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Hydrochemical characteristics and evaluation of surface water of Shatt Al-Hilla, Babil Governorate, Central Iraq

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Abstract

The current study aimed to assessing the water quality and discussing the hydrochemical characteristics and seasonal variation of surface water on the aspect of metals in Shatt-Al-Hilla, Babil Governorate, Central Iraq. Water samples were collected from eleven sampling sites of Shatt Al-Hila for wet season in March (18/3/2018), and a dry season in July (30/7/2018).

Surface water samples were analyzed for physiochemical parameters such as water temperature pH, EC, TDS, major ions $(Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{-2-}, CI^-, and HCO_3^-)$, nutrients $(NO_3^-, and PO_4^{-3-})$ for both seasons and DO for one season. Additionally, trace elements as Fe, B, Pb, Zn, Mn, Cr, Cu, Co, Ni, and Cd were also analyzed. Suitability of water for drinking and agricultural uses also evaluated.

Shatt Al-Hilla water type was classified as Ca^{2+} -HCO₃⁻ water type at wet season, and only (3) samples where Na⁺ is dominant than Ca²⁺ and classified as Na⁺-HCO₃⁻. While at dry season, (6) samples classified as Na⁺-Cl⁻ water type, and (5) samples where Ca⁺ is dominant than Na⁺ and classified as Ca²⁺-Cl⁻. Water classification based on Piper diagram shows that all samples are alkaline with increasing in the portions of alkalis and prevailing sulfate and chloride. Most water samples from Shatt Al-Hilla during the wet and dry seasons are unsuitable for drinking purposes according to results of anions and cations and trace elements, and within "excellent type" for livestock and poultry drinking and it lies within a permissible class based on EC limit for irrigation.

Keywords: Shatt Al-Hilla, Surface water, Major ions, Trace elements.

الخصائص الهيدروكيميائية وتقييم المياه السطحية في منطقة شط الحلة، محافظة بابل، وسط العراق

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الخلاصة

تهدف الدراسة الحالية إلى تقييم نوعية المياه ومناقشة الخصائص الهيدروكيميائية والتغير الموسمي للمياه السطحية اضافة لتواجد العناصر الأثرية في شط الحلة، محافظة بابل، وسط العراق. حيث تم جمع 11 عينة ماء من شط الحلة خلال الموسم الرطب في شهر اذار (2018/3/18)، و11 عينة خلال الموسم الجاف في شهر حزيران (2018/7/30). تم تحليل عينات المياه السطحية لمعرفة الخصائص الفيزوكيميائية مثل درجة حرارة الماء ، الأس الهيدروجيني (pH)، التوصيلية الكهربائية (EC)، الاملاح الذائبة الكلية (TDS) والاوكسجين الذائب في الماء (DD) ، وكذلك الأيونات الرئيسية (, Cl³, Na⁺, K⁺, SO₄^{2–}, Cl⁻, Cl⁻, Mg²⁺, Na⁺, K⁺, SO₄^{2–}, Cl⁻, NJ²) بالإضافة إلى العناصر الأثرية مثل (PA) (and HCO₃⁻ - Cl⁻, MG²⁺, NA⁺, K⁺, SO₄^{2–}, Cl⁻) بالإضافة إلى العناصر الأثرية مثل (NO₃⁻, and PO₄⁴⁻)

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لمجريت دراسة هيدروكيميائية للمياه السطحية لشط الحلة خلال الموسم الرطب والاستخدامات الزراعية الأخرى. أجريت دراسة هيدروكيميائية للمياه السطحية لشط الحلة خلال الموسم الرطب والجاف لتقدير تأثير الملوثات على جودة المياه. صنفت نوعية المياه في شط الحلة خلال الموسم الرطب ك⁻ Ca²⁺ HCO³ ، باستثناء ثلاث عينات فقط حيث يكون ⁺Na أكثر وفرة من⁺²Ca وصنفت نوعية المياه ك⁻ Na² – HCO³ ، بينما في الفترة الجافة كان الـ+Na اكثر وفرة من ⁺²Ca حيث صنغت ك⁻¹CD⁴ ، و (5) عينات حيث يكون ⁺²Ca²⁺ , وفرة من ⁺Na اكثر وفرة من ⁺²Ca حيث صنغت ك⁻¹Cl²⁺ ، و (5) عينات حيث يكون ويبين تصنيف المياه على أساس (مخطط بايبر) أن جميع العينات قلوية مع وفرة الكبريتات والكلوريدات .معظم عينات المياه خلال الموسمين كانت غير صالحة لشرب الانسان حسب نتائج الأيونات الموجبة والسالبة والعناصر الأثرية ولكن جميع العينات ولكلا الموسمين صنفت من "النوع الممتاز" لشرب الماشية و الدواجن ، ويتقع ضمن الفئة "المسموح بها" لاستخدامات الري اعتمادا على نسبة الملوحة بدلالة التوصيلية الكهريئية.

