	8.20	2710	1355	197	5.5	141	63	273	492	2.6	166
Shanafiya	S6	8.10	3940	1970	394	6	173	47	357	748	3	231
Samawa	S7	8.00	4820	2410	562	6.7	185	41.6	621	750	3.1	235
Nasiriya	S8	8.14	5320	2660	465	7.6	208	145	716	865	2.2	234

All Concentrations are in ppm; EC is given in µS/cm

Table 2: Concentration of major ions (Wet period).

Station	Site	pH	EC	TDS	Na^{2+}	K^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	HCO_3^{-}
Hindiya	S1	7.6	1500	750	65	1.3	121	46	205	167	2	136
Kifel	S2	7.5	1890	945	107	1.2	138	50	204	296	4.9	138
Kufa	S3	7.3	2410	1205	185	1.2	135	60	238	426	2.9	147
Abu Skheer	S4	7.5	2320	1160	125	1.6	154	59	202	402	1	204
Mishkhab	S5	7.4	2640	1320	178	1.1	136	88	254	479	4.9	169
Shanafiya	S6	7.5	3890	1945	405	4.8	172	45	359	723	4.8	220
Samawa	S7	7.4	4060	2030	465	3.5	160	32	462	676	7	218
Nasiriya	S8	8	5310	2655	500	5.1	200	160	702	839	5	229

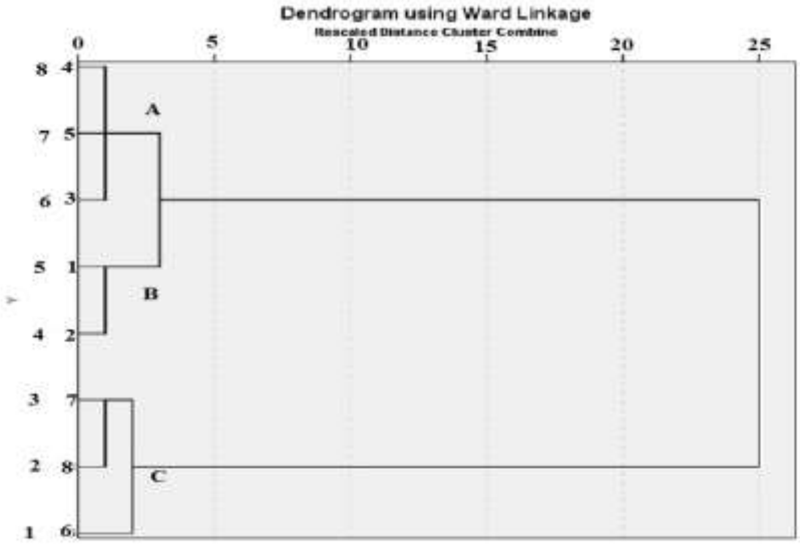

Fig. 2. Dendrogram viewing clustering of sample sites (Dry period).

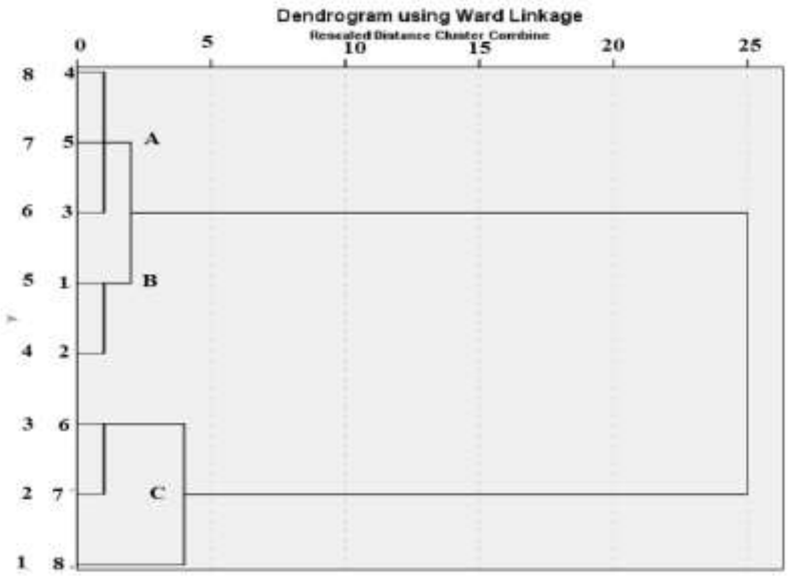

Fig. 3. Dendrogram viewing clustering of sample sites (Wet period).

