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Seasonal Fluctuations in Physicochemical Characteristics as Indicators of Water Pollution in Al- Hilla River, Middle of Iraq

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ABSTRACT: Water is the most important element in shaping the Earth and regulating the climate; it is one of the most significant compounds affecting life. Assessing water properties and quality is essential for promoting human health and ecosystems. This study aimed to evaluate the physical and chemical properties of the Hilla River water in three sites were in the center of Hilla before entering the center ,in the middle of the center , and after leaving the center. These three sites were selected during the wet and dry seasons, and thirteen environmental factors were included(temperature of the air and water, electrical conductivity, pH, dissolved oxygen, calcium, magnesium, total hardness, and alkalinity, orthophosphate, nitrite, nitrate, and biochemical oxygen demand). The study found that the EC was 1.254 (µs/cm) and that the greatest average air and water temperatures were 26.25°C and 26.583°C, respectively, during the dry season during the wet season, pH was 7.489 during the wet season, pH 7.489 in wet, DO(7.9mg/l) in wet season , BOD_5 (2.889 mg/l)in wet, T ALK(156.111mg$CaCo_3$/L)in wet season, TH (427.222 mg$CaCo_3$/L) in wet season ,Ca(126.708 mg$CaCo_3$/L) in dry season, Mg (43.658 mg$CaCo_3$/L)in dry season ,NO_2(0.065mg/l) during the rainy season, NO_3 (3.071 mg/l) in wet season, PO_4(1.11mg/l) in wet season . Overall, the findings provide valuable baseline data on the water quality of Shatt Al-Hilla River and can support future monitoring and sustainable water resource management.

Graphical Abstract

INTRODUCTION

Rivers are among the most affected ecosystems due to various human activities, such as drinking, cooking, industry and agriculture. These activities have a significant impact on the lives of organisms in rivers. River water is usually at its best at its source, but becomes increasingly polluted as it flows through different lands and is used for various purposes [1].Rivers play a vital role in the sustainability of water resources, particularly in arid and semi-arid regions, where surface water is often the primary source of supply. In Iraq, surface water resources, especially the Tigris and Euphrates rivers and their tributaries, constitute the country's main water source[2].The Hilla River is an important natural waterway essential for numerous water applications. It is located in the Iraqi province of Babylon. Babylon, with a population of over two million, relies on this river as its primary source of fresh water[3].

The most readily available and accessible water sources for domestic use in developing nations are surface waterways like rivers, lakes, and streams. A vast array of amenities, such as drinking, irrigation, recreation, power generation, and habitat for fisheries with substantial economic value, are offered by surface water sources to the human population. Domestic, industrial, and agricultural wastes are the main sources of surface water contamination through runoff and direct dumping [4].

Most of water bodies are now polluted as a result of urban expansion, industry, and man-made problems caused primarily by population growth[5].

Point source pollution occurs when the source of water pollution is identified or when the pollutants entering the water come from a specific source, such as a ditch, pipe industry, storm drain, wastewater treatment plant, etc. [6]. Municipalities' and industries' point sources are the greatest danger to water quality. Water quality is also impacted by mining, urbanization, and farming[7]. Nonpoint source pollution occurs when the source of water pollution is unknown or does not originate from a single, distinct source [8]. They are very difficult to control and can arise from a variety of sources, including industrial waste, fertilizers, pesticides, etc. [9].

MATERIAIS AND METHODS

Al-Hilla River is a branch of the Euphrates River. It starts from the city of Saddat al-Hindiyah, with a summer discharge rate of 200m³/s, and a winter discharge rate of 245 m³/s. The al-Hilla River is 101 km ,long and passes through Babil Governorate. Its total area is 420,000 hectares, and its discharge rate varies according to the agricultural needs of Babylon , Qadisiyah, and Muthanna Governorates. 36 main canals branch off from the river banks within the boundaries of Babylon Governorate, each with a length of 511.6 km [10] .Three important locations were chosen, in the Hilla shore to conduct the study. These areas were in the center of Hilla before entering the center, in the middle of the center, and after leaving the center.