1. Introduction

Over the past decades, with the rapid urbanization and an increased, agriculture activity in Babil governorate, more water resources for irrigation and domestic uses is required. These developmental activities, coupled with the decrease in water amount as a result of building large dams in upstream river increased the risk of contamination of the surface waters in the area. The evaluation of water quality and hydrochemical characterizes has become a critical part of water resource studies, planning and management [1]. The Euphrates River was divided into Al-Hindia River and Shatt Al-Hilla River, after crossing the Al-Hindia barrage [2]. Shatt Al-Hilla is considered the main water resource for all drinking, domestic use, and agricultural activities in Babil Governorate. Drain waters containing pesticides and fertilizers and effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies with huge quantities of inorganic anions and trace elements [3]. The main objective of this study is to identify the hydrochemical characterize and evaluate the water quality of Shatt Al-Hilla, in order to improve the information available for better preservation and management of water resources.

2. Study Area

The study area is located in Babil Governorate, Central Iraq, between longitudes $(43^{\circ} 42^{\circ} \pm 45^{\circ} 50^{\circ})$, and latitudes $(32^{\circ} 7' \text{ N} \pm 33^{\circ} 8^{\circ})$ as shown in Figure-1. The total area of Babil Governorate is 5119 Km², representing 1.3% of the total area of Iraq [4]. Shatt Al-Hilla is waterway with a length of 104 Km in Babil Governorate, runs southeast and passes through the Babil province to Diwaniyah province [5]. Shatt Al-Hilla is an important water resource in Babil province, where it passes through large areas, and it is divided into several rivers and stream [6]

3. Methodology and materials

The water samples collected from (11) different sites along Shatt Al-Hilla, from Al-Hindia barrage to the south of Hilla City during wet and dry seasons (18/3/2018 and 30/7/2018) respectively (Table-1 and Figure-1). The samples collected on a scientific basis, using polyethylene bottles with a capacity of (1) liter. Surface water samples analyzed for physiochemical parameters such as water temperature pH, EC, TDS, DO, major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻, and HCO₃⁻), and nutrients (NO₃⁻, and PO₄³⁻) for both seasons except DO just for one season. Additionally, trace elements include Fe, B, Pb, Zn, Mn, Cr, Cu, Co, Ni and Cd also analyzed.



Figure 1-Location map of study area and water sampling sites along Shatt Al-Hila

No	Longitude	Latitude	City	Sample Site name
1	44°17'52.99"E	32°40'60.0"N	Sada	Under bridge
2	44°19'47.33"E	32°38'50.68''N	Sada	Fish pond
3	44°23'43.99"E	32°35'60.0"N	Mahaweel	Albomustafa
4	44°25'9.42"E	32°32'59.96"N	Mahaweel	Alboalwan
5	44°25'11.57"E	32°31'47.31"N	Mahaweel	Babil city
6	44°25'42.88"E	32°31'0.69"N	Hilla	Western Zoer
7	44°26'4.31"E	32°30'1.05''N	Hilla	Al-Saha
8	44°26'26.43"E	32°28'45.84''N	Hilla	Saad bridge
9	44°28'32.47"E	32°26'6.64"N	Hilla	Alaffar
10	44°29'23.14"E	32°25'4.06"N	Hilla	Almaimir
11	44°30'4.48"E	32°24'30.68''N	Medhatia	Dora barrage

 Table 1-Location of water samples along Shatt Al-Hilla

4. Results and discussion

4.1. Physicochemical parameters

Physiochemical parameters results of Shatt Al-Hilla water samples during dry and wet seasons compared with Iraqi [7] and WHO standards [8] as shown in Table-2. Generally, the mean temperature values for water samples in the study area vary between 16.7°C in the wet season (18 March 2018) and 32.7°C for the dry season (30 July 2018) as shown in Table-2 and Figure-2.

S. No.		W	et seaso	n		Dry season			
	TDS ppm	EC μs/cm	DO	pН	T∘C	TDS ppm	EC μs/cm	pН	T∘C
1	581	1163	7.1	7.83	18.9	568	1148	7.33	31.9
2	583	1165	7.2	8.2	18.6	563	1141	7.33	31.9
3	604	1208	7.2	7.9	18.5	561	1138	7.32	32.5
4	596	1194	7.5	7.84	17.4	455	1137	7.31	34
5	574	1147	7.6	7.75	16.8	545	1135	7.36	33.3
6	574	1145	7.5	8.11	16.9	539	1134	7.34	33.2
7	574	1148	7.8	7.58	16.9	535	1136	7.33	33.3
8	573	1148	7.4	8.03	17.6	531	1134	7.34	33.2
9	572	1137	8.2	7.9	16.2	530	1130	7.5	33.4
10	580	1155	8.4	7.71	13.2	528	1129	7.5	32.2
11	571	1155	8.5	8.22	12.9	560	1138	7.6	30.3
Range	571- 604	1137- 1208	7.1- 8.5	7.71- 8.22	12.9- 18.9	455- 568	1129- 1148	7.31- 7.6	30.3- 34
Mean	580	1160	7.7	7.91	16.7	547	1136	7.38	32.7
IQS	1000	1530	>5	6.5-8.5		1000	1530	6.5- 8.5	
WHO (2008)	1000	-	-	6.5-8.5	-	1000	-	6.5- 8.5	-

Table 2-Physiochemical parameter results of Shatt Al-Hilla water samples

During the dry season, pH ranges from 7.31-7.60 with a mean of 7.38 whereas it is recorded from 7.71 to 8.22 with a mean of 7.9 during the wet season (Table-2 and Figure-3). pH values were measured in the field using a portable conductivity and pH meter. In general, pH of water samples was slightly alkaline in nature. Specific Electrical conductivity (EC) is the ability of 1cm³ of water to

conduct electrical current, at a temperature of 25°C measured by micromhos/cm (µmohs/cm) depends on the concentration of soluble salts and the temperature of the water [9]. In Shatt Al-Hilla, EC of the surface water samples of wet season ranged from 1137-1208 µs/cm, with a mean of 1160 µs/cm. And it ranges from 1129-1148 µs/cm with a mean of 1136 µs/cm during the dry season (Table-2 and Figure-4). According to the water classification based on EC. It is clear that Shatt Al-Hilla water characterized as weakly mineralized water as shown in the Table-3.

