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Study the Hardness and Some Ions in Central Karbala Drinking Water Treatment Station

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Abstract

This study included the compromised the containing Hardness and some ions of treated water in central Karbala drinking water treatment station with Iraqi and international drinking water criteria. Also, this study was attempted to focus on probable pollution sources. The Hardness and other waters salts Sulphates (SO₄), Chloride ion (Cl⁻), Calcium ion (Ca⁺²), and Magnesium ion (Mg⁺²) tests criteria were determined on water samples taken from Al-Hussainia River water source, treated drinking water during October-November 2013 to August - September 2014. Study results revealed an increasing in Total hardness (TH), sulfate, chloride, calcium, in winter (December- January) 2014. In addition, the results showed a decrease in above mentioned criteria in (August-September) 2014. Study finding revealed that the values of chloride, calcium, sulphate, were out of the Iraqi and the international standards water. While total hardness, magnesium, and chloride concentrated were within Iraqi and international acceptable standards.

Keywords: Drinking water, Karbala, Hardness and Salts.

دراسة العسرة وبعض الايونات في محطة ماء كربلاء المركزية

يعرب فالج خلف الفتلاوي ، يحيى هاشم ياس

قسم علوم الحياة ، كلية العلوم ، جامعة بغداد ، بغداد ، العراق.

الخلاصة

شملت الدراسة تقييم محتوى المياه من العسرة وعدد من الأيونات مع معايير مياه الشرب العراقية والدولية. كما شملت الدراسة عدد من الفحوصات مثل العسرة والكالسيوم والمغنيسيوم والكلورايد والكبريتات لعينات المياه المأخوذة من مصادر المياه نهر الحسينية ومحطة كربلاء المركزية لتصفية مياه في المدينة خلال أكتوبر- نوفمبر 2013 إلى أغسطس - سبتمبر 2014. كما وكشفت نتائج الدراسة إلى زيادة في العسرة والكالسيوم والمغنيسيوم والكلورايد والكبريتات في فصل الشتاء وانخفاضها في الأشهر الحارة وخصوصاً (أب وأيلول). كما كانت قيم الكلوريد، والمغنيسيوم، والكبريتات أعلى من المواصفة العراقية و الدولية، بينما العسرة الكلية والمغنيسيوم ضمن المواصفات العراقية والعالمية.

Introduction

Water is an important resource to sustain life, and a satisfactory must be of adequate, safe, accessible, and available to all populations [1]. Karbala is an important Iraqi holy city depends on Al-Hussainia river waters for drinking water after treating in central Karbala drinking water treatment station. Al-Hussainia river water quality ranges from poor to very poor and central Karbala drinking water treatment station is old and there are many problems in quality and quantity drinking water

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production [2]. In this study we identifying the values of hardness and some ions properties of water in Al-Hussainia River and the central Karbala drinking water treatment station, and compared the concentration of pollutants with international and Iraqi specifications.

Hardness is one of the important chemical characteristics to determine the suitability of water for domestic drinking and industrial purposes. Hardness is caused principally due to the dissolved contents of carbonates and sulphates of calcium and magnesium; at times to a lesser degree, presence of chlorides, nitrates and sometimes iron and aluminum is effective in causing hardness. It is expressed as ppm in terms of calcium carbonate [3].

Calcium and magnesium are the major common ions in freshwater due to their existent in rocks and sediments [4]. The calcium occurs in water due to presence of limestone, gypsum and dolomite. Calcium and magnesium are the major scale forming constituents in raw water. Calcium is an essential element for Human and for plant growth. Magnesium is an essential element for human beings, but higher levels of magnesium are harmful as they act as cathartics and diuretics in man [5].