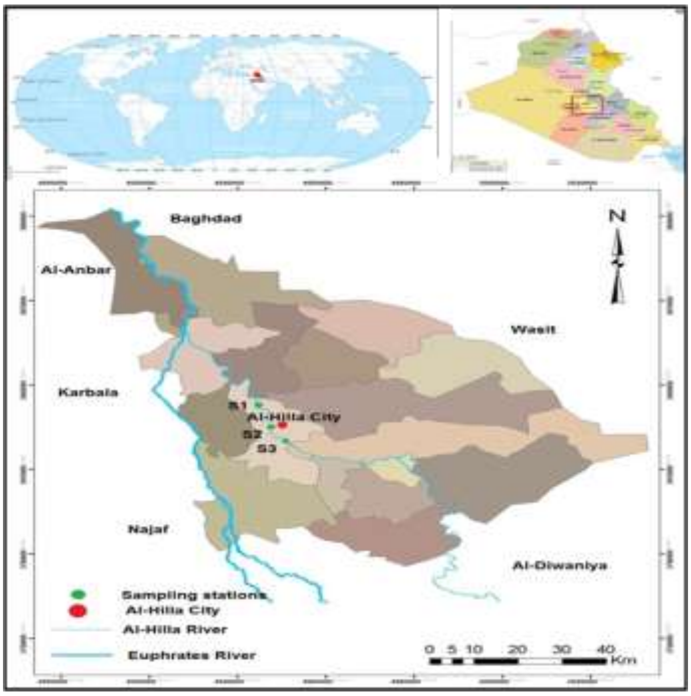

Figure 1. Map of study sites for Al-Hilla river.

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Water Samples

Water samples were collected from December 2024 to June 2025 at three important sites on the Al -Hilla river. To conduct physical and chemical properities for a period of 7 months. during two seasons, the first season is the wet(December 2024, ,January2025, February2025) and the second season is the dry(March,April,May,June2025).

Field measurements:

1- Temperature(T): Temperature In this study, water temperature (WT)and air temperature(AT) were measured directly at the sampling sites using a mercury thermometer(1-100°c).
2- pH : The pH was measured using a WTW pH meter directly in the field after calibrating the device using three buffer solutions at concentrations of 4, 7, and 9.
3- Electrical conductivity(EC): The electrical conductivity of water was measured directly in the field using a WTW electrical conductivity meter and the results were expressed in units of(μs/cm).

Laboratory Measurements:

1- Dissolved oxygen(D.O): The Winkler method is used to measure dissolved oxygen in water samples . The result is expressed in mg/L. Fill the Winkler bottle with river water, then close the bottle tightly. Add 2 ml of manganese sulfate to the bottle, then add 2 ml of basic iodide and mix the sample by inverting the bottle several times. Then we add 2 ml of sulfuric acid and stir it several times. Then we take 200 ml of the sample and titrate it with sodium thiosulfate until it turns a color. Add 2 ml of starch solution until a blue color is formed. Continue titrating slowly until the sample becomes clear to remove the blue color [11].
2- Biological Oxygen Demand (BOD5): The Biological Oxygen Demond was assigned to the winkler method [11] ,to measure dissolved oxygen by taking darkness Winkler bottles and BOD5 was calculated as follows BOD5 (mg/L) = primtive dissolved oxygen - final dissolved oxygen.
3- Total alkalinity (T ALK): Was measured by titrating 100 ml of the sample to be studied with (0.02 N) sulfuric acid(H_2SO_4) using phenolphthalein and methyl red reagents. The results were expressed in mg($CaCO_3$)/L [11].
4- Total hardness(TH) : Was estimated by titration with 2NaEDTA (0.01N) solution using Erichrom Black T (EBT) as an indicator and the result was expressed in mg($CaCO_3$)/L [12].
5- Calcium (Ca): Hardness of calcium estimated according to [12], by titrating with 2NaEDTA (0.01N) solution and adding NaOH (1N) solution, using Murexid dye as an indicator, and expressing the results in mg($CaCO_3$)/L units.
6- Magnesium: The following equation and the mathematical method[12] were used to obtain the magnesium values:

mg $Mg^{+}2$/ *L*=[*mEq hardness* / L-mEqca^{+}2/L]*12.16

mEq hardness/*L*=*[mg hardness]**0.01988
mEqCa $^{+2}$=[*mgCa* $^{+2}$]*0.0499
And expressing the results in mg/L units.