Water quality

All samples, for the wet and dry periods, have basic pH values, with a range between 7.3 to 8.20. According to WHO (2011), the permissible limits for the total dissolved ion concentrations of drinking water is 1000 mg/l. However, the TDS values of 16 samples for both periods vary between 750 and 2660 mg/l (Table 3). Between eight sites only S1 and S2 are within the permissible limits for both periods.

Sodium ion concentrations are within the acceptable limits in the first five sites (S1, S2, S3, S4 and S5). The concentrations of magnesium ion in all sites are outside the permissible limits. The concentrations of chlorine ions are within the acceptable limits in the first six sites and outside the permissible limits in the last two sites S7 and S8. Sulfate concentrations in the first and second sites only are within the permissible limits, while the concentrations of carbonates are within the permissible limits for all sites (Table 1, 2, and 3).

Through Stiff Diagram (Fig. 4), it is noticed that there is a clear increase in the concentrations of sodium and chloride ions at the final site of the section (S8) when compared to the first site (S1), and a decrease in the concentrations of carbonate and calcium ions is noted. It is considered a normal result due to the saline drainage waters that are discharged into the river especially at site S6, as well as ion exchange processes.

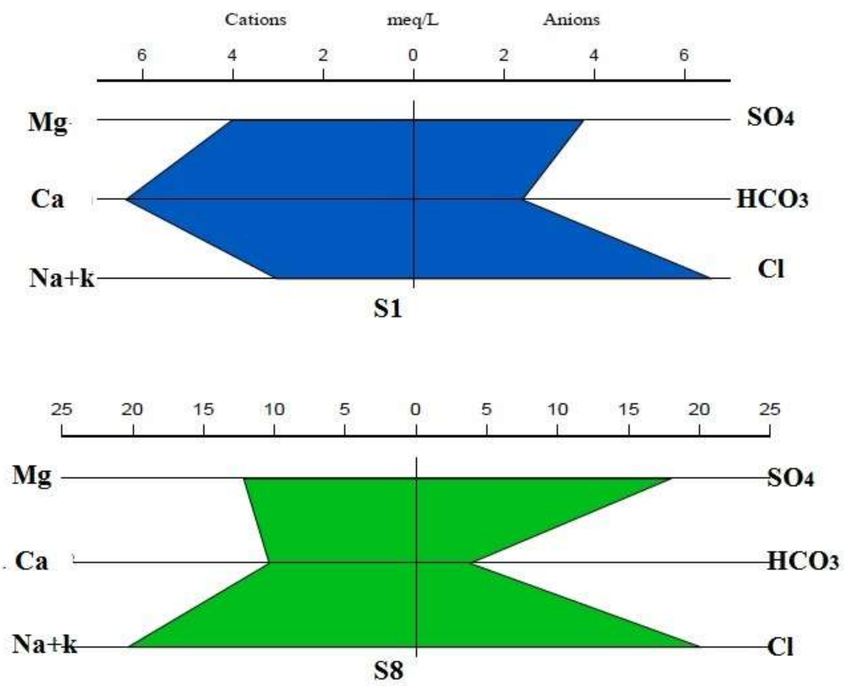

Fig. 4. Stiff diagram for the S1 (first sampling site) and S8 (Last site).

Table 3: Hydrochemical parameter range and permissible limit.

Element	Dry period range	Wet period range	WHO
pH	8-8.2	7.3-7.8	6.6 - 8
EC	1640-5320	1500-5310	1000
TDS	820-2660	750-2655	1000
Na^{2+}	67-562	65-500	200
K^{+}	4-7.6	1.1-5.1	-
Ca^{2+}	123-208	121-200	300
Mg^{2+}	49-145	46-160	30
Cl^{-}	211-716	202-710	400
SO_4^{2-}	181-865	167-839	400
HCO_3^{-}	123-209	121-200	500

Geochemical Variation

To know the water quality and the geochemical changes in the course of the Euphrates River, Piper and Dorov Plots are used (Figs.5 and 6) (Piper, 1944). The water types are limited to Classes 2, 3 and 5. The water type for sites S1, S2, S5 and S4 is Ca-Cl, while the water quality for sites S5 and S7 is Na-Cl type, and for sites S3 and S8 Ca-Mg- Cl.