EC(µc/cm)	Mineralization	• = =	
<1000	Very weakly mineralized water	4000-6000	Moderately mineralized water
1000-2000	Weakly mineralized water	6000-10000	Highly mineralized water
2000-4000	Slightly mineralized water	>10000	Excessively mineralized water

 Table 3-Water classification based on electrical conductivity [10]

The TDS concentration of the surface water during wet season ranging from 571 ppm to 604 ppm with mean values 580 ppm and from 528 ppm to 568 ppm with mean values 547 ppm in the dry season (Table-2 and Figure-4). The variations in the EC and TDS concentrations attributed to the anthropogenic activities represented mainly by effluent from agricultural activates and drain wastewater to the river directly without treatment in many locations.



Figure 2-Variation of water temperature in the surface water of Shatt Al-Hilla



Figure 3-Variation of pH values in the surface water of Shatt Al-Hilla samples



Figure 4-Variance of the electrical conductivity and TDS values of the water samples.

5.Major ions of surface water

The chemistry of water is depended mainly on major ion concentrations. All water samples were analyzed for major cations (Ca²⁺, Mg ²⁺, Na⁺, and K⁺), major anions (SO₄⁻², Cl⁻ and HCO₃⁻), and minor anions (NO₃⁻ and PO₄³⁻). The results of the major and minor ions of Shatt Al-Hilla water samples in both seasons are summarized in the Table-4.

Shatt Al-Hilla water samples (Wet season) in ppm									
Major ion	Ca ²⁺	Mg^{2+}	Na^+	\mathbf{K}^+	${{{ m SO}_{4}}^{2-}}$	Cl	HCO ₃ ⁻	NO ₃ ⁻	PO4 ³⁻
Min	78	20.4	91.8	8.60	202	118.3	187.7	0.65	0.063
Max	110	36.7	113.7	13.8	250	155.1	241.3	2.26	0.361
Mean	91.15	30.5	98.37	11.22	230.8	136.36	216.7	1.49	0.188
SD	8.98	5.07	5.9	1.78	18	14.47	17.85	0.75	0.079
		Shatt A	l-Hilla w	ater samp	les (Dry s	eason) in p	pm		
Min	144.6	59	160	4.8	287	329	123	4.3	0.35
Max	151	69	173	6,5	315	354	174	11.4	0.64
Mean	139	63.5	167.5	5.6	301.5	341	146.5	8.1	0.43
SD	3.6	2.8	3.8	0.5	7.9	8.66	13.8	3.7	0.07

Table 4-Statistical data of major ions in Shatt Al-Hilla water samples

Calcium (Ca^{2+})

Most Calcium in surface water comes from streams flowing over limestone, gypsum, and other calcium-containing rocks and minerals. Evaporates rocks containing gypsum and anhydrite are also most important sources of calcium soluble in water [9]. During wet season, Ca²⁺ranges from 78 to 110 ppm with 91.15 ppm in mean, while in the dry season, it ranges from 144.6 ppm to 151 ppm with mean 139 ppm (Table-4 and Figure-5). In dry period, Ca²⁺concentrations are higher than concentrations in wet period, this can be attributed to many factor as increase evaporation, absent of precipitation which dilute river water, increase photosynthesis in summer season compared to winter season. The pH of river water is influenced by many factors, especially by photosynthesizing organisms. These organisms commonly cause diurnal and seasonal fluctuations, with higher pH values on summer days and lower values at night and during other periods of low photosynthetic activity [9].

The increase of Ca^{2+} is consistent with the increase of SO_4^{2-} , both ions are produced by dissolving the secondary gypsum in the sediments.



Figure 5-Variation of major cations in the Shatt Al-Hilla water samples

Magnesium (Mg²⁺)

Magnesium is one of the widespread elements in the earth's crust. It is present in all natural waters [11]. Mg^{2+} ranges from 20.4 to 36.7 ppm with a mean of 30.5 ppm during the wet season, while during the dry season, it ranges from 59 ppm to 69 ppm with a mean of 63.5 ppm (Table -4 and Figure-5). The relatively high values of magnesium are attributed to the presence of carbon dioxide in the region, which dissolves magnesium from dolomite and carbonic minerals. In addition, common Clay minerals (mornormolinate) in the study area contain high concentration of magnesium.

