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Assessment of Contamination along the Tigris River from Tharthar-Tigris Canal to Azizziyah, Middle of Iraq

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Abstract: The Tigris River is the second-longest river in Western Asia and runs through heavily populated areas, especially in Baghdad city with nearly 8 million inhabitants. The water demand is at its highest levels, nevertheless the Tigris discharge has severely declined in the last decades; combined with the fact that the wastewater quantities are increasing, and the wastewater treatment plants are experiencing a deficiency. Four sites were chosen: the Tharthar-Tigris Canal which is located in the north part of Baghdad city, Baghdad city, the Diyala River conjunction with the Tigris River site, and Al-Azizziyah site in the south of Baghdad city near Kut government, to determine the effect of the decreasing Tigris River flow on the water quality and to identify the sources of pollution. In this research, the used method evaluates the concentration of the contaminants along the course of the Tigris River to determine the source of the contaminants as the novelty of this research. The data include the discharge of The Tigris River, a hydrochemical analysis, such as major ions and trace elements, and biological parameters (BOD_5, COD, *E. coli* bacteria, and coliform bacteria MPN/100 mL) as contamination indicators. Multivariate statistical techniques (factor analysis) were applied to evaluate spatial variations, for the years 2005 to 2020, and Phreeqc software was used to assess the saturation indices determine the dominant geochemical processes source responsible for surface water quality. The dominant minerals of the Tigris River were gypsum, anhydrite, and halite. The Tigris River is within the permissible limits for drinking, except at the Tharthar-Tigris Canal and Diyala River, and the main water quality deterioration factors of the Tigris River were recognized as: total dissolved solids, *E. coli* bacteria, fecal coliform bacteria, BOD_5, and COD. By applying the SPSS program, two factors were identified. The first anthropogenic factor discharged into the river represents 71.27% of the variance and is comprised of agricultural land wastewater and sewage water. While the second factor represents 17.02%, indicated by the variables Ca^{2+}, K^{+}, Mg^{2+}, and $SO_4{}^{2-}$. This factor accounts for the chemical weathering of rocky components. It is recommended that a periodic monitoring system is needed to follow up on pollution levels and water quality for the Tigris River, by conducting seasonal surveys.

Keywords: Tigris River; contamination; bacteria; surface water; Iraq

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1. Introduction

The Tigris River is a vital resource of water for domestic use and economic activities in Iraq. The evaluation of water quality in Iraq has become a critical issue in recent years, especially due to the concern that fresh water will be a scarce resource in the future and it is always susceptible to pollution [1].

The Tigris River is the second longest river in Western Asia. It is 1850 km long, originating from eastern Turkey, enters Baghdad city from the north heading toward the south as a part of the alluvial plain with an average flow rate of 540 m^3/s for the period 2005–2020. The bed comprises mainly fine sand, silt, and clay [2]. The Tigris River runs through heavily populated areas especially in Baghdad city with nearly 8 million inhabitants [3]. The water demand is at its highest level, nevertheless the Tigris River discharge has severely declined in the last decades; combined with the fact that the wastewater quantities are increasing and the treatment plant is experiencing deficiency [4].

Contamination of the Tigris River water by the transmission of toxic pollutants as a result of anthropogenic activities such as domestic wastewater, hospitals, and industrial factories which discharge their wastewater directly into the river without any real treatments pass through Baghdad city and threaten the ecosystem for plants and living organisms [5]. Such untreated wastewater inputs contaminate the river water with trace element contaminations and by many contaminant indicators such as COD, BOD_5, and other biological parameters [6–9]. Excess intake of essential trace elements in drinking water may lead to adverse health effects [10]. In particular, elements such as cadmium, chromium, copper, zinc, and lead have significant biological toxicity and are harmful to human health. For example, if their concentration goes above the necessary amount, they are harmful to the liver, kidney, digestive system, blood system, nervous system, and brain [10,11].

Considering the increasing need for drinking water and the stringent concentration limits of their dissolved constituents, and due to their toxicity, non-biodegradability, and persistency, heavy metals can exert adverse effects on the environment and other ecological receptors. It is mandatory to develop and apply efficient remediation systems based on geochemical considerations [12,13]. Therefore, various methods have been developed and used to decrease heavy metals concentrations in ecosystems. These technologies can be categorized in physicochemical processes such as ion exchange, reverse osmosis, membrane filtration, adsorption, precipitation, electrolytic removal, and biological processes involving activated sludge and phytoremediation [14–17]. In the future it is recommended to apply the nanofiltration/reverse osmosis (NF/RO) technologies for the Tigris River water to remove dissolved ions such as divalent ions(SO_4^{2+}, Ca^{2+}, Mg^{2+}, Na^+) from contaminated water [18–20].

Some widely used adsorbents for the removal of metal ions include clay minerals, activated carbon, biomaterials, industrial solid wastes, and zeolites [15]. An approach that can be used to sustain the surface water is monitoring the sources of the contaminants and trying to decrease their effects.

Wastewater discharges without any treatment in rivers, sewage effluent from domestic waste, garbage dumped into the river, or washing and/or effluent human/animal tools are a major source of fecal microorganisms, including pathogens [21,22]. For example, some strains of *E. coli* bacteria (*Escherichia coli*), are pathogenic, which means that they can cause infection that leads to diarrhea, urinary tract infections, respiratory illness, and pneumonia; coliform bacteria are capable of invading and multiplying in the intestinal epithelial cells of the distal large bowel in humans [23].

Anthropogenically derived water pollution from BOD_5 and COD are another major perturbation in aquatic ecosystems that results in an increased influx of pollutants and nutrients into aquatic systems and significantly disrupts the structure and function of natural microbial assemblages, leading to reduced species diversity, increased heterotrophy, and a rise in the number of potentially harmful microbes [22,24,25].

The selected area extends from Tharthar-Tigris Canal which is located in the north part of Baghdad city to Al-Azizziyah city in the south of Baghdad city near Kut government within the following geographical coordinates ranges (33°55′07″–32°54′30″ N and 44°22′16″–45°4′0″ E), (Figure 1).

The chosen Tigris River course is due to the effect of high salinity from the discharging water of Tharthar-Tigris Canal on the Baghdad site, in addition to the effects of human activities (hospitals, industrial factors, domestic wastewater, and others). Furthermore, the Contamination of the Al-Rustimiyah treatment plant located on the Diyala River has an important effect on water quality and contamination that affect the Tigris River southern course that is vital for the southern governorates, Waset, Misan, and Basra. The Al-Rustimiyah treatment plant has limited capacity of wastewater treatment; hence, the overload wastewater is discharging into the river without any treatment.

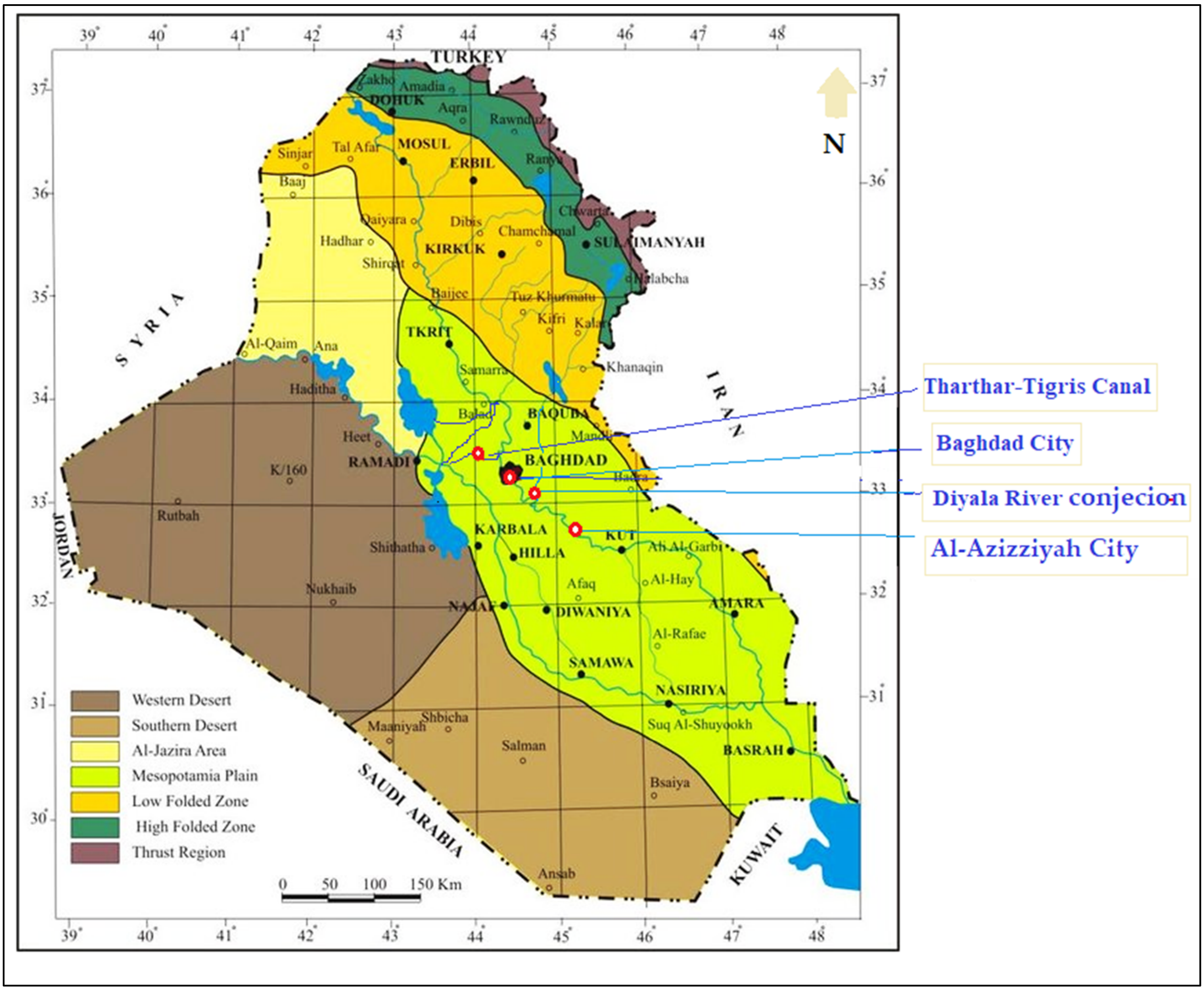

Figure 1. Location map of the Tigris River in the study area [26].