Through the Dorov plot (Durov, 1948), all the water samples are distributed within field 5. It is evident that all the water samples for the sites illustrate the prevailing fact that there are mixing processes, these processes lead to the non-dominance of any type of cations or anions. The hydrochemical processes are closer to ion exchange processes than reversible ion exchange (Lloyd and Heathcote, 1985).

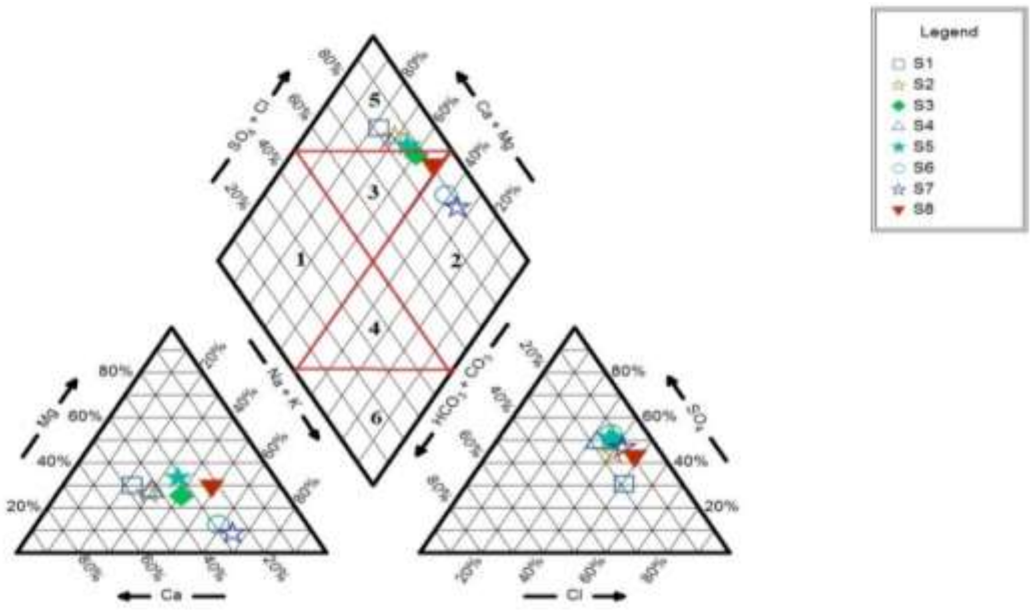

Fig. 5. Piper plot.

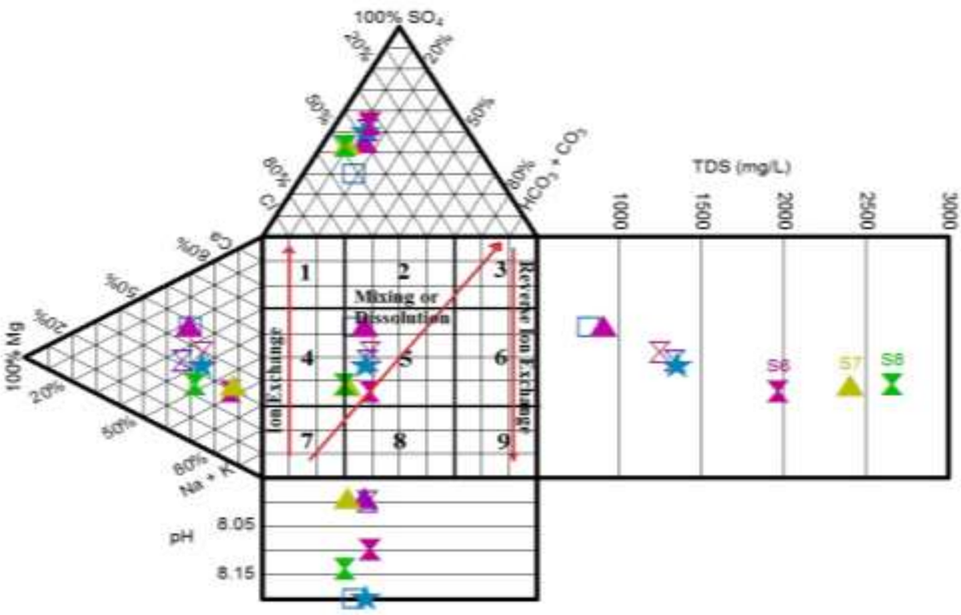

Fig. 6. Durov Plot.