7- Nitrite(NO_2): Methodology ,In a 25 ml calibrated flask, add 1 ml of 0 1% p-aminophenylmer captoacetic acid solution and 2 ml of the 1% N-(1 naphthyl) ethylenediamine dihydrochloride solution to an aliquot of sample solution containing 0 50-20 pg of nitnte (0 02-0 80 p p m when diluted to 25 ml). A bluish violet color develops ,and remains stable for 48 hours after being set aside for at least 15 minutes for full color development ,and diluted to the appropriate level with distilled water. Check the absorbance in 1-cm cuvettes at 565 nm against a reagent blank made in the same way but without nitrite. Create a nitrite calibration graph in this way[13].
8- Nitrate(NO_3) : To measure nitrates, use the method APHA (2017) described in flowing, nitrite ion standard (1000 mg NO3-/L), HCl , were the materials employed. Using a Shimadzu UV-1800 reader spectrophotometer, the sample was analyzed at wavelengths of 220 nm and 275 nm. Before being measured using a UV-Vis spectrophotometer, 1 mL of 1 M HCl was added to the sample ,and standard solutions. The calibration standard solution has concentrations of 0, 10, 20, 30, 40, and 50 mg/L. The difference between the absorbance data at 220 nm and, many absorbance data at 275 nm was used to create the calibration curve [14] .
9- Orethrophosphate(PO_4): To obtain suitable portions of the standard solution, 1 ml of ammonium molybdate and 0.4 ml of hydrazine sulfate were added, and the solution was made up to 10 ml with twice-distilled water in a standard measuring vessel. The standard measuring vessels were kept in a heating water bath for 30 minutes. The water bath

temperature was set at 60 °C. During heating, a blue color appeared due to the formation of the ammonium phosphomolybdate complex. After heating for 30 minutes, the solution was cooled and its absorbance was measured at a wavelength of 830 nm. A blank experimental solution was used to perform a baseline correction[15].

Statistical Analysis

Statistical analysis was performed using the(JASP package, version 17). ANOVA analysis of factors and locations during the study period. Principal Component Analysis (PCA) was used to identify patterns of variation in the variables over the study period.

RESULT & DISCUSSIONS

Variations in stream temperature are primarily contingent upon heat exchange between the water body and overlying air characterized by air temperature, solar radiation, relative humidity, cloud cover, and wind speed [16,17]. High water temperatures were recorded during the dry season, with an average of 26.583(±3.397)°C. During the wet season, temperatures were lower, with an average of 12.889(±1.167)°C. The highest water temperature was recorded at 31°C at site 3 and the lowest was(11°C) in site 1. There is a significant variation between the seasons but not between the sites. There are many factors that affect the variation in water temperature values such as temperature, running water, and other weather conditions[18]. Air temperature (AT) values 26.250(±3.841)°C during the dry season and the wet season 11.00(±3.905)°C. The highest values were recorded during the dry season. The highest air temperature was recorded at (31°C) at sites 1 and 2 and the lowest was(7°C) in site 1. The results show a significant variation between seasons $p<0.05$, but no significant variation between sites $p>0.05$. This demonstrates how the river's surface water temperatures rose in the summer and fell in the winter, precisely matching the ambient air temperatures this is consistent with a study [19,20].

Is considered an indicator for monitoring water quality, as it is a measurement of substances dissolved in an aqueous solution that relates to the ability of substances to conduct electricity [21]. EC recorded its highest values in the wet season with an average of (1.254µs/cm) and its lowest value in the dry season with an average of(1.201 µs/cm). The results showed that there is no significant variation between the seasons $p > 0.05$. as it recorded its highest value of 1.234(±0.059)µs/cm in site 3 and its lowest value of 1.207(±0.069) µs/cm in site 2. The results showed that there is no significant variation between the seasons $p > 0.05$ and also that there is no significant variation between the sites $p>0.05$ Electrical conductivity is a measure of the amount of dissolved salts in water, and is closely related to total dissolved solids ,It also increases in areas where industrial and agricultural activity is prevalent[22].