The used methods in this research, are to evaluate the concentration of the contaminants along the course of the Tigris River to determine the source of the contaminants, analyzing the results, explaining the reasons behind the contamination on the hydrochemistry of Tigris River for the years 2005 to 2020 as the novelty of this research.

The aim of this study is to determine the concentration of major ions, trace metals such as: Cu, Cd, Zn, Pb, Fe, and Cr, and biological parameters analysis such as BOD_5, COD, *E. coli* bacteria and fecal coliform bacteria, that are considered good indicators of the surface water pollution, to assess the environmental pollution of the Tigris River annually during 2005–2020 along the river from Tharthar-Tigris Canal to Al-Azizziyah city.

The geology of the Tigris River in the studied sites, started from the Tharthar-Tigris Canal which it consists of the Fat'ha Formation (Middle Miocene) that is comprised of alternating beds of anhydrite, gypsum, halite, and salt, inter-bedded with limestone, marl, and relatively fine-grained clastic, and Euphrates limestone (Middle Miocene) which is comprised of shelly dolomitized limestone. At Baghdad to the south of the Al-Azizziyah sites, the river passes through the recent and quaternary sediments [27], (Figure 2).

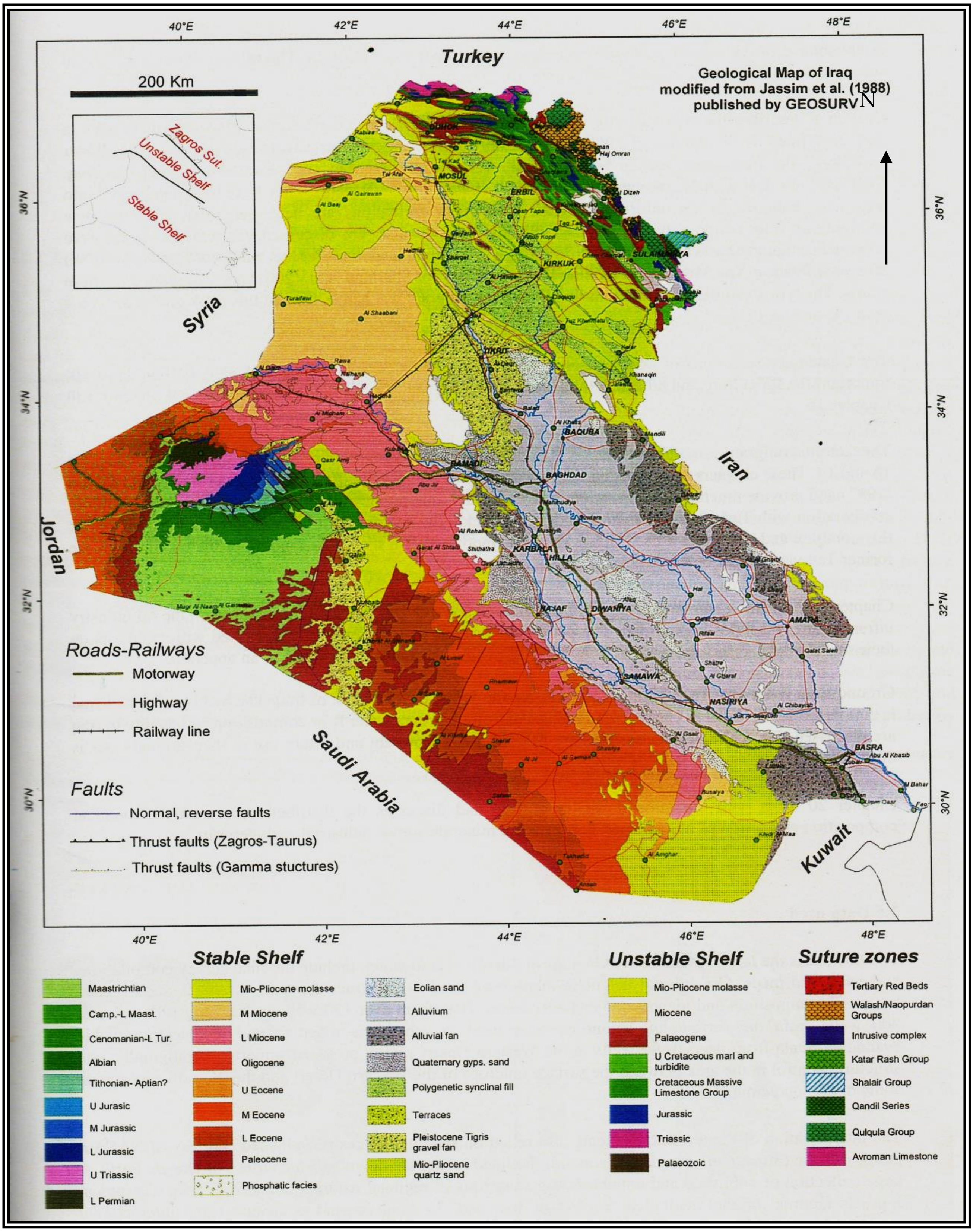

Figure 2. Geological map of Iraq including the Tigris River [27].

2. Materials and Methods

Four sites were chosen: the Tharthar-Tigris Canal, Baghdad, Diyala River conjunction with the Tigris River, and Al-Azizziyah, to determine the effect of decreasing Tigris River flow on the water quality and to identify the sources of pollution for the period (2005–2020) [26].

The reason for selecting this path is that the Tharthar-Tigris Canal is connected to the Tigris River as an outlet canal feeds back from the Tharthar lake, (which is used for water storage and flood relief). The Tharthar-Tigris Canal passes through gypsiferous soil (Gypcrete) that extends from Tharthar Lake to the Tigris River, with the Tharthar Lake saline water which impacts the quality of the Tigris River at the city of Baghdad. The Baghdad site was chosen because it is the capital of Iraq and the biggest city that has many domestic wastewater, industrials factories, and hospitals, which drain the untreated water directly into the Tigris River. The Diyala River conjunction site with the Tigris River was chosen because of the existence of Al-Rustimiyah wastewater treatment plant that affects Diyala River quality by pouring the overloaded untreated municipal wastewater that exceeds its operational capacity to the Diyala River. The Al-Azizziyah site represents the final mixture of the Tigris River flow with the other three selected sites that pass to the southern provinces.

The historical data applied in this research were evaluated and tested for independence, steadiness, and homogeneity [26]. The data include the discharge of the Tigris River, the hydrochemical analysis such as major ions and trace elements, biological parameter indicators such as BOD_5, COD, *E. coli* bacteria and, the most probable number for coliform bacteria MPN/100 mL, (Tables 1–3).The Phreeqc software (version 3.7.3) was applied to assess the saturation indices to determine the dominant geochemical processes responsible for surface water quality deterioration. In addition, multivariate statistical techniques, (factor analysis) were applied using the SPSS 26.0 program to evaluate spatial variations, and to interpret measured water quality within the studied sites. The application of the factor analysis (FA) helps in the interpretation of complex data matrices better understand the water quality and ecological status of the studied systems, and allows the identification of possible factors/sources that influence water systems [28].

Moreover, the Aq. QA software program was used for plotting piper and Schoeller diagrams to display the relative concentrations of the different ions (epm). The hydrochemical formula was computed as an average formula based on a water type formula which was referred according to the Ivanov 1968 method. Plotting Total Ionic Salinity (TIS) was performed as proposed by [29]. The results of the current study were compared with the previous studies to highlights the deterioration of the Tigris River quality in recent years due to the effects of climate change, as well as the construction of dams within the riparian counties [5,30–34].

3. Result and Discussion

3.1. Hydrologic Properties of the Tigris River

The results show that the annual flow of the Tigris River for the period (2005–2020) ranged between (15.96 and 98.02) m^3/s with a mean annual flow (46.71) m^3/s for the Tharthar-Tigris Canal, (Figure 3A). While for the Baghdad site, the range was between (399.84 and 711) m^3/s with a mean annual flow (525.50) m^3/s(Figure 3B); for Diyala River the range was between (8.1 and 136) m^3/s with a mean annual flow (50.97) m^3/s(Figure 3C); and for the Al-Azizziyah site the range was between (132 and 303) m^3/s with a mean annual flow (213.86) m^3/s(Figure 3D). The annual flow of the Tigris River decreased through time in all stations, especially at the Baghdad site (it was 711 m^3/s in 2005 and become 399.84 m^3/s in 2020), due to the climatic change and building dams on the Iraqi–Turkey border as noticed by [35].