Sodium (Na⁺)

The sodium ion is one of the most reactive metals present in nature. Sodium concentration is important in classifying irrigation water [12]. During the wet season, Na^+ ranges from 91.8 to 113.7 ppm with 98.37 ppm in mean, while during the dry season, it ranges from 160 ppm to 173 ppm with 167.5 ppm in mean as shown (Table-4 and Figure-5). The increase in sodium ion concentrations is consistent with increased salinity and increased concentration of **CI**, that indicating the source of this is chloride salts and the agricultural soil around the river.

Potassium (K⁺)

Rivers generally contains about 2-3 ppm potassium [13]. Potassium is highly soluble, therefore it is not easily removed from water except by ion exchange [14].

During the wet season, potassium ranges from 8.60 to 13.8 ppm with 11.22 ppm in the mean. During a dry season, it ranges from 4.8 to 6.5 ppm with 5.6 ppm in mean (Table 4 and Figure 5). It can be observed that potassium concentration is lower than sodium, because, potassium ion is larger than

sodium ions and therefore has less adsorption than sodium in ion exchange, and also the high resistance to weathering of potassium-containing minerals such as Potassium Feldspar[15].

Chloride (Cl⁻)

Dissolution of evaporitic minerals such as halite and gypsum is a major source of Cl⁻, Na⁺, and SO4²⁻ in average river water. The chloride concentration for Shatt Al-Hilla water samples varied between 118.3 ppm to 155.1 ppm and 136.36 in mean at the wet season and between 329 to 354ppm and 341ppm in mean at the dry season (Table-4 and Figure-6). High concentration of Cl⁻ in both seasons, because chloride content is increased in water by evaporation and salts chloride has high solubility, such as (Halite). Thus, the falling rain (even if a few) dissolves chloride salts and increases water content.



Figure 6-Variation of major anions in the Shatt Al-Hilla water samples.

Bicarbonate (HCO₃)

The pH range 7.3-8.7 of the analyzed Shatt Al-Hilla water samples for wet and dry seasons indicating the dominant of bicarbonate ion. HCO_3^- ion is the dominant species between pH 6.3 and 10.3 [16]. Bicarbonate concentration within the collected water samples range between 187.70 ppm 241.3 ppm and with a mean of 216.7 ppm at the wet season, and it ranges between 123 ppm to 174 ppm and with a mean of 146.5 ppm in the dry season (Table-4 and Figure-6). The increase in **HCO**₃⁻ for both seasons can be attributed to the effect of (CO₂) in the atmosphere and in soil and carbonate rock solutions. In addition, the process of respiration and decay of plants after their death, CO₂ is released[15].

Sulfate (SO_4^{2-})

Sulfate is one of the major dissolved components of rain [17]. The maximum level of sulfate suggested by WHO [8] for drinking water quality is 250 mg/l and 400 mg/l in IQS [8]. The mean concentration of sulfate in Shatt Al-Hilla water samples in the wet season is 230.8 ppm and ranging from 202 to 250 ppm, during the dry season, sulfate ranges from 287 ppm to 315 ppm with 301.5 ppm in mean (Table-4 and Figure-6). Sulfates are dominant in the wet period in most aquatic samples

and their value changes irregularly with the flow direction, due to the fact that sulphates are part of the soil content of study area. The different dilution and watering processes showed a difference in the increase or decrease in concentration of sulphate during the two seasons.

6. Nutrients

Phosphate (PO₄³⁻)

Phosphate existed in water in a soluble form, is originated from rocks in addition to its existence in agricultural runoff, industrial wastes, municipal sewage [18]. The PO_4^{3-} concentration for water samples varies between 0.063 to 0.361 ppm and between 0.35 to 0.64 ppm for wet and dry season respectively (Table-4 and Figure-7). The concentration of PO_4^{3-} at dry season is greater than wet season, due to the effect of evaporation and low water level as well as the pollution by chemical fertilizers, and the increase is associated with the increase of NO_3^{2-}

Nitrate (NO₃⁻)

The concentration of NO₃⁻ for water varies between 0.65 - 2.26 ppm with a mean of 1.49 ppm and between 4.3 - 18.4 ppm with a mean of 9 ppm during wet and dry seasons respectively (Table-4 and Figure-7).. High concentrations of NO_3^{2-} were recorded in some samples near agricultural activity areas and animal grazing. Generally NO_3^{-} concentrations of most water samples collected from Shatt Al-Hilla water during both seasons are negligible or so small to be considered and lower than the above mentioned standards.



Figure 7-Variation of nutrients in Shatt Al-Hilla water samples.

7. Trace elements of surface water

The potential contamination of river waters with trace elements is very harmful due to their nonbiodegradable nature, long biological half-lives and their potential to accumulate in different body parts [19]. The natural sources of trace elements are the weathering of the rocks and soil. Some of these metals are essential for all living organisms and be toxic at high concentrations; other metals are toxic even at a relatively low concentration [20]. The water samples were analyzed for trace elements (Zn, Pb, Cu, Cd, Ni, Cr, Co, Mn, Fe and B). The results of trace elements concentration in ppb of Shatt Al-Hilla water samples during wet and dry seasons are systemized in the Table-5.