The results of the current study showed a slight increase in pH in the wet season, with an average of 7.489(±0.414), and a lower pH in the dry season, with an average of 7.175(±0.463). The highest value was recorded at site S1 7.343(±0.624), and the lowest value was recorded at site S3 7.243(±0.395) . This indicates no significant variation between seasons and between sites $P>0.05$. Domestic and industrial wastewater being dumped into the river, which contains many acidic elements, could be a cause of this decline[23] . This indicates no significant variation between seasons. Iraqi water bodies are characterized by pH levels approaching eight, indicating the presence of bicarbonates and carbonates[24].

Dissolved oxygen results indicate that the wet season value of (7.900(±0.278) mg/l) is higher than the dry season value of(6.533(±1.05) mg/l). The highest value of (7.771(±0.799) mg/l) was recorded at site S3 and the lowest value of(6.743(±1.005) mg/l) in site1 . The results showed a significant variation between seasons and a between sites $p<0.05$. Due rainfall, untreated city water, industrial water, irrigation water, and natural hydrological processes are some of the causes of the rise in the Al-Hillah River's total dissolved solids content[25]. Higher temperatures and increased organic matter resulting from economic activity are expected to lead to lower levels of dissolved oxygen[3] . The results showed a significant variation between seasons . Variations in dissolved oxygen levels in the river during the study period were attributed to biodegradation of organic matter or low water levels at these stations[26].

The current study recorded an average BOD_5 for the wet season of 2.889 (±0.535)mg/l which is higher than the dry season of 0.617(±0,321)mg/l. with the highest of 1.786(±1.438)mg/l recorded at site S3 and the lowest of1.486(±1.092)mg/l at site S1. There is a significant variation between seasons and there is no significant variation between sites $p>0.05$. Biochemical oxygen demand (BOD5) is one of the most important indicators of water quality. It is a rough estimate of the amount of decomposing organic matter in the aquatic environment[27].

The total alkalinity values of Al Hillah river in the current study for the wet season were recorded at an average of156.11(±10.833) mg/l, which is higher than the dry season, where it was recorded in the dry season at 151.667 (±6.513mg/l. Highest average was at site S1 at 158.571(±9.88) mg/l, and low at site S2 at(147.857(±6.986)mg/l) . There is no significant difference between seasons $P>0.05$, while there is a significant difference between locations $P<0.05$. The monthly variation in alkalinity values observed during the current research can be explained by the significant influence of river water levels on alkalinity values [28].

The current study recorded higher values of total hardness for the wet season with an average of(427.222(±27.513)mgCaCo₃/L). Increased TH is a result of rainfall and agricultural activities, and untreated sewage and other pollutants can also lead to increased TH in rivers(10).Than the dry season values with an average of (390.417(±17.249) mgCaCo₃/L), where the highest value was recorded at (415.714(±29.781)at site S1 and the lowest value was recorded at 398.571 (±27.495 mgCaCo₃/L)at site S2. The results showed a significant variation between seasons ($p<0.05$) and no significant variation between sitesP>0.05.This may be due to the effect of sedimentation, filtration and the addition of disinfectants[29].

Calcium concentrations of Al-Hillah river were recorded in this study as high during the dry season with an average of(126.708(±6.178) mgCaCo₃/L), and low during the wet season with an average of (118.589(±8.802) mgCaCo₃/L). Highest average was at site3 and the lowest was recorded at S2(118.643(±9.116) mgCaCo₃/L) The results showed that there was a significant variation between the seasons and there was no significant between the sites $p>0.05$. Ca concentrations are higher during dry periods than during wet periods for several reasons, including increased evaporation, less rainfall diluting river water, and increased photosynthesis during summer compared to winter[30] .