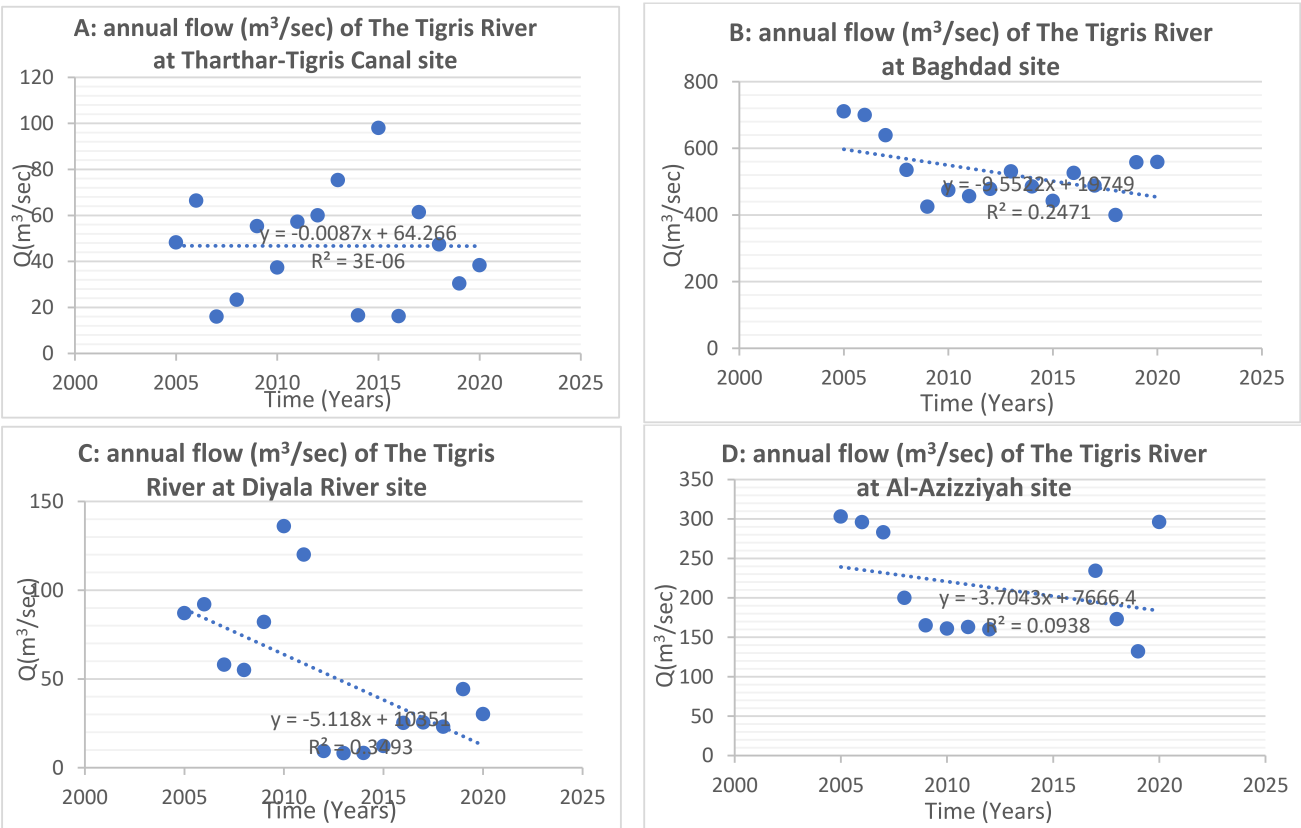

Figure 3. Annual flow (m^3/s) of the Tigris River for the period (1990–2020), (**A**) annual flow (m^3/s) of Tharthar-Tigris canal, (**B**) annual flow (m^3/s) for Baghdad site, (**C**) annual flow (m^3/s) for Diyala River, and (**D**) annual flow (m^3/s) for Al-Azizziyah site [35].

3.2. Hydrochemical Characteristics of The Tigris River

The results of the Major ions and Trace Elements of the Tigris River for the period (2005–2020) from Tharthar-Tigris Canal to Al-Azizziyah sites are tabulated (Tables 1–3) and (Figures 4 and 5) and standard deviation (STDV) recorded for each parameter. Temperature values range between (16.32–23), (12.4–28) C at Tharthar- Tigris Canal and Baghdad site, While, at Diyala River and Al-Azizziyah site ranges between (17.6–33) and (19.6–32) C.

TDS was used as an indicator test to determine the general quality of the water. The concentration of TDS can be related to the electrical conductivity of the water, but the relation is not a constant [36]. WHO (2018) stated that the median value of TDS in drinking water is 1000 mg/L. TDS concentration of the Tigris River varies between (847 and 1601.8) ppm with a mean (1089.4) ppm at the Tharthar-Tigris Canal, while at the Baghdad site it varies between (640 and 815) with a mean (621) ppm. As for the Diyala River and Al-Azizziyah sites it varies between (1268 and 2554) and (620 and 2112.4) ppm with a mean (2003) and (984.3), respectively. For the Tharthar-Tigris Canal site, these may be attributed to an increase in the salinity of the Tharthar Lake which is due to high evaporation and the passing of this canal through gypsum soil as well as the drain water which comes from agricultural lands. As for high concentrations in the Diyala River which are believed to be due to the effects of the untreated water from Russtumia treatment site which are thrown directly into the river. TDS concentration of the Tigris River is within the permissible limits of [37] standards and Iraqi standards [38], except at the Tharthar-Tigris Canal and the Diyala River sites of the Tigris River where they exceed the standards. Temperature values for all sites of the Tigris River are within the permissible limits of [38].

Table 1. Hydrochemical analysis of the Tigris River sites (ppm) for the period (2005–2020) [26].

Site	Parameters	TDS	T C	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
Tharthar-Tigris Canal	Range	847–1601.8	16.32–23	72.9–232	14–391	81–524	2.5–8	107–192	67–1104	55–207
	Mean	1089.4	19.61	138.12	102.55	135.25	11.11	166.78	527.32	114.89
	ST.DV	130	1.22	16.88	4.56	24.5	0.13	16.3	58.11	15.24
Baghdad	Range	640–815	12.4–28	34–128	13.2–150	12–140	1.2–5.5	17–121	106–1152	36–153.5
	Mean	621	21.83	56.37	44.88	66.98	9.06	69.47	233.81	89.61
	ST.DV	88.6	0.98	14.3	5.7	28.3	1.3	12.3	67.3	19.4
Diyala River	Range	1268–2554	17.6–33	12–212	43.2–936	40.5–600	5-37.5	92.3–650	113–1114	56–151
	Mean	2003	25.95	131.34	126.44	296.48	11.89	324.66	754.92	63.29
	ST.DV	50.3	1.12	11.8	4.2	60.3	5.9	16.3	30.4	21.6
Azizziyah	Range	620–2112.4	19.6–32	44–256	19–214	25–433	1.5–5.8	12–764	154–742.8	85.2–123
	Mean	984.3	27.89	102.54	61.83	126	6.3	176.26	306.39	89.85
	ST.DV	145	1.45	10.2	11.6	42.2	0.7	22.8	28.9	13.4
WHO, 2018	ppm	1000		200	150	100	12	250	250	-
IQS, 2009	ppm	1500	<35	200	150	100	12	350	400	-

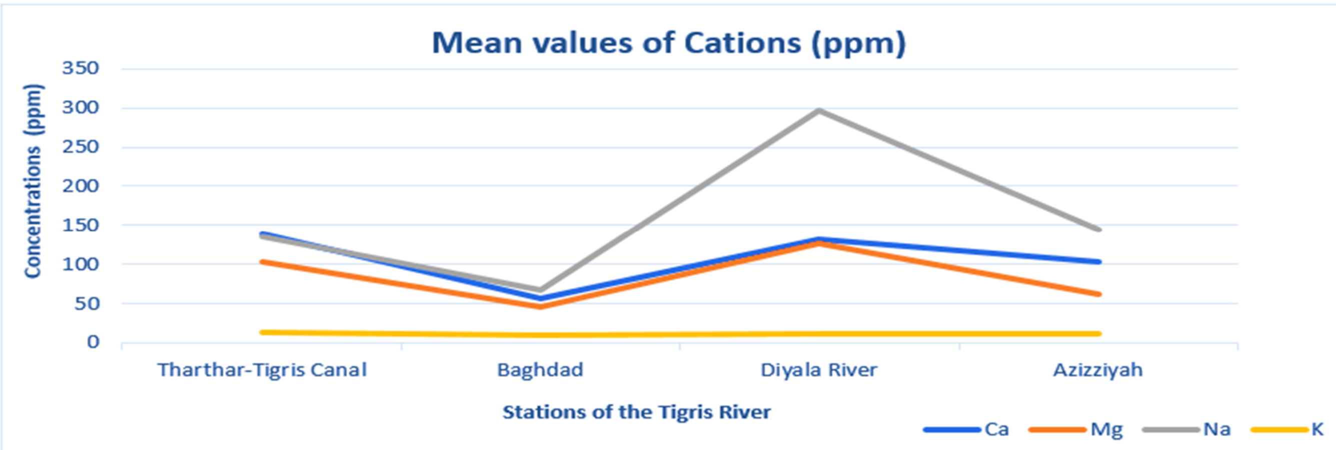

Figure 4. Mean values of annual cations (ppm) along the Tigris River for the period (2005–2020) [26].