Hydrochemical Processes

There are three dominant natural chemical processes that control the chemistry of surface water represented by evaporation, rainfall and interaction between water and river bed processes (Gibbs, 1977). From Figure (7), it is clear that the natural processes affecting the chemistry of Euphrates River water are evaporation processes, followed by interaction processes between water and sediments. Also, it is found that sodium concentrations during the wet season are higher than during the dry period. This is the result of very high-water releases for the purpose of rice agriculture, whose cultivation requires large and continuous amounts of water and continuous drainage throughout the agricultural season. Unfortunately, this drained water is returned to the river to be used again without treatment, due to the large water deficit in the country. This leads to a reduction in salt concentrations contrary to expectations as the salinity increases during the winter season due to the lack of water imports, lack of drainage water and shortage of rainfall, which leads to water salinization in addition to an increase in evaporation during the two seasons.

In the Gibbs plot, there are three dominant natural chemical processes that control the chemistry of surface water represented by evaporation, rainfall and interaction between water and river bed processes (Gibbs, 1977). The samples are distributed in locations characterized by TDS values of about 1000 mg/l or more. The equivalent ratio of sodium ion (Na^+ / Na^+ + Ca^{2+}) tends to be less. From Figure (7), it is clear that the natural processes affecting the chemistry of Euphrates River water are evaporation processes, followed by interaction processes between water and sediments.

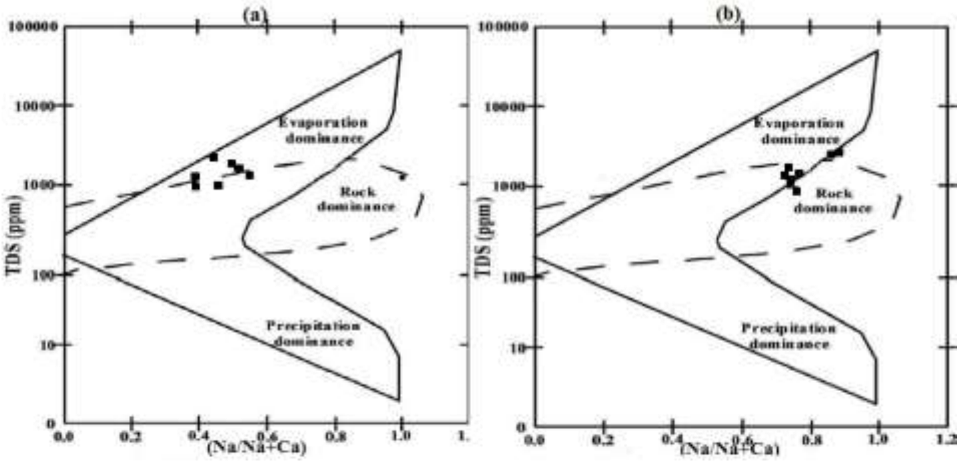

Fig. 7. Gibbs Plot which represents the natural processes that determine the chemistry of a river's water

Heavy Metal Pollution Index

Tables (4 and 5) show the concentrations of iron, cadmium and lead ions are present in the river waters at high levels far from the permissible limits. This indicates that the river's water is polluted with these metals. The high increase in the concentrations of these elements is due to the wastes that are discarded by the cities sited along the river, as well as the drainage water, which is discarded directly without treatment from the surrounding agricultural lands.

The heavy metal pollution index and the weighted values (Wi) have been calculated according to what is previously stated in the materials and methods for all the eight stations and the values are shown in Table (6). It is found that the pollution index values for all water samples in the selected stations on the river are very high, with an average of (4613.129). This value is very far from the HPI value of 100. Based on the foregoing, the level of pollution is very high in this section of the river. These results indicate that the river water is polluted and poses a threat to public health.

Table 4. Heavy metals concentration in (ppm).

Site	Pb	Co	Cu	Fe	Cd	Mn
S1	0.02	0.4	0.93	2.09	0.17	0.23
S2	0.07	0.3	1.2	2.1	0.2	0.3
S3	0.1	0.5	0.89	2.2	0.2	0.29
S4	0.14	0.45	1.2	2.6	0.3	0.32
S5	0.17	0.39	1.7	2.5	0.23	0.35
S6	0.2	0.5	1.8	2.7	0.21	0.41
S7	0.26	0.56	2	3.1	0.35	0.45
S8	0.35	0.55	2.4	3	0.421	0.52
Permissible limit	0.01	0.01	2	0.3	0.003	0.4

Table 5. Relative weight of heavy metal pollution in Euphrates River.