The results recorded a slight increase in the concentration of magnesium in Al-Hilla river waters during the dry season with an average of 43.658 (±4.711) mgCaCo₃/L compared to the wet season with an average of 43.456 (±5.75) mgCaCo₃/L. Site S3 recorded the highest of (47.043(±4.653) mgCaCo₃/L), and Site S1 recorded the lowest reading with a concentration of 39.843(±4.411) mgCaCo₃/L . The results showed that there was no significant difference between seasons $p>0.05$ and there was a significant difference between sites ($p<0.05$). Human activities, such as runoff from farms or discharges from wastewater treatment plants, can cause elevated magnesium levels in the river, these sources have the potential to increase the amounts of magnesium and other minerals in the river[10].

Phosphate concentrations in Al-Hilla River waters were recorded during the study period for the dry season with an average of 0.912(±0.776) mg/l, while it increased in the wet season with an average of 1.110(±1.01) mg/l. The highest reading was recorded at 1.125(±0.901)mg/l at site S1 and the lowest value was 0.81(±0.743)mg/l at site S2 . The results showed no significant variation between seasons and sites $p>0.05$, Phosphate existed in water in a soluble form, is originated from rocks in addition to its existence in agricultural runoff, industrial wastes, municipal sewage[31].

Nitrite concentrations in Al Hillah River recorded a slight increase during the wet season with an average of(0.065 (±0.089)mg/l) compared to the dry season of(0.047(±0.011) mg/l). where the highest average was(0.065(±0.077)mg/l)at site S2 and the lowest concentration was(0.039(±0.019)mg/l) at site S1 .The study showed that there is no significant variation between seasons and locations $p>0.05$.

Nitrate concentration in the Hilla River is highest in the wet season with an average of 0.171(±0.49) mg/l and lowest in the dry season with an average of 0.097(±0.063) mg/l. where the highest value was recorded at 0.134 (±0.076) mg/l at site 3 and the lowest value was recorded at 0.122 (±0.064) mg/l at site1. Household waste, chemical fertilizers, sewage, industrial waste, and decomposing plant and animal matter ,are the main causes of nitrate pollution in rivers[32].

Table 1 Concentration of some physicochemical properites of Hilla River water during study seasons.

Factors	Seasons	Mean	SD	Minimum	Maximum
AT (Ċ)	Dry	26.25	±3.841	20	31
AT (Ċ)	Wet	11	±3.905	7	19
WT(Ċ)	Dry	26.583	± 3.397	21	31
WT (Ċ)	Wet	12.889	±1.167	11	14

EC (µ.s/cm)	Dry	1.201	±0.04	1.13	1.27
EC (µ.s/cm)	Wet	1.254	±0.079	1.13	1.34
pH	Dry	7.175	±0.463	6.3	7.7
pH	Wet	7.489	±0.414	6.7	8.1
DO (mg/l)	Dry	6.533	±1.05	5.1	8.9
DO (mg/l)	Wet	7.9	±0.278	7.5	8.3
BOD_5 (mg/l)	Dry	0.617	±0.321	0.2	1.2
BOD_5 (mg/l)	Wet	2.889	±0.535	2.4	4.2
TALK (mg $CaCo_3$/L)	Dry	151.667	±6.513	140	165
TALK (mg $CaCo_3$/L)	Wet	156.111	±10.833	140	175
TH (mg $CaCo_3$/L)	Dry	390.417	±17.249	365	425
TH (mg $CaCo_3$/L)	Wet	427.222	±27.513	390	470
Ca (mg $CaCo_3$/L)	Dry	126.708	±6.178	118.4	138.2
Ca (mg $CaCo_3$/L)	Wet	118.589	±8.802	98.8	127
Mg (mg $CaCo_3$/L)	Dry	43.658	±4.711	33.1	49.6
Mg (mg $CaCo_3$/L)	Wet	43.456	±5.75	36.5	51.3
NO_2 (mg/l)	Dry	0.047	±0.011	0.031	0.061
NO_2 (mg/l)	Wet	0.065	±0.089	0.014	0.236
NO_3 (mg/l)	Dry	0.097	±0.063	0.034	0.203
NO_3 (mg/l)	Wet	0.171	±0.049	0.074	0.218
po_4 (mg/l)	Dry	0.912	±0.776	0.014	2.475
po_4 (mg/l)	Wet	1.11	±1.01	0.053	2.717

Table 2 Concentration of some physicochemical properites of Hilla River water during study sites.