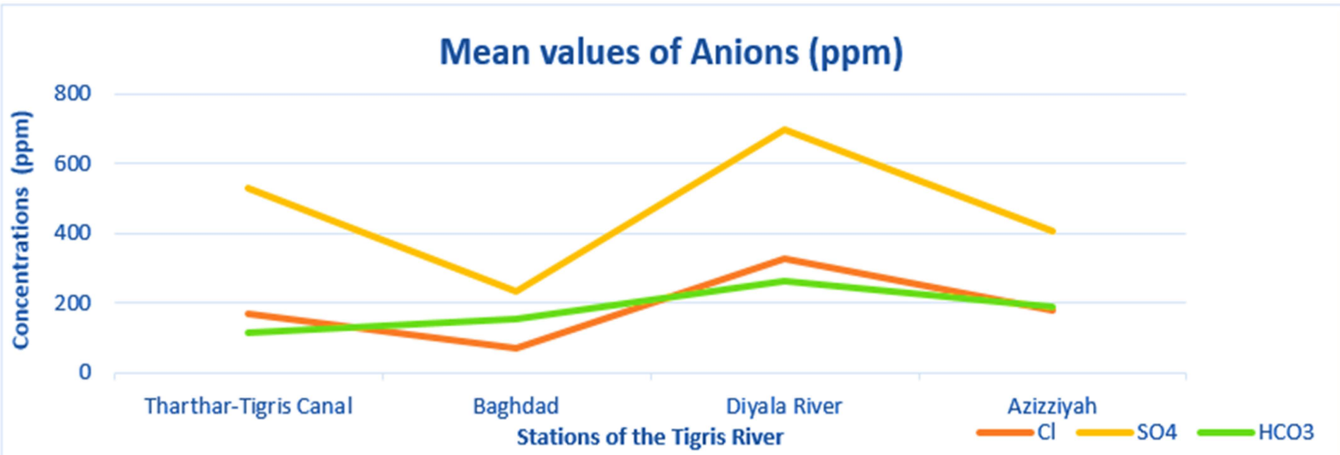

Figure 5. Mean values of annual antions (ppm) along the Tigris River. For the period (2005–2020) [26].

Table 2. Trace elements concentration (ppm) in The Tigris River for the period (2005–2020) with standard limits of drinking water.

Site	Trace Elements	Cu	Cd	Zn	Pb	Fe	Cr
Tharthar-Tigris Canal	Maximum	0.01	0.002	0.01	0.003	0.09	0.008
	ST.DV	0.001	0.0004	0.03	0.0004	0.001	0.003
Baghdad	Maximum	0.02	0.002	0.05	0.006	0.2	0.02
	ST.DV	0.001	0.001	0.022	0.002	0.011	0.03
Diyala River	Maximum	0.03	0.002	0.09	0.008	0.28	0.04
	ST.DV	0.012	0.001	0.009	0.002	0.091	0.02
Al-Azizziyah	Maximum	0.07	0.002	0.06	0.008	0.25	0.03
	ST.DV	0.01	0.011	0.02	0.033	0.016	0.067
[37]	ppm	1.5	0.005	3	0.01	0.3	0.05
[38]	ppm	1	0.003	1	0.01	0.3	0.05

Table 3. The biological analysis of the Tigris River for the period (2005–2020) [26].

Site	Biological Analysis	COD mg/L	BOD_5 mg/L	Fecal Coliform Bacteria MPN/100 mL	*E. coli* Bacteria MPN/100 mL
Tharthar-Tigris Canal	Range	0.3–2.3	0.09–9.3	480–24,961	100–198,630
	Mean	1.07	1.16	25,483	9162
	ST.DV	0.01	0.02	121	451
Baghdad	Range	0.1–3.6	0.1–10.5	100–120,330	100–155,310
	Mean	0.98	1.73	6617	13,408
	ST.DV	0.33	0.43	154	325
Diyala River	Range	2–18.8	0.22–282	95–>241,940	330–241,961
	Mean	5.77	44.69	28,396	14,445
	ST.DV	1.67	11.3	133	234
Azizziyah	Range	0.3–16	0.22–222	73.8–16,000	97–241,960
	Mean	2.2	15.71	2078	11,830
	ST.DV	0.25	0.14	169	467
[39]		-	-	5 cells/100 mL	5 cells/100 mL

3.2.1. Major Ions

The calcium (Ca^{2+}) concentration of the Tigris River ranges between (72.9 and 232) ppm for the Tharthar-Tigris Canal site. As for the Baghdad, Diyala River, and Al-Azizziyah sites the ranges are (34–128), (12–212) and, (44–256) ppm, respectively. Ca^{2+} concentrations were higher in the Tharthar-Tigris Canal and Diyala River than the others, this may be attributed to an increase evaporation and decrease in water supply and may indicate the land's geological composition of the Tharthar-Tigris Canal.

Magnesium (Mg^{2+}) concentration varies between (14a and 391) ppm at the Tharthar-Tigris Canal. As For the Baghdad, Diyala River, and Al-Azizziyah sites, magnesium concentration varies between (13.2 and 150), (43.2 and 936), and (19 and 214) ppm, respectively. Mg^{2+} concentration increased in the Tharthar-Tigris Canal and Diyala River sites, this increase can be attributed mainly to the effluent of wastewater from urban and agricultural areas. The sodium (Na^{+}) concentration of the Tharthar-Tigris Canal site varies between (81 and 524) ppm. As for the Baghdad, Diyala River, and Al-Azizziyah sites the ranges are between (12 and 140), (40.5 and 600), and (25a and 433) ppm, respectively.

Potassium (K^+) concentration of the Tharthar-Tigris Canal site ranges between (2.5 and 8) ppm. As for the Baghdad, Diyala River, and Al-Azizziyah sites the ranges are between (1.2 and 5.5), (5 and 37.5), and (1.5 and 5.8) ppm, respectively.

Chloride (Cl^-) concentration varied between (107 and 192) ppm at the Tharthar-Tigris Canal site. As for the Baghdad, Diyala River, and Al-Azizziyah sites the ranges are between (17 and 121), (92.3 and 650), and (12 and 764) ppm, respectively. Sulfate ($SO_4{}^{2-}$) concentration of the Tharthar-Tigris Canal varies between (67 and 610.7) ppm. As for the Baghdad, Diyala River, and Al-Azizziyah sites the ranges are between (106 and 509), (113 and 1114), and (154 and 742.8) ppm respectively. Bicarbonate ($HCO_3{}^-$) concentration varies between (55 and 207) ppm for the Tharthar-Tigris Canal. While, for Baghdad, Diyala River, and Al-Azizziyah sites the ranges between are (36–153.5), (65–151), and (85.2–123) ppm respectively.

Ca^{2+}, Mg^{2+}, and K^+ concentrations in the study area are within the permissible limits of WHO (2018) standards and Iraqi standards (IQS, 2009). Na^+ and $SO_4{}^{2-}$ concentrations along the Tharthar-Tigris Canal and Diyala River sites exceed the permissible limits of WHO (2018) standards and Iraqi standards (IQS, 2009). Cl^- concentration of the Tigris River is within the permissible limits of [37,38] standards, except at the Diyala River site which exceeds the standards. The high concentrations of Na^+, Cl^-, and $SO_4{}^{2-}$ may be due to man-fabricated activities and natural resources such as lithology in the basin. $HCO_3{}^-$ concentration of the Tigris River depends on the annual rainfall and controlling discharges from the reservoirs.

3.2.2. Trace Elements

The trace elements in natural water are defined as those elements that have a concentration of less than 1 ppm, which means that the trace elements are not considered in the calculation of the total dissolved salts in natural waters because their quantities are not significant compared with the total major ions. The following trace elements, Cu, Cd, Zn, Fe, Cr, and Pb were investigated. The concentrations of these trace elements ae range from zero to their maximum values (Table 2). The results show a relative increase in the maximum values at the Diyala River and Al-Azizziyah sites. When comparing the trace elements between [37,38] standards the results reflect that all the concentrations of these trace elements along the Tigris River are below permissible limits.

The source of these trace elements may be from anthropogenic inputs into soils from different sources, such as agricultural fertilizers, atmospheric deposition, traffic emission, and sewage sludge [39]. In general, it is believed that the analyzed trace elements are controlled by parent or source rocks, climatic conditions, pyogenic processes, and drainage where the soils and surface sediments of Mesopotamia terrains are immature with little modifications or alterations by pyogenesis and have undergone degradation by fluvial processes. Salinization of the upper part of the Mesopotamia sediments is induced by poor drainage, little rainfall, and very high evaporation rates. The Major ions and trace elements concentration in the surface water appear to have been mainly influenced by the type of source rocks of the Tigris River and its tributaries [39,40].

3.2.3. Biological Parameters of the Tigris River

The Biological analysis includes BOD_5, COD, fecal coliform bacteria, and *E. coli* bacteria and are tabulated in Table 3. BOD_5 is an indication of poor water quality, and it is a measure of the amount of oxygen consumed by the bacteria that decompose organic matter to both waste and surface water. The results of BOD_5 were ranged between (0.092 and 9.3) and (0.1 and 10.5) with a mean value (1.16) and (1.73) mg/L at the Tharthar-Tigris Canal and Baghdad sites, respectively. The Diyala River and Al-Azizziyah sites were ranged between (0.22 and 282), and (0.22 and 222) with a mean value (44.69) and (15.71) mg/L respectively. COD is an indication of poor water quality and it is a measure of the amount of chemicals that consume dissolved oxygen. The results of COD of the Tigris River were ranged between (0.3 and 2.3) and (0.1 and 3.6) with a mean value (1.07) and (0.98) mg/L at the Tharthar-Tigris Canal and Baghdad sites, respectively. As for the Diyala River and Al-Azizziyah the ranges were between (2 and 18.8), and (0.3 and 16) with a mean value (5.77) and (2.2) mg/L, respectively. The results of the present study show that the BOD_5 and COD values are within the limit of clean water of the [37], except for the Diyala River and Al-Azizziyah sites which are higher due to municipal wastewater discharges to the river, and as more water is used for irrigation purposes the returned irrigation water is expected to seep back into the irrigation network. Ref. [23], concluded that the coliform bacteria are the best indicators for the assessment of recent fecal pollution, mainly caused by raw and treated sewage, and diffuse impacts from the farmland and pasture. According to the [37], the bacterial coliform should be eliminated in water treatment in order to make water acceptable for drinking. The results showed the high variability in the levels and number of bacteria indicators in the Tigris River that may be due to the variation in environmental conditions such as turbidity, temperature, salinity, dissolved oxygen, and organic matter [41]. The results of coliform bacteria of the Tigris River ranged between (480 and 24,961) and (100 and 120,330) with a mean value of (25,483) and (6617) mg/L at the Tharthar-Tigris Canal and Baghdad sites, respectively. As for the Diyala River and Al-Azizziyah sites, they ranged (95–241,940), and (73.8–16,000) with a mean value (28,396) and (2078) mg/L, respectively, the results of all sites exceed the WHO (2018) limits for suitability.