The chloride ion is available in all natural water at different concentrations. The sedimentary rocks the main source of chloride ion as well as rainwater and melting snow. In addition, agricultural, industrial, and domestic wastewaters discharged to surface waters are a source of chlorides. Sewage contains large amounts of chloride, as do some industrial effluents [6, 7]. The measurement of chloride (Cl_2) is necessary to determine the suitability of water for domestic, industrial or agricultural uses [8]. Excess presence of Chloride in water leads to gastrointestinal disease, diarrhea, and skin allergies [3].

Sulphates exist in nearly all natural waters, the concentrations varying according to the nature of the terrain through which they flow. They are often derived from the sulphides of heavy metals (iron, nickel, copper and lead) [9]. The Iraqi waters distinguished by the presences of a high concentration of SO_4 ions, the sulphur has a great bio important of many organism, it is one of the main elements in forming proteins and plants growth [10,11].

Materials and methods

Samples collection and studied stations

Sampling of hardness and some ions variables were performed from fourteen sites bimonthly were carried out from October 2013 until September 2014, to represent all months. Sampling usually started at 9 am and was completed at 2pm.

The samples were taken from:

1- **S1**: Samples were collected before the station from a place of the river before the stations in 1.5 Km as showed in figure 1. The samples were collected in three replicates, first one (2, 3) meter far from the left side of the river and the other (2, 3) meter from the right side of the river and the third replicate from the middle of the river.



Figure 1-Location of Karbala central Karbala drinking water treatment

S2: Samples were collected from the inside of the station after the chlorination and before pumping to the city areas

❖ Water sample for chemical analysis collected in polyethylene containers with a volume of 5 liters under water surface about (20-40) cm after rinsing the container with water sample twice before filling, then kept at 15°C in refrigerator [1].

Total Hardness (TH)

The method described by [13]. It was used for the purpose of measuring the values of total hardness, by taking 10 ml of the sample and diluted to 50 ml with distilled water, then added one ml of ammonia regulator solution where the pH is 10. After the addition of a few of dry indicator (Erichrom black T) use as reagents and titrated against EDTA solution normally 0.05, and calculated values often by the following equation:

$$\text{Total hardness as CaCO}_3 = A \times B \times 1000/\text{ml of sample}$$

Where:

A = number of titration moles

B = number of grams of calcium carbonate equivalent 100 ml of EDTA titrated.

Sulphates (SO₄⁻²)

The method described by [14], where 5 ml of the sample diluted to 100 ml of distilled water, 5 ml of conditioning reagent (HCl, NaCl, glycerol, alcohol, distil water) was added to the sample, and 0.15 mg of powder of barium chloride BaCl₂ was added, then the absorption was determined by using UV-spectrophotometer at wave length 420nm, then the absorption was read on the above mentioned wavelength which makes the barium sulphate minutes stuck. The amount of sulphates is calculated from the difference between the two readings after making a trend of calibration from standard sulphuric acid solution (H₂SO₄). The results are expressed in units of mg /L.

Chloride ion (Cl)

Chloride ion concentration was measured in the samples in a manner titration using silver nitrate according to the method called Argentometric Nitrate Method, where 10 ml of the sample diluted to 100 ml of distilled water, and 1 ml of potassium chromate solution as indicator was added. The sample titration against silver nitrate solution of 0.041normal until the appearance of light yellow colour, redoing the same procedure on 100 ml of distilled water. The volume of silver nitrate consumed was recorded in the case of distilled water. The second reading was subtracted of the first, and then the formula described in APHA (1998) was applied to calculate the concentration of chloride ion, as follows:

$$\text{Cl mg/L} = (A-B) (N) \times 35450 / \text{ml of sample}$$

Where A = first reading of the sample

B = first reading of the Blanck

N = normality of silver nitrate.

Calcium ion Ca⁺²

The method described by [13], was used. It is called (EDTA Titrametric Method), where 10 ml of the sample diluted to 50 ml by distilled water, and then two ml of NaOH of one normal added to the sample to adjust pH to 12-13, meroxide reagent added in amount of 0.2 gm. The samples titrated against (0.01) EDTA-Na₂ molar until the color changes from pink to purple which indicates the end of the reaction. Calcium ion and calcium hardness in terms of calcium carbonate were calculated according to the following equation:

$$\text{Ca}^{++} \text{ mg / L} = A \times B \times 40.08 / \text{ml of sample}$$

Where A = size of the titrated sample

B = grams of calcium carbonate equivalent of 1 ml of EDTA.