Wet season										
Element	B	Fe	Mn	Zn	Cu	Cd	Ni	Pb	Cr	Со
Unit	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Min.	198	175	140	117	71	69	96	70	84	56
Max.	430	401	250	280	145	167	149	164	124	101
Mean	339	399	200	202	114	109	120	126	109	81
SD	80.1	75.7	35.3	55.9	23.5	32.5	19.8	25.3	12.6	13.9
				Dr	y season					
Min.	179	185	95	103	68	65	76	73	82	34
Max.	429	380	251	271	149	129	118	150	126	86
Mean	344	290	193.4	199	110	95.5	100	121.1	104.4	67.4
SD	85.5	75.8	60.1	58.4	30.6	22.9	14.1	23.7	14.9	18.9

Table 5-Trace elements of Shatt Al-Hilla water samples

Boron for Shatt Al-Hilla water samples during the wet season is 198 ppb to 430 ppb with mean is 339 ppb, ppb and a dry season is 179 ppb to 429 ppb with mean 344 ppb (Table-5 and Figure-8). The increase of boron concentration compared to the rest of trace elements due to the weathering of tournaline minerals as well as its presence in industrial and wastewater due to the use of boron in cleaning aid[15].

Iron is one of the most abundant metals of the Earth's crust. The added fertilizers to the agricultural soil also supply a considerable amount of [21]. During the wet season, Fe ranges from 175 ppb to 401 ppb with 399 ppb in mean, but during the dry season, it ranges from 185 ppb to 380 ppb with 290 ppb in the mean (Table-5 and Figure-8). The mean concentrations of Fe at wet season are higher than dry season, in addition to the presence of Fe in the sediments, the presence of Fe in the water can be attributed to organic waste and the remains of decaying plants in the soil.

Manganese, the major anthropogenic sources of Mn include municipal wastewater discharges, sewage sludge, mining and mineral processing, combustion of fossil fuels [22]. Concentrations of dissolved Mn in Shatt Al-Hilla water samples varies between 140 and 250 ppb with a mean of 200 ppb for the wet season, and between 95 and 251 ppb with a mean of 193.4 ppb for dry season (Table-5 and Figure-8).

Zinc is a common contaminant in surface and groundwater, runoff, and industrial waste [16]. Zn concentration, during a wet season, ranges from 117 ppb to 280 ppb with 202 ppb in mean, but during the dry season, it ranges from 103 ppb to 271 with 199 ppb in mean (Table-5 and Figure-8). The mean concentrations for Zn at wet season are higher than dry season, this can be attributed to agricultural events and the use of fertilizers.

The weathering of **copper** deposits is the main natural source in the aquatic environment [16]. The concentration of Cu in Shatt Al-Hilla water samples for wet season varies between 71 ppb and 135 ppb with a mean of 114 ppb, and between 68ppb and 149 ppb with a mean of 110 ppb for dry season (Table-5 and Figure-8). High Cu in wet season may be attributed to domestic sewage, run-off from agriculture and urban area where Hilla City characterized by intensive human activities, although Cu in both seasons is within the limits allowed in [7] and [8].



Figure 8-Variation of trace elements in the Shatt Al-Hilla water samples.

Lead originates naturally from its minerals such as galena (PbS), anglesite (PbSO₄) and cerussite (PbCO₃) [23]. During wet season, lead ranges from below detection limit 70 ppb to164 ppb with 126 ppb in the mean. but in the dry season, it ranges from below detection limit 73ppb to 150 ppb with 122 ppb in mean (Table 5 and Figure-8). Lead concentrations in aquatic samples of the study area were high and exceeded the permissible limits for drinking water. This increase in concentrations can be attributed to agricultural processes, land us, fusel fuel as well as industrial emissione .

Cadmium, during a wet season, Cd ranges from 69 ppb to 167 ppb with 109 ppb in average (Table 4.8), but during the dry season was decreased and it ranges from 65ppb to 129 ppb with 109 ppb in mean (Table-5 and Figure-8). Although the concentration of Cd is the lowest for trace elements but exceeded the limits of Iraq standards [7] and WHO[8]. This can be explained by its presence in the rocks and river sediments, or may be polluted by industrial pollutants in cadmium (electroplating, dyes, printing ink)

Chromium in Shatt Al-Hilla water samples range from 85ppb to 124 ppb with a mean of 109 ppb, in the wet season and from 82 ppb to 126 ppb with a mean of 104.5 ppb in the dry season (Table 5 and Figure-8). All the results of Cr exceeded the permissible limits for drinking water. This increase in concentrations can be attributed to the untreated domestic and industrial water, runoff from agricultural land.

Cobalt concentration of Shatt Al-Hilla water samples during wet season ranges from 56 ppb to 101 ppb with a mean of 81 ppb, and from 34 ppb to 86 ppb with a mean of 67.4 ppb during the dry season (Table-5 and Figure-8). The results show that cobalt is the least trace element found in Shatt Al-Hilla and that all samples are within the permissible limits for drinking water

Nickel for Shatt Al-Hilla water samples during the wet season is 96 ppb to 149 ppb with mean is 120 ppb, and during the dry season is 76 ppb to 118 ppb with mean 100 ppb season (Table-5 and Figure-8). The values for the wet season are higher than for dry season and that all values have exceeded the permissible limit for drinking water. The high presence in the environment is attributed to human activity [9] especially agricultural, for its presence in Iraqi fertilizers.