The results of *E. coli* bacteria of the Tigris River ranged between (100 and 198,630), and (100 and 155,310) with a mean value (9162) and (13,408) mg/L at Tharthar-Tigris Canal and Baghdad sites, respectively. As for the Diyala River and Al-Azizziyah sites, the results ranged (330–241,961), and (97–241,960) with a mean value (14,445) and (11,830) mg/L respectively. The Tigris River at the Al-Azizziyah site (south of Baghdad city) may represent the total mixing of all the above sites water due to agricultural activities and the release of wastewater directly into the river, which causes a rapid increase in the values of biological parameters at the Al-Azizziyah site.

3.3. Hydrochemical Formula of the Tigris River

The type of water varies from time to time along the study period. The formula of water classification depends on the ratio of the main ions expressed by epm % units which has more than 15% availability [42]. The cations are at the base of equation, while anions are above with pH and TDS values, as shown in Equation (1).

$$\mathrm{TDS}\left(\frac{\mathrm{mg}}{\mathrm{l}}\right)\frac{\left(\mathrm{SO4^{2-}}\cdot \mathrm{Cl^-}\ \cdot \mathrm{HCO_3}-\right)\mathrm{epm\%}}{\left(\mathrm{Na^+}\ \cdot \mathrm{Ca^{2+}}\cdot \mathrm{Mg^{2+}}\ \cdot \mathrm{K^+}\right)\mathrm{epm\%}}\mathrm{pH} \quad (1)$$

By applying the water type formula on the hydrochemical parameters for each year, the water type is classified between $NaSO_4$ (80%) and $CaSO_4$ (20%) at Tharthar-Tigris Canal. While Baghdad city is classified between $MgSO_4$ (5%), $NaSO_4$ (45%), and $CaSO_4$ (40%). As for Diyala River, the water type is classified as $NaSO_4$ (100%) and for Al-Azizziyah city, the classification is $NaSO_4$ (70%) and $CaSO_4$ (30%). Therefore, the general water type of the Tigris River for the period (2005–2020) is classified as $NaSO_4$-water type.

Ref. [43], proposed a trilinear diagram for water classification for both cation and anion compositions of water quality data; it is consists of two trilinear and a diamond plot. A Piper diagram shows not only graphically the nature of the water but also dictates its relation to other sites, and can identify the geologic unit that has chemically similar water through applying this classification, it is found that the water type of all sites are classified as (e) which represents the prevailing sulphate and chloride (Figure 6).

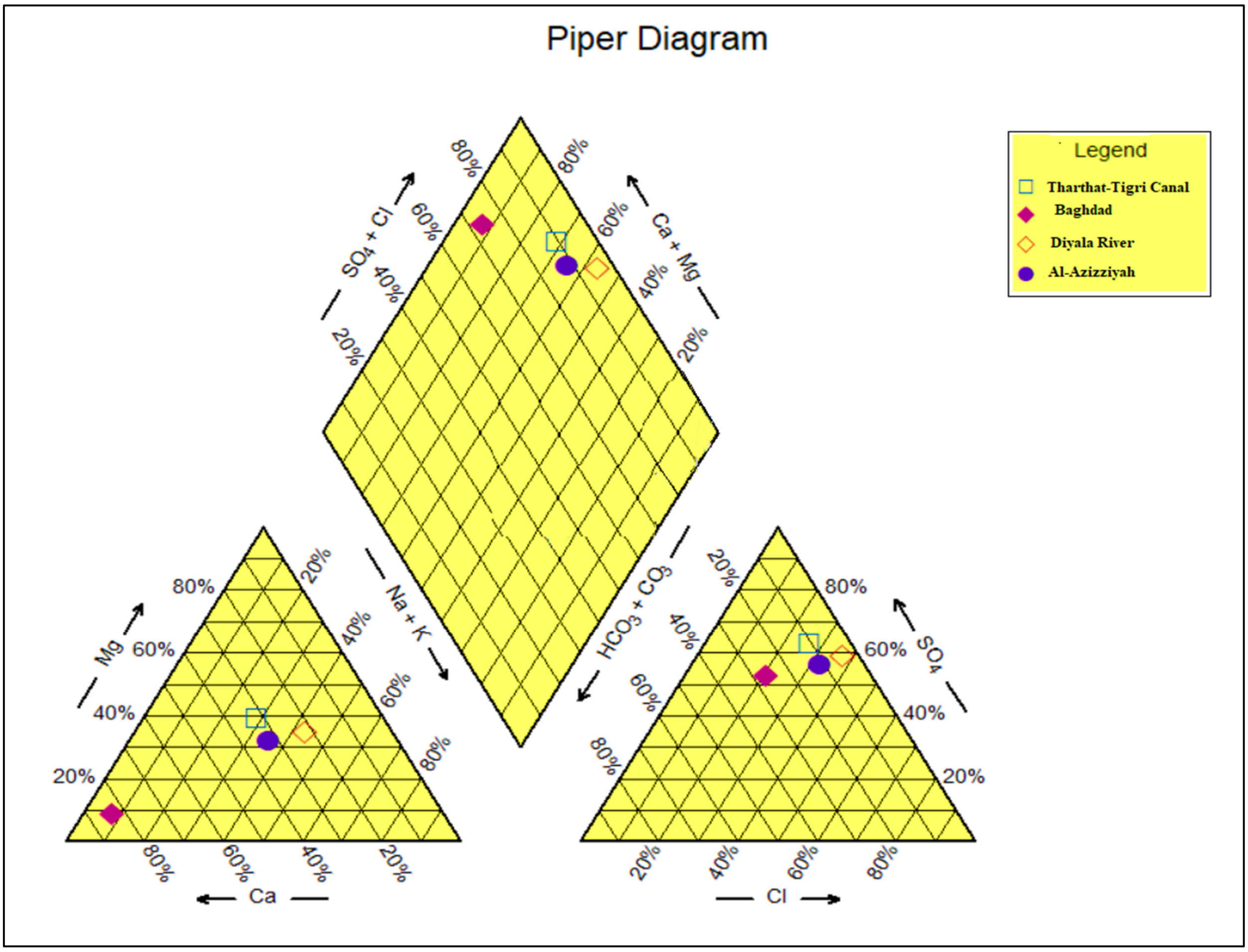

Figure 6. Piper diagram of the Tigris River sites for the period (2005–2020).

Schoeller diagrams are also used to show the relative concentrations of anions and cations typically expressed in milliequivalents per liter [44]. based on the average values of hydrochemical parameters of the Tigris River. At the Tharthar-Tigris Canal site, the cations are in the order of abundance as $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$ while the anions reveal an order of abundance as $SO_4^{2-} > Cl^{-} > HCO_3^{-}$. While, at the Baghdad site, the cations are in the order of abundance as $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ while the anions reveal an order of abundance as $SO_4^{2-} > HCO_3^{-} > Cl^{-}$. At the Diyala River site the cations are in the order of abundance as $Na^{+} > Mg^{2+} > Ca^{2+} > K^{+}$ while the anions reveal an order of abundance as $SO_4^{2-} > Cl^{-} > HCO_3^{-}$. Finally, at the Al-Azizziyah site, the cations are in the order of abundance as $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ while the anions reveal an order of abundance as $SO_4^{2-} > Cl^{-} > HCO_3^{-}$ (Figure 7). The Al-Azizziyah site (south of Baghdad city), is believed to represent the total mixing of all the above sites water.

3.4. Surface Water—Rock Interaction

The hydrochemical functions may reflect the river characterization by concluding the rock-water interaction [45]. Some of these functions are applied in this study to differentiate the effects of various weathering processes with the four studied sites (Table 4). The results indicate that the ratio of rCa^{2+}/rMg^{2+} with the average value (1.65) is between the effects of saline groundwater (0.14) and rainwater (7.14) [46]. Such a finding reflects the dissolution of carbonate constituents under acidic pH conditions. While the ratio rNa^{+}/rCl^{-} shows that the Na^{+} concentration is relatively high compared with the Cl^{-} value represented by the average value (1.1). This finding indicates a presence of another source of Na^{+} rather than halite that provides evidence of dissolution of terrestrial minerals during partial leaching such as the clay minerals (Table 5). The dissolution of the gypsum and anhydrite in the water are indicated by the rSO_4^{2-}/rCl^- ratio [47]. Such a result is in accordance with [48], finding that the rSO_4^{2-}/rCl^- ratio is (2.3) in the Tharthar-Tigris Canal, (2.5) in Baghdad site, (1.6) in the Diyala River and (1.7) Al-Azizziyah site (Figure 8).