Factor	Sites	Mean	±SD	Min	Max
AT (Ċ)	S1	19.143	±10.04	7	31
AT (Ċ)	S2	19.857	±8.764	9	31
AT (Ċ)	S3	20.143	±8.275	9	30
WT (Ċ)	S1	20.714	±7.697	11	30
WT (Ċ)	S2	21	±7.789	12	30
WT (Ċ)	S3	20.429	±7.976	12	31
EC (μ.s/cm)	S1	1.23	±0.071	1.15	1.34
EC (μ.s/cm)	S2	1.207	±0.069	1.13	1.33
EC (μ.s/cm)	S3	1.234	±0.059	1.17	1.32
pH	S1	7.343	±0.624	6.3	8.1
pH	S2	7.343	±0.391	6.6	7.8
pH	S3	7.243	±0.395	6.5	7.6
DO (mg/l)	S1	6.743	±1.005	5.1	7.8
DO (mg/l)	S2	6.843	±1.152	5.3	8
DO (mg/l)	S3	7.771	±0.799	6.6	8.9
BOD_5 (mg/l)	S1	1.486	±1.092	0.3	2.9
BOD_5 (mg/l)	S2	1.5	±1.292	0.2	3
BOD_5 (mg/l)	S3	1.786	±1.438	0.4	4.2
TALK (mg $CaCo_3$/L)	S1	158.571	±9.88	145	175
TALK (mg $CaCo_3$/L)	S2	147.857	±6.986	140	160
TALK (mg $CaCo_3$/L)	S3	154.286	±6.075	150	165

TH (mg $CaCo_3$/L)	S1	415.714	±29.781	380	470
TH (mg $CaCo_3$/L)	S2	398.571	±27.495	365	450
TH (mg $CaCo_3$/L)	S3	404.286	±29.921	370	460
Ca (mg $CaCo_3$/L)	S1	122.871	±5.174	112.5	127.5
Ca (mg $CaCo_3$/L)	S2	118.643	±9.116	98.8	126
Ca (mg $CaCo_3$/L)	S3	128.171	±8.168	115	138.2
Mg (mg $CaCo_3$/L)	S1	39.843	±4.411	33.1	48
Mg (mg $CaCo_3$/L)	S2	43.829	±3.653	36.5	47.4
Mg (mg $CaCo_3$/L)	S3	47.043	±4.653	37.3	51.3
NO_2 (mg/l)	S1	0.039	±0.019	0.014	0.059
NO_2 (mg/l)	S2	0.065	±0.077	0.017	0.236
NO_2 (mg/l)	S3	0.06	±0.066	0.017	0.205
NO_3 (mg/l)	S1	0.122	±0.064	0.05	0.203
NO_3 (mg/l)	S2	0.13	±0.073	0.042	0.214
NO_3 (mg/l)	S3	0.134	±0.076	0.034	0.218
Po_4(mg/l)	S1	1.125	±0.901	0.232	2.717
Po_4 (mg/l)	S2	0.81	±0.743	0.014	1.745
Po_4 (mg/l)	S3	1.054	±1.035	0.127	2.475

Principal components analysis(PCA):

PCA is used to enumerate the relationships between the chemical and physical variables of water. Figure 2 shows the chemical and physical variables of water correlated to varying degrees and summarized into four main components: PC1, PC2, PC3, and PC4. Each line between the components and variables represents the strength and direction of the relationship. The green line indicates a positive relationship, meaning that an increase in the variable is accompanied by an increase in the main component. The red line indicates a negative relationship, meaning that an increase in one variable is accompanied by a decrease in the main component. The thickness of the line indicates the strength of the correlation between the variable and the component.. showed that the first principal component was strongly associated with several physical and chemical factors in the river water during the study period. WT and AT recorded a strong inverse correlation, while BOD_5, DO, and TH recorded a strong direct correlation. PC2 was negatively correlated with PO4 and NO3, and positively correlated with Mg and EC and NO3. PC3 recorded a direct correlation with NO3 and Ca, and an inverse correlation with TALK. PC4 recorded a direct correlation with pH .