8. Hydrochemical formula

The hydrochemical formula of surface water in Shatt Al-Hilla is determined according to Kurlolov's formula. This formula depends on the ratio of the main ions, (cations and anions) expressed by equivalents per million epm %, that are arranged in descending order which have more than (15%) ratio of availability [24].

Applying Kurlolov's formula of Shatt Al-Hilla surface water data shows that Ca^{2+} - Na^+ - Mg^{2+} - HCO_3^- - SO_4^{2-} - CI^- are the dominant hydrochemical formula in water samples for the wet seasons, and classified as Ca^{2+} - HCO_3^- water type (Table-6). There are only three samples (1,7, 9), where the Na⁺ is more dominant than Ca^+ and classified as Na^+ - HCO_3^- (Table-6). At dry season, when applying Kurlolov's formula of Shatt Al-Hilla surface water data, shows that Na^+ - Ca^{2+} - Mg^{2+} - $CI^-SO_4^{2-}$ - are the dominant hydrochemical formula in water samples (six samples), and classified as Na^+ - CI^- water type, and (5) samples, where the Ca^{2+} is dominant than Na^+ and classified as Ca^{2+} - Cl (Table-6).

S. NO.	Ca ²⁺	Mg ²⁺	Na^+	\mathbf{K}^+	HCO ₃ -	SO4 ²⁻	Cl	Hydrochemical formula	Water type		
	Wet season (epm %)										
1	37.5	17.3	42,1	3.0	37.5	30	32.2	Na+-Ca2+Mg2+-HCO3Cl- SO42	Na+HCO3-		
2	39.1	20.1	37.5	3.1	38.2	36.41	25.6	Ca2+-Na+-Mg2+ -HCO3- SO42Cl-	Ca2+HCO3-		
3	39.5	23.4	34.2	2.7	40.8	28.1	30.2	Ca2+-Na+-Mg2+- HCO3Cl- SO42	Ca2+HCO3-		
4	41.5	20.2	35.2	2.9	40	31.6	28.0	Ca2+-Na+-Mg2+ HCO3- SO42Cl-	Ca2+HCO3-		
5	36.5	25.4	35.3	2.5	41.1	33.0	25.4	Ca2+-Na+-Mg2+- HCO3- SO42Cl-	Ca2+HCO3-		
6	39.4	22.4	35.66	2.1	40.9	32.2	26.4	Ca2+-Na+-Mg2+- HCO3- SO42Cl-	Ca2+HCO3-		
7	34.0	25.0	38.8	2.1	39.6	28.4	31.8	Na+-Ca2+Mg2+- HCO3Cl- SO42	Na+HCO3-		

Table 6-Hydrochemical formula and water type of surface water samples.

8	36.9	25.2	35.6	2.2	44.3	28.4	27.1	Ca2+-Na+-Mg2+ HCO3- SO42Cl-	Ca2+HCO3-
9	36.8	24.3	36.88	1.8	36.5	34.7	28.1	Na+-Ca2+Mg2+- HCO3- SO42Cl-	Na+HCO3-
10	42.4	20.2	35.2	2.0	35.7	33.6	30.5	Ca2+-Na+-Mg2+ HCO3- SO42Cl-	Ca2+HCO3-
11	43.8	20.2	33.8	2.0	38.5	33.9	26.8	Ca2+-Na+-Mg2+ HCO3- SO42Cl-	Ca2+HCO3-
						Dry Se	ason ((epm %)	
1	36.3	26.2	36.7	0.85	13.9	32	49.6	Na+-Ca2+Mg2+ Cl SO42-	Na ⁺ Cl-
2	37	25.6	36.9	0.6	12.9	34.3	52.3	Ca2+-Na+-Mg2+ Cl SO42-	Ca ²⁺ Cl-
3	36.37	26.8	36.32	0.7	13.1	33.4	53.0	Ca2+-Na+-Mg2+ Cl SO42-	Ca ²⁺ Cl-
4	36.49	26.65	36.5	0.7	13.3	33.9	51.6	Na+-Ca2+Mg2+- Cl SO42-	Na ⁺ Cl-
5	36.5	26.1	36.8	0.7	11.9	34.4	53.3	Na+-Ca2+Mg2+- Cl SO42-	Na ⁺ Cl-
6	36.6	25.9	37	0.6	12.4	33.8	53.1	Na+-Ca2+Mg2+- Cl SO42-	Na ⁺ Cl-
7	36.54	25.8	37.0	0.6	11.9	33.9	53.5	Na+-Ca2+Mg2+- Cl SO42-	Na ⁺ Cl-
8	37.76	26.5	36.3	0.6	12.5	34.1	52.7	Ca2+-Na+-Mg2+ Cl SO42-	Ca ²⁺ Cl-
9	36.46	26.1	36.71	0.6	13.8	33.9	51.1	Na+-Ca2+Mg2+- Cl SO42-	Na ⁺ Cl-
10	36.20	27.2	35.8	0.7	12.4	34.7	52.5	Ca2+-Na+-Mg2+- Cl SO42-	Ca ²⁺ Cl-
11	36.37	26.9	36.3	0.7	13.1	34.8	50.7	Ca2+-Na+-Mg2+ Cl SO42-	Ca ²⁺ Cl-

9. Water classification according to Piper Diagram

Piper diagram is presented by using geochemical data and it is based on four main cations (Ca²⁺, Mg²⁺, Na^{+,} and K⁺) and three main anions (HCO₃²⁻, SO₄²⁻ and Cl⁻) presented in milliequivalent per liter (meq /l). Piper, [25] has proposed a tri-linear diagram that permits the classification of water into seven types. Water classifications according to Furtak & Langguth (1965) are displayed in Table-7 and Figure-9. Water classification based on Piper diagram, during both seasons show that all the collected of Shatt Al-Hilla water samples are located in the upper half of the rhombic-shaped (class e) which means that water is prevailing sulfate-chloride (Figure-10). Therefore, it is evident that all the samples and for both seasons are alkaline with increasing in the portions of alkalis with prevailing sulfate and chloride.