The graphic relation of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ is close to the 1:1 line as normal case if the dissolutions of calcite, dolomite, and gypsum are the dominant reactions in the water [49,50]. The points are shifted to the left due to a large excess of calcium and magnesium relative to sulfates and bicarbonates. The reverse is true when the ion exchange tends to shift points to the right due to an excess of $SO_4^{2-} + HCO_3^-$.The sites of the Tigris River are shifted relatively to the left as a result of calcium and magnesium excess relative to sulfates and bicarbonates (Figure 8).

The study of the geochemical properties aims to facilitate the understanding and interpretation of all evolutionary trends, especially in the surface water system, when they are interpreted in conjunction with maps of hydrochemical divisions and their distribution. When taking into account the salinity, the water samples were plotted on Total Ionic Salinity (TIS) (Figure 9A). For surface water sites, their majority present a TIS between 10 and 30 meq/L (Apollaro, et al., 2022). For the Tharthar-Tigris Canal, Baghdad, and Al-Azizziyah sites TISs were ranged between (20 and 40 meq/L). Whereas the Diyala River site, the TIS was above (40 meq/L).

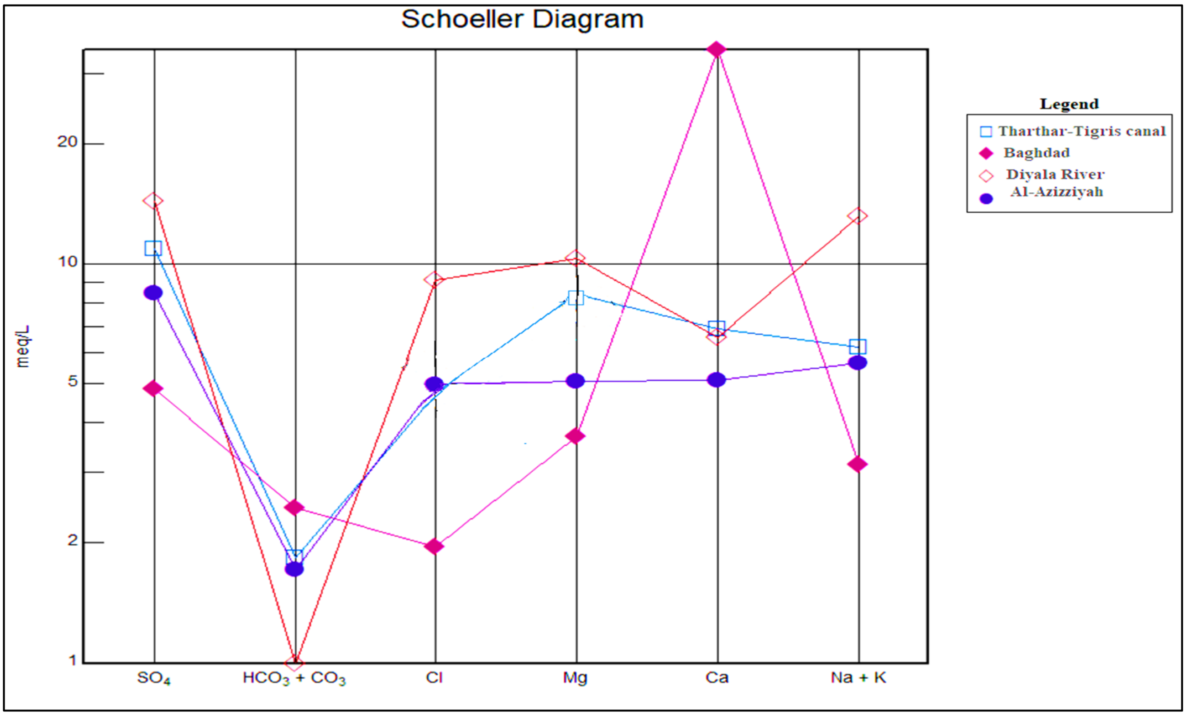

Figure 7. Schoeller diagram of the Tigris River sites for the period (2005–2020).

Table 4. Hydrochemical function (epm) of The Tigris River sites for the period (2005–2020).

Sites	rCa^{2+}/rMg^{2+}	rSO_4^{2-}/rCl^-	$Ca^{2+} + Mg^{2+}$	$SO_4^{2-} + HCO_3^-$	rCl^-	rNa^+/rCl^-	rNa^+
Tharthar-Tigris Canal	0.8	2.3	15.3	12.8	4.7	1.3	5.9
Baghdad	9.4	2.5	38.2	7.4	2.0	1.5	2.9
Diyala River	0.6	1.6	16.9	15.5	9.1	1.4	12.9
Azizziyah	1.0	1.7	10.1	10.2	5.0	1.1	5.5
Jamil, 1977		2.1				1.1	

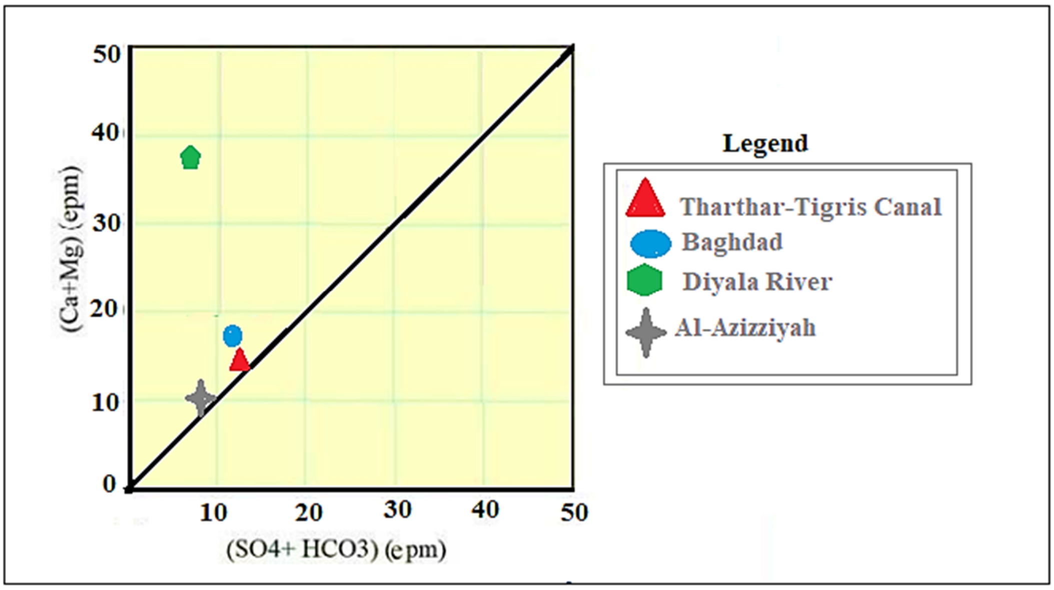

Figure 8. Relation between of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ in the Tigris River sites.

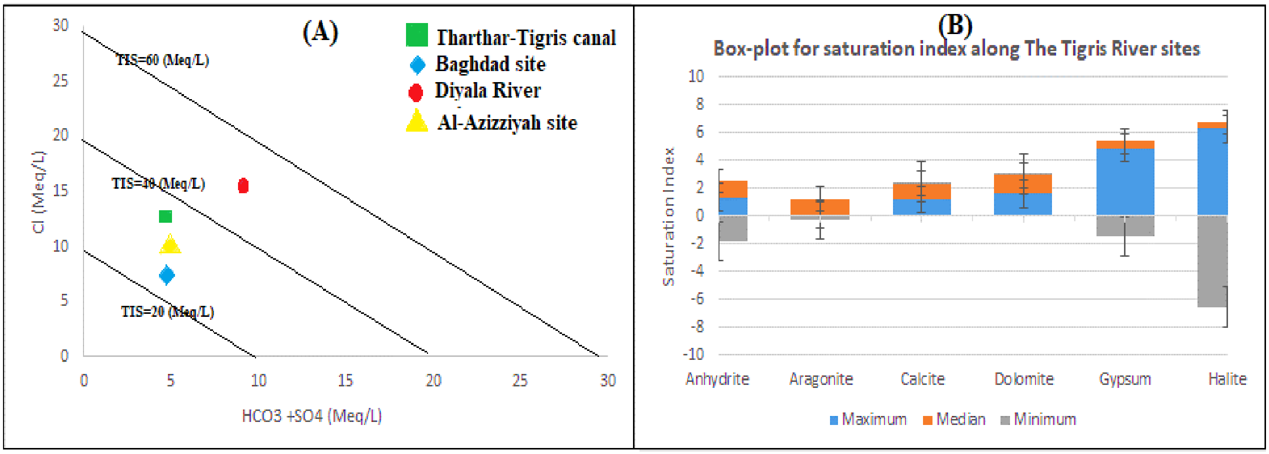

Figure 9. (**A**) Total Ionic Salinity (TIS) diagram. (**B**) Boxplot for saturation indices.

Phreeqc software [51] was used to assess the saturation indices for the Tigris River path. The results are shown in the boxplot (Figure 9B). For the Tharthar-Tigris Canal SI-gypsum, SI-anhydrite, and SI-halite were relatively high values, whereas, SI-calcite and SI-dolomite were above zero and in contrast SI-aragonite was negative. As for the Baghdad site, SI-calcite and SI-dolomite were higher values, SI-aragonite was above zero, and SI-gypsum, SI-anhydrite, and SI-halite were negative. For Diyala River, SI-anhydrite and SI-halite were relatively high values, SI-calcite and SI-dolomite were above zero, and SI-aragonite and SI-gypsum were negative. Finally, at the Al-Azizziyah site SI-anhydrite and SI-halite were relatively high values, SI-aragonite, SI-calcite and SI-dolomite were above zero, and (SI-gypsum) was negative. Such results confirm that some water samples are oversaturated or close to equilibrium calcite, dolomite, anhydrite, gypsum and halite in contrast to aragonite due to geological rock composition and due to reaction between water and bedrock.