Heavy metals	W_i	Unit weightage (W_i)	Standard permissible value according to WHO, 2011 in (ppm) after (Rakotondrabe et al., 2017)
Pb	1	20	0.05
Co	1	100	0.01
Cu	1	0.666	1.5
Fe	1	3.333	0.3
Cd	1	200	0.005
Mn	1	2.5	0.4
		∑ 326.5	

Table 6. HPI values in Euphrates River.

Sites	W_i	$\sum W_iQ_i$	HPI
S1	326.5	1081652	3312.8
S2	326.5	1105374	3385.5
S3	326.5	1306665	4002.03
S4	326.5	1658742	5080.3
S5	326.5	1319872	4042.4
S6	326.5	1351336	4138.8
S7	326.5	1974214	6046.5
S8	326.5	2251765	6896.7

The clear discrepancy in values and the unexpected rise is due to the locations of the water samples on the rivers that may be close to sources of pollution, as well as due to drainage projects that flow directly into the river from all the agricultural lands surrounding the river.

The SAR values are plotted on the US salinity diagram (Fig. 8a), and it is found that the sites S1, S2, S3, S4 and S5 are in the field of low to medium concentrations. Where the water in these locations is suitable for irrigation in various types of soils. While it is found that the last three sites of the river section (S6, S7 and S8) are located within the high concentration field, and this indicates the high levels of sodium ions concentrations, and therefore attention must be paid, because this water cannot be used for all types of soils and only those with high porosity.

According to the Na% with electrical conductivity (Fig. 8b), it is found that the last 3 sites (S6, S7 and S8) are not suitable for irrigation, while the other sites (S1, S2, S3, S4 and S5) fall within the good to doubtful ranges.

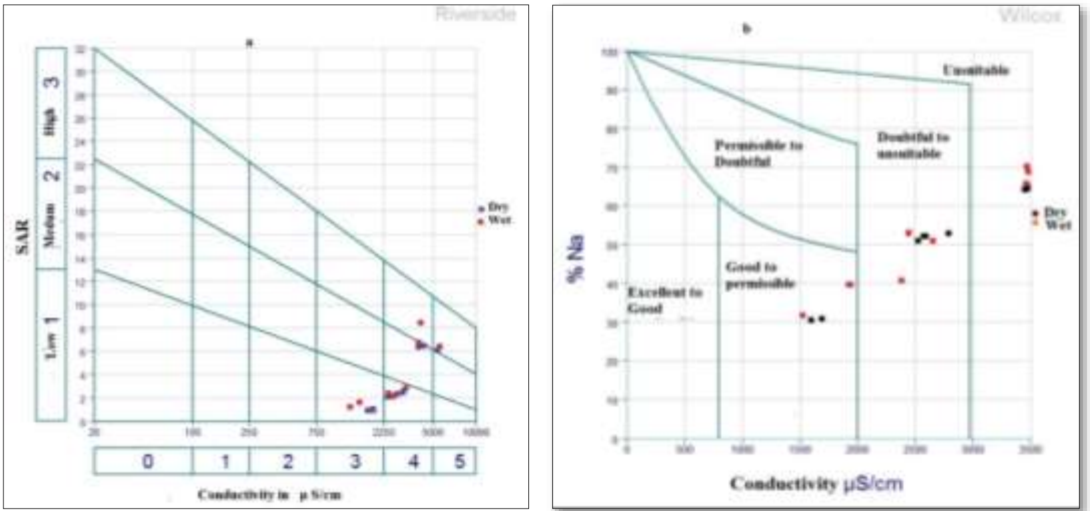

Fig. 8. Riverside and Wilcox plots for Irrigation water.

Conclusion

The hydrogeochemical nature of the river water is verified by conducting analyses for the major cations, anions and some heavy metals. Cluster hierarchical statistical analysis proved that water samples are divided into only two main groups and subgroups, which indicates the occurrence of chemical mixing processes of similar chemical component. Also, Stiff diagram indicates the predominance of sodium and chlorine ions at the last site (S8), as a result of mixing of drainage water and salty groundwater. The Piper plot shows a state of chemical mixing processes. Dorov diagram shows that all the river samples are located within the mixing field among more than one water type. Through a Gibbs diagram, it is found that water samples are distributed in the rock dominance. Heavy metal pollution index indicates that the river water is highly polluted with heavy metals. From the Welcox and Riverside diagrams, it is found that the river's water quality is deteriorating at sites S6, S7, and S8, and that use of this water is harmful.

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