Table 7-Water classification based on the Piper diagram after [26]

Water Types	Subdivision
Normal earth alkaline water	
With prevailing bicarbonate	a
With prevailing bicarbonate and sulfate or chloride	b
With prevailing sulfate or chloride	С
Earth alkaline water with increased portions of alkalis	
With prevailing bicarbonate	d
With sulfate and chloride	e
Alkaline water	
With prevailing bicarbonate	f
With prevailing sulfate-chloride	g



Figure 9-Piper diagram according to Furtak & Langguth [26]



Figure 10-Piper classification for water samples.

10. Suitability of water for different uses10.1. Evaluation of water quality for drinking

Drinking water quality standards of WHO [8] and Iraq [7] are used as a basis for the water quality evaluation of the present study samples for drinking use. Most water samples from Shatt Al-Hilla during the wet and dry season are not suitable for drinking purposes according to results of anions and cations and trace elements (Table-8).

Devenuetor	TT *4			Wet sea	son)	Dry season)		
Parameter	Unit	IQS (2009)	WHO (2008)	min	max	min	max	
W.T.	°C			12.9	18.9	30.3	34.0	
рН		6.5-8.5	6.5-8.5	7.7	8.2	7.3	7.8	
DO	ppm	-	-	6.9	8.5			
EC	ppm			1137	1208	1129	1128	
TDS	ppm	1000	1000	571	604	455	568	
Ca ²⁺	ppm	150	100	78	110	144	151	
Mg^{2+}	ppm	100	125	20.4	36.7	59	69	
Na ⁺	ppm	200	200	91.8	113.7	160	173	
K ⁺	ppm		12	8.6	13.8	4.8	6.5	
SO4 ²⁻	ppm	400	250	202	250	287	315	
Cl-	ppm	350	250	118.3	155.1	329	354	
HCO ₃ ⁻	ppm			187.7	241.3	132	174	
NO ₃	ppm	50	50	0.65	2.26	4.3	18.4	
PO ₄ ³⁻	ppm			0.063	0.361	0.35	0.64	
Fe	ppb	300	<3000	173	401	185	380	
Pb	ppb	10	10	70	164	73	150	
Zn	ppb	3000	3000	117	280	103	171	
Mn	ppb	100	400	140	250	95	251	
Cr	ppb	50	50	84	124	82	126	
Cu	ppb	1000	2000	71	145	68	149	
Со	ppb			56	101	34	86	
Ni	ppb	20	70	96	149	78	118	
Cd	ppb	3	3	96	167	65	129	
* Adap	oted from	([27] Environ	mental Protectio	n Agency. IQS	5 [7] and W	HO [8].		

Table 8-Comparing surface water samples of Shatt Al- Hilla during wet and dry seasons with standard water quality criteria and previous study

The maximum value of calcium, and chloride (major ions) exceeded the limits of Iraq standards [7] and WHO [8] and Sulfate, minimum value of calcium and chloride exceeded the limits of WHO at dry season. While at wet season maximum value of calcium, potassium, exceeded the limits of WHO [8].

Lead, Chromium, Nickel and Cadmium exceeded the limits of Iraq standards [7] and WHO [8] at both seasons. While Iron and Manganese exceeded only the limits of Iraq standards [7] at both seasons. So most water samples from Shatt Al-Hilla during the wet and dry season are not suitable for drinking purposes according to results of anions and cations and trace elements (Table-8).

10.2. Evaluation of water quality for livestock

Criteria for livestock suitability usually takes into account the type of livestock, daily water requirements of each species as well as information on the toxicity of specific substances to the different species. The recommended limits presented in Table-9 include an appropriate margin of safety. According to water quality for livestock and poultry [28], all surface water samples for the dry and wet seasons are within "excellent type" (Tables-9).

Water Salinity (EC) (µS/cm)	Rating	Remarks
<1500	Excellent	Usable for all classes of livestock and poultry.
15 00– 5000	Very Satisfactory	Usable for all classes of livestock and poultry. May cause temporary diarrhoea in livestock not accustomed to such water; watery droppings in poultry.
5000 - 8000	Satisfactory for Livestock Unfit for Poultry	May cause temporary diarrhoea or be refused at first by animals not accustomed to such water. Often causes watery faeces, increased mortality and

Table 9-Water quality for livestock and poultry uses [28]

		decreased growth, especially in turkeys.
	Limited Use for	Usable with reasonable safety for dairy and beef cattle, sheep,
9000 11000	Linited Use for	swine and horses. Avoid use for pregnant or lactating
8000 - 11000	LIVESTOCK	animals.
	Unfit for Poultry	Not acceptable for poultry.
		Unfit for poultry and probably unfit for swine. The
		considerable risk in using for pregnant or lactating cows,
11000 16000	Very Limited Use	horses or sheep, or for the young of these species. In general,
11000 - 10000		use should be avoided although older ruminants, horses,
		poultry, and swine may subsist on waters such as these under
		certain conditions.
> 16000	Not	Risks with such highly saline water are so great that it cannot
>16000	Recommended	be recommended for use under any conditions.