3.5. Result of SPSS

A factor analysis was applied to twelve water quality parameters from the four surface water quality monitoring sites situated in the Tigris River during (2005–2020) using

SPSS [52,53]. The correlation matrix of variables was generated and the factors extracted by the centroid method, rotated by Varimax rotation [54]. The selected parameters for the estimation of surface water quality characteristics in SPSS were total dissolved solids (TDS), Major ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, $SO_4{}^{2-}$, and $HCO_3{}^{-}$ and biological analyses such as BOD, COD, fecal coliform bacteria, and *E. coli* bacteria. Next, the Pearson correlation coefficient matrix was used for the determination of the correlation between the variables. Then, these correlation coefficients were examined to decide if factor analysis can be applied to the variables. As a result, the factor analysis method was found to be applicable. The correlation matrix of the water quality parameters was obtained from the extraction method: (Principal Component Analysis (PCA)) and Rotation Method: (Varimax with Kaiser Normalization).

The data of the chemical and biological analyses of the waters of the Tigris River were entered into the statistical program (SPSS). In order to determine the most important factors affecting them, and it was found that conducting a factor analysis of the samples indicates that there are two main factors that affect the concentrations of the main variables. The results of the factorial analysis of the samples indicated that there are two main factors that represent more than 88% of the variance. The first factor represents 71.27% of the variance, with an Eigen value of about 5.70, while the second factor represents 17.02%, with an Eigen value of about 1.4 (Table 5). The Eigen value provides a measure of the significance for the factor, which with the highest Eigen value is the most significant. Eigen values of 1.0 or greater are considered significant [55].

The First Factor (F1):

This factor constitutes a large proportion of the total variance (71.27%), and it is a unipolar factor and is represented by the strong positive loading of the following variables (COD, BOD, fecal coliform bacteria, *E. coli* bacteria, TDS, $HCO_3{}^{-}$, Cl^{-}, Na^{+},$SO_4{}^{2-}$) (Figure 10). This factor is an abnormal factor (Anthropogenic factor) represented by what is thrown into the river of agricultural land wastewater, waste, and sewage water.

Table 5. Loading and (variance), (Eigen values) and (communalities) for the first and second factors of the samples.

Rotated Component Matrix [a]		
Parameters	Component	
	F1	F2
COD	0.969	0.223
BOD	0.962	0.192
$HCO_3{}^{-}$	0.957	
Fecal Coliform Bacteria	0.916	0.216
TDS	0.900	0.418
E. coli Bactria	0.887	0.432
Na^{+}	0.874	0.480
Cl^{-}	0.818	0.559
Ca^{2+}	0.243	0.970
K^{+}		0.965
Mg^{2+}	0.584	0.772
$SO_4{}^{2-}$	0.640	0.767
Eigen values	5.70	1.41
Variance (%)	71.27	17.02
Cumulative (%)	71.27	88.29

[a] Rotation converged in 3iterations.

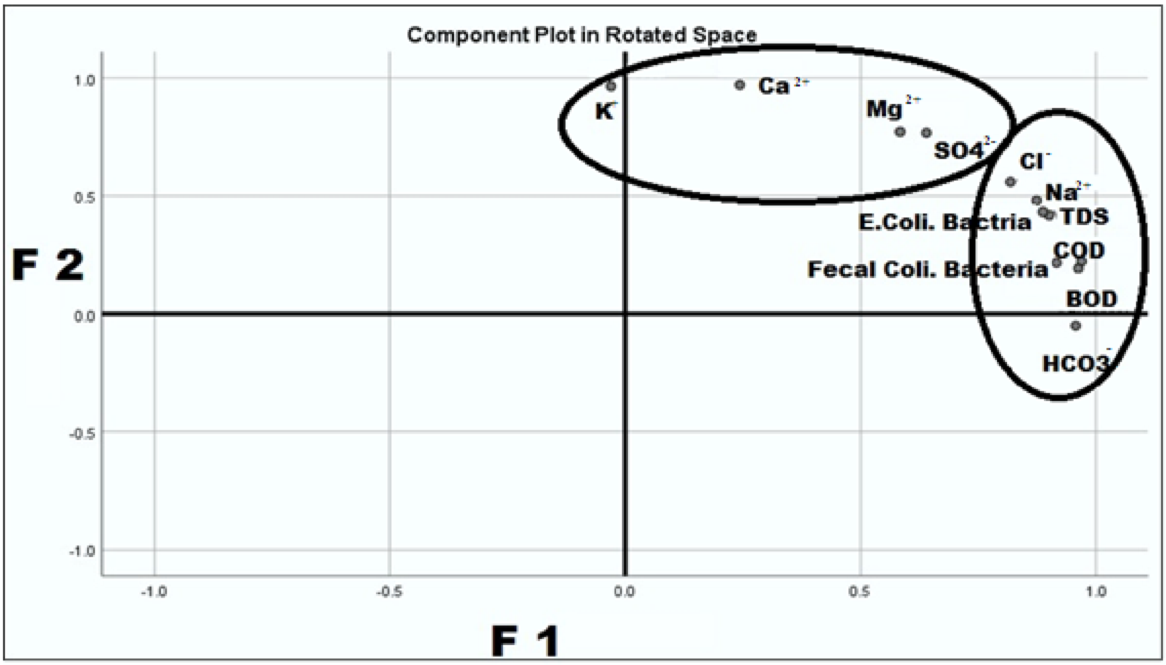

Figure 10. The relationship between the first and second factors.

The Second Factor (F2):

This factor constitutes (17.02%) of the total variance, and is considered to have a limited effect relative to the first factor. It is a unipolar factor and is represented by the weak positive loading of the following variables: Ca^{2+}, Mg^{2+}, K^{+}, and SO_4^{2-}. This factor accounts for the chemical weathering of rock components and is widespread in The Tigris River Basin. The rainfall leads to the transfer of weathering products from different types of rocks and from all parts of the basin to the Tigris River. The process transfers the dissolved load within different rock layers (the sedimentary rocks mainly represented by carbonate rocks, gypsum, marl, and the quaternary sediments). This factor indicates a natural factor represented by the weathering of the rocky components of the river basin.

4. Discussion

The high concentrations of TDS values clearly indicate the high pollution loads that are related to the input of untreated wastewater directly into the river as well as pouring the contaminated surface drainage from irrigation, industrial, and domestic activities (Tables 2–4).

The salinity varies within the studied sites depending on nature, geographic location, and the affected factors within each site such as: soil variation, agriculture, and population density, etc. Accordingly, it was noticed that the salinity within the Tharthar-Tigris Canal site is higher than that of the Baghdad site and becomes higher in the Diyala River site where there is an input of untreated sewage water from the Rustamiya wastewater, consequently the final mean water salinity is indicated within the Azizziyah site. The major ions behave equally as the salinity. In general, it was noticed that the Diyala River has the maximum values of salinity as well as the major ions. The percentage of the major ions along the Tigris River reflected that it is in the following order $SO_4^{2-} > Cl^{-}$ for all sites except the Baghdad site that reflect $SO_4^{2-} > HCO_3^{-} > Cl^{-}$ (Table 6). Such a finding may indicate the limited effect of the Tharthar-Tigris Canal on Tigris River at Baghdad site, but its water deteriorated due to the Diyala River discharge.

Table 6. Rate of the major ions of the Tigris River water for the period (2005–2020).

Site	Tharthar-Tigris Canal		Baghdad		Diyala River		Azizziyah		WHO, 2018
Parameters	**ppm**	**%**	**ppm**	**%**	**ppm**	**%**	**ppm**	**%**	
TDS	1089.4		621		2003		984.3		1000
Ca^{2+}	138.12	12.7	56.37	9.1	131.34	6.5	102.54	10.3	100
Mg^{2+}	102.55	9.4	44.88	7.2	126.44	6.3	61.83	6.1	125
Na^{+}	135.25	12.4	66.98	10.8	296.48	14.8	126	14.6	200
K^{+}	13.11	1.2	9.06	1.5	11.89	0.6	6.30	1.2	12
Cl^{-}	166.78	15.3	69.47	11.2	324.66	16	176.26	17.8	250
SO_4^{2-}	527.32	48.4	233.81	37.7	754.92	37.6	406.39	41.2	250
HCO_3^{-}	114.89	10.5	89.6	24.7	63.29	13	89.85	9.04	—

By comparing the results of this research with the water suitability standards for drinking, it was found that Tigris River water at the Baghdad site is suitable for drinking and deteriorated after its connection with Diyala River where it is unsuitable for drinking [37,38].

Moreover, the comparisons of this study results with previous studies shows that most of the parameters are relatively higher than the result of previous studies and these values exceeded the standard of WHO, 2018 and IQS, 2009 for drinking water [30–34], (Figure 11). This finding may reflect the deterioration of Tigris water with time due the climate change effects, low river discharge, and relatively high contamination within the past two decades.