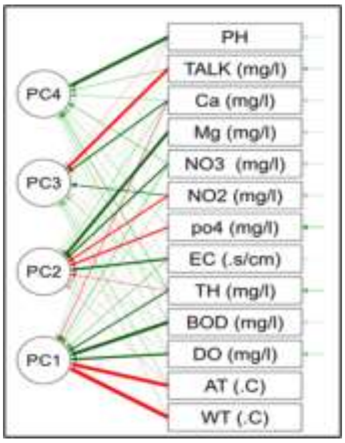

Figure 2. Path diagram of Principal Component Analysis physicochemical properites in the study |period.

Principal component analysis (PCA) of environmental factors in the Hilla River water showed that PC1 explained 35.76% of the total variance among the measured variables Figure 3 . A strong positive correlation was found between PC1 and each of the following: DO, BOD, NO2NO3, pH, EC, T, Alk, TH, and PO4. PC1 represented a group of factors associated with organic pollution and nutrients[33] . Where it is concentrated in the wet season. Seasonal changes in rainfall, surface runoff, cross-flow, groundwater flow, and inflow and outflow flows strongly affect river discharge and thus the concentration of pollutants in river water[17] .In contrast, WT AT Ca Mg was negatively correlated with PC1, representing thermal and mineral conditions that often rise during the dry season. Iraq's hot, dry summers and cold, rainy winters[34].

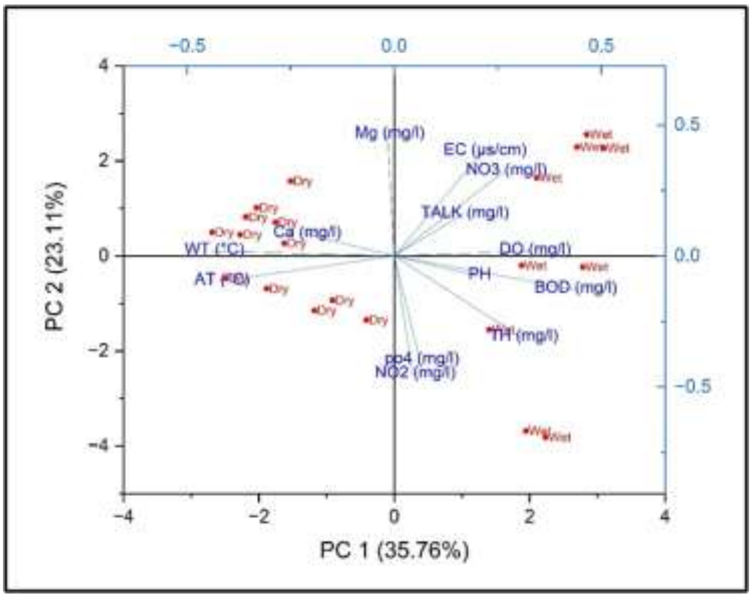

Figure 3. Analysis of the main components of water.

CONCLUSION

The Hilla River exhibits remarkable spatial and seasonal variations in physical and chemical factors due to both natural processes and human activities. Agricultural runoff and domestic wastewater discharge can pose potential risks to the aquatic ecosystem if not properly managed. Continuous monitoring, improved wastewater treatment, and the adoption of effective water management strategies are recommended to maintain and protect river water quality.

AUTHOR CONTRIBUTIONS

T. Hyder conducted the experiments, collected the data, and performed the analyses. J.M. Salman conceived the study idea, designed its objectives and editing the manuscript. M.J. Yase contributed to writing, reviewing, and editing the manuscript, as well as discussing the results.

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CONFLICT OF INTEREST

The authors declared that there is no conflict of interests regarding the publication of this manuscript.

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