10.3. Evaluation of water quality for irrigation Salinity Hazard

The most influential water quality guideline on crop productivity is the salinity hazard as measured by electrical conductivity (EC). Almost all Shatt Al-Hilla water samples of the wet and dry season lie within "Permissible" class based on Suggested limits of EC value for irrigation (Table-10).

Table 10-Classification the suitability of water for irrigation according to ele	ectrical conductivity [29]
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Classes of water	Electrical Conductivity (dS/m)*				
Class 1, Excellent	< 0.25				
Class 2, Good	0.25 - 0.75				
Class 3, Permissible ¹	0.76 - 2.00				
Class 4, Doubtful ²	2.01 - 3.00				
Class 5, Unsuitable ²	>3.00				
* decisiemen/m,(dS/m)at 25° C = millimho/cm, mmho/cm, 1 dS/m = 1000 μ S/cm.					
¹ Leaching needed if used. ² Good drainage needed and sensitive plants					

Sodium Hazard

Classification of irrigation waters with respect to SAR is based primarily on the effect of exchangeable sodium on the physical condition of the soil. In addition, sodium-sensitive plants may suffer damage as a result of sodium accumulation in plant tissues. The Sodium Adsorption Ratio (SAR) calculated based on the following formula [27]

$$SAR = \frac{(Na^{+})}{\sqrt{\frac{1}{2}[(Ca^{2+}) + (Mg^{2+})]}}$$

All water samples of Shatt Al-Hilla, based on SAR values, in wet and dry season, lie within "Medium " class of the irrigation water [28] as shown in Tables-(11, 12).

Table 11-SAR value of Shatt Al-Hilla water samples during wet and dry seasons

Season	No	1	2	3	4	5	6	7	8	9	10	11	Min	Max	Average
Wet season	R	11	10	9.8	9.6	10.1	10.3	10.7	10	10.8	9.8	9.5	9.5	11	10
Dry season	SA	13.3	13.3	13.3	13.4	13.5	13.4	13.3	13.2	13.5	13.6	13.6	13.2	13.6	13.4

Table 12-Class	sification of the irrigation w	water according to sodium hazard based on SAR values [29	
			_

SAR values	Sodium hazard of water	Comments
1-9	Low	Use on sodium sensitive crops must be cautioned
10-17	Medium	Amendments (such as gypsum) and leaching needed
18-25	High	Generally unsuitable for continuous use
≥26	Very high	Generally unsuitable for use

Conclusions

Shatt Al-Hilla water samples characterized within the category weakly mineralized water based on electric conductivity results. All water samples are considered as "Fresh water" and there is a gradual decline when comparing the results of TDS with the previous years at the (Al-Hilla station.

Shatt Al-Hilla water type shows that $Ca^{2+}Na^+-Mg^{2+}-HCO_3^-SO_4^{2-}-Cl^-$ are the dominant hydrochemical formula in wet seasons, and classified as $Ca^{2+}-HCO_3^-$ water type, there are only three samples where the Na⁺ is more dominant than Ca+ and classified as Na⁺- HCO₃⁻. While at the dry season, Shatt Al-Hilla water type, shows that Na⁺-Ca²⁺ --Mg²⁺- Cl⁻ - SO₄²⁻ are the dominant hydrochemical formula in water samples (six samples), and classified as Na⁺ -Cl⁻ water type. Additionally, (5) samples, where the Ca⁺ is more dominant than Na+ and classified as Ca²⁺- Cl.

According to water classification based on the Piper diagram, all water samples of- Shatt Al-Hilla are located in (class e). Therefore, it is evident that all the samples for both examined conditions are alkaline with increasing in the portions of alkalis with prevailing sulfate and chloride.

The maximum value of calcium, and chloride (major ions) exceeded the limits of Iraq standards (IQS 2009) and WHO (WHO,2008b) and sulfate, minimum value of calcium and chloride exceeded the limits of WHO at dry season . While at wet season maximum value of calcium, potassium, exceeded the limits of WHO (WHO,2008b),.Lead, Chromium, Nickel and Cadmium exceeded the limits of Iraq standards(IQS 2009) and WHO(WHO,2008b) at both seasons. While Iron and Manganese exceeded only the limits of Iraq standards(IQS 2009) at both seasons. So most water samples from Shatt Al-Hilla during the wet and dry season are not suitable for drinking purposes according to results of anions and cations and trace elements. All Shatt Al-Hilla water samples for the dry and wet season are within "excellent type" According to water quality for livestock and poultry, and season lies within " Permissible" class based on suggested limits of EC value for irrigation. All Shatt Al-Hilla water samples for wet and dry season lie within class "Medium " of the irrigation water based on SAR values.

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