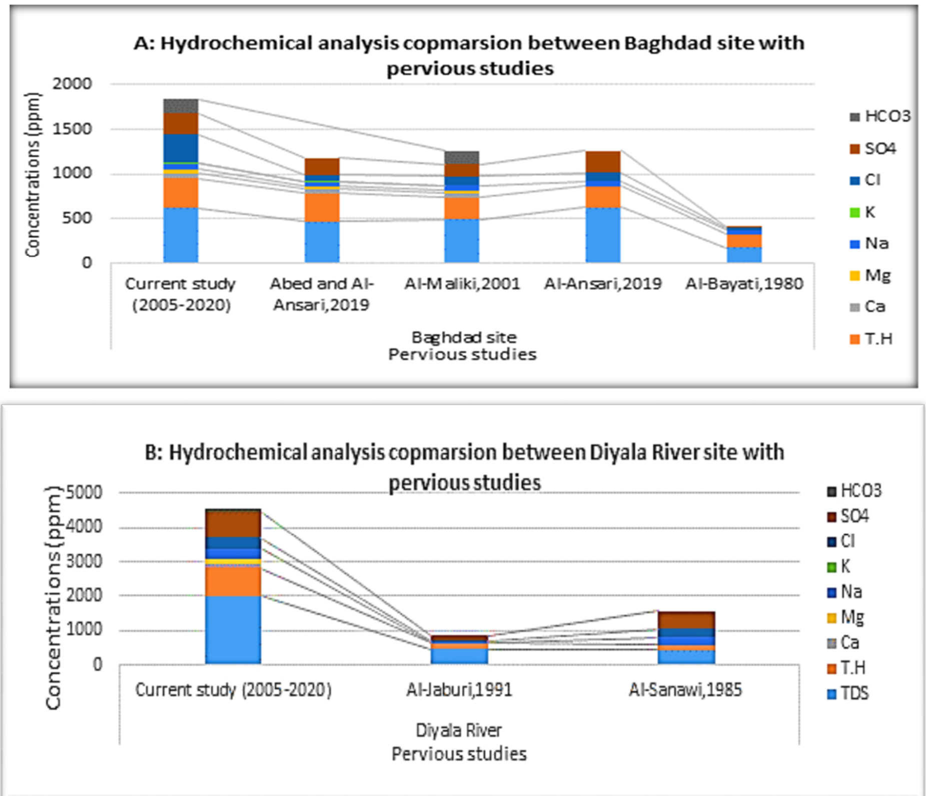

Figure 11. *Cont.*

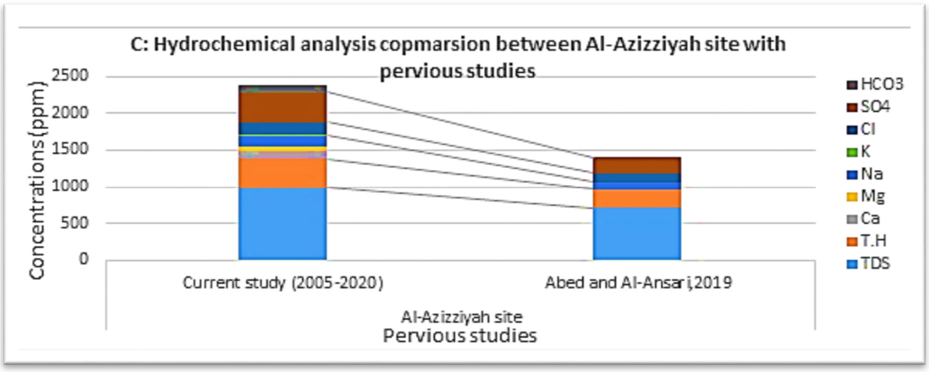

Figure 11. Comparison between the hydrochemical analysis of the current study data with the previous studies, (**A**) Baghdad site, (**B**) Diyala River, and (**C**) Al-Azizziyah site.

Applying Phreeqc software [51], is reflected that the cation exchange, as well as the dissolution/precipitation of gypsum, anhydrite, and halite were responsible for the geochemical processes. The results show that the geological composition can affect the water quality of the Tigris River especially at the Tharthar-Tigris Canal. The mean, maximum, and minimum of the saturation index of minerals along the path of the Tigris River are presented in Table 7. Additionally, anthropogenic activities such as untreated sewage discharge and fertilizer usage also had striking effects on the hydrochemistry of the Tigris River.

Table 7. Mean, Maximum, and Minimum values of saturation index of minerals along the Tigris River (2005–2020).

Minerals	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum	Halite
Maximum	1.33	0.09	1.19	1.6	4.88	6.26
Median	1.205	1.16	1.16	1.33	1.16	0.4875
Minimum	−1.79	−0.24	0.1	0.11	−1.45	−6.53

5. Conclusions

Four sites were chosen: the Tharthar-Tigris Canal, Baghdad, Diyala River conjunction with the Tigris River, and Al-Azizziyah, to determine the effect of the decreasing Tigris River flow on the water quality and to identify the sources of pollution for the period (2005–2020). The annual flow of the Tigris River decreased through time due to climatic change and dams on the Iraqi–Turkey border, in addition to the increasing water consumption due to high population growth rates. TDS values were higher at Tharthar-Tigris Canal and Diyala River, for Tharthar-Tigris Canal site, these may be attributed to an increase in the salinity of Tharthar Lake which is due to high evaporation and the passing of this canal through gypsum soil as well as the drain water which comes from agricultural lands. As for high concentrations in the Diyala River site that they are due to the effects of the untreated water from Al-Rustimiyah treatment site which are thrown directly into the river. TDS concentration of the Tigris River is within the permissible limits of WHO (2018) standards and Iraqi standards (IQS, 2009), except at the Tharthar-Tigris Canal and Diyala River sites of the Tigris River which they exceeded the standards. Temperature values for all sites of the Tigris River are within the permissible limits of IQS, 2009. Ca^{2+}, Mg^{2+}, and K^{+} concentrations in the study area are within the permissible limits of WHO (2018) standards and Iraqi standards (IQS, 2009). Na^{+} and SO_4^{2-} concentrations along the Tharthar-Tigris Canal and Diyala River sites have exceeded the permissible limits of WHO (2018) standards and Iraqi standards (IQS,2009). Cl^{-} concentration of the Tigris River is within the permissible limits of WHO (2018) standards and Iraqi standards (IQS, 2009) except at Diyala River site which exceeds the standards. The high concentrations of Na^{+}, Cl^{-}, and SO_4^{2-} maybe due to man-fabricated activities and natural resources such as lithology in the basin. HCO_3^- concentration of the Tigris River depends on the annual rainfall and the controlling of discharges from the reservoirs. The trace elements along the Tigris River are below permissible limits. The concentrations of coliform and fecal coliform bacteria along the Tigris River were more than the international permissible levels recommended by WHO (2018). The dominant water type of the Tigris River is classified as sodium sulphate and Magnesium sulphate ($NaSO_4$ and $MgSO_4$). It is noted that there is a movement in the quality of the river water toward increasing salinity in the south.

By comparing these results with the local and international water suitability standards for drinking, it was found that the Tigris River water at the Baghdad site is suitable for drinking and deteriorated after its connection with Diyala River where it is unsuitable for drinking (IQS, 2009, WHO, 2018). The Total Ionic Salinity (TIS) of the Tigris River sites (Tharthar-Tigris Canal, Baghdad, and Al-Azizziyah) ranged between (20 and 40 meq/L), whereas the Diyala River site had a relatively higher TIS above (40 meq/L). By using Phreeqc software to assess the saturation indices and determine the dominant geochemical processes source responsible for surface water quality for the Tigris River path, the dominant minerals in the Tigris River were relatively high values of SI-gypsum, SI-anhydrite, and SI-halite at Tharthar-Tigris Canal, SI-calcite and SI-dolomite at Baghdad site, and SI-anhydrite, and SI-halite at Diyala River and Al-Azizziyah sites. Selection of the correct parameters and use of them in multivariate statistical technique in water quality monitoring studies is an important to be used in environmental studies to prevent pollution. Results from the factor analysis show that Tigris River water had two factors. The first factor (F1) is with 71.272% of the total variance and was strong positive loading composed with the following variables: COD, BOD, HCO_3^-, fecal coliform bacteria, TDS, *E. coli* bacteria, Na^+, Cl^-, Mg^{2+}, and SO_4^{2-}. The second factor (F2) is of weak positive loading composed with the following variables: Ca, K^+, Mg^{2+}, and SO_4^{2-}. The contribution to different sources can be from the nature of the studied site, anthropogenic stresses, industrial activities which carry domestic and industrial wastewater of the city in addition to deficiency of water resources due to climatic change and dam construction of the riparian countries.

Recommendations: Strict measures should be taken in order to control the levels of pollutants discharged into the Tigris River and to reduce the dissemination of the Coliform and fecal coliform bacteria to protect human health. Tigris River water needs further treatment, especially at the south of Baghdad city, for that a periodic monitoring system should be established to follow up on pollution levels and water quality for the Tigris River, by conducting seasonal surveys. In addition, the treatment of the wastewater of the Al-Rustimiyah plant must be improved by applying the conventional methods that are generally employed for water, which can be grouped into adsorption, ion exchange, coagulation/precipitation, and membrane-based technologies and construct a desalination plant. Nano filtration/reverse osmosis (NF/RO) technologies can be used for water desalination to remove dissolved ions into the water of the Tharthar-Tigris Canal. Finally, local governments can form effective policies, such as reducing industrial discharge and agricultural fertilizer in addition to wastewater discharge.

Author Contributions: A.S.O.: data processing and validation, software, formal analysis, data curation, writing—original draft preparation, writing—review and editing. M.A.-D.: supervision, project administration, conceptualization, investigation, visualization, data curation, writing—original draft preparation, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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