Magnesium ion Mg⁺²

Magnesium ion concentration was calculated according to the equation described in [13]:

$$\text{Mg}^{+2} \text{ mg / L} = (\text{Total hardness} - \text{Calcium hardness}) \times 0.243$$

Results and discussions

Total Hardness (TH)

The current results found that the highest value for TH was 360.66 and 353.00 mg/L in winter (December- January) 2014 at S1 and S2 respectively, while the lowest value was 201 and 320 mg/L in (August-September) 2014 at Station 1 and 2 figur.2 and 3. The statistical analysis showed a significant difference among months and a significant difference among stations at (P<0.05) Appendix

1. The positive and direct correlation among TH Sulphates (SO_4), Chloride ion (Cl^-), Calcium ion (Ca^{+2}), and Magnesium ion (Mg^{+2}) Ca^{+2} in present study table 1

Higher values of total hardness in Al-Hussainia River due to the major increase occurred after receiving the untreated domestic sewage and industrial waste of Karbala city. The increase levels hardness in winter and spring and decrease in summer due to the dilution in salts concentration in flood period [15]. On the other hand, the erosion of soils toward Euphrates River as a results of rain falls in the cold months and reaching the pollutants to river water from the municipal wastes close to the river [16], as well as the agricultural wastes from the nearby lands, all of that lead to raising the rates of hardness in the waters, and this turn affects in the Al-Hussainia river because it is a one branches of the Euphrates River.

Kevin [17] had divided water sample into four types depending on total hardness as: the concentration less than 50mg/l calcium carbonate as non-hard water, the water has values ranged from 50 to 100 mg/l is moderate hard water, values from 100 to 200 mg/l is hardness water, and more than 200 mg/L calcium carbonate as a very hard water, according to present study finding, it can be classify Al-Hussainia river water as very hard water.

The concentration of TH was within the permissible limit by Iraqi standard specification for drinking water 2001 No. (417), which was 500 mg/L, and within WHO standards (2004) [18], which was 500 mg/L Appendix 2.

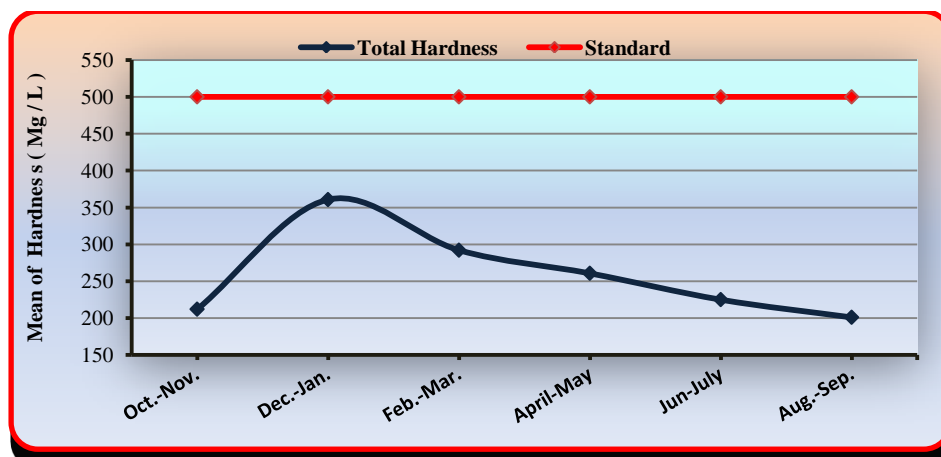


Figure 2-The variations of Total Hardness (TH) values in Al- Hussainia River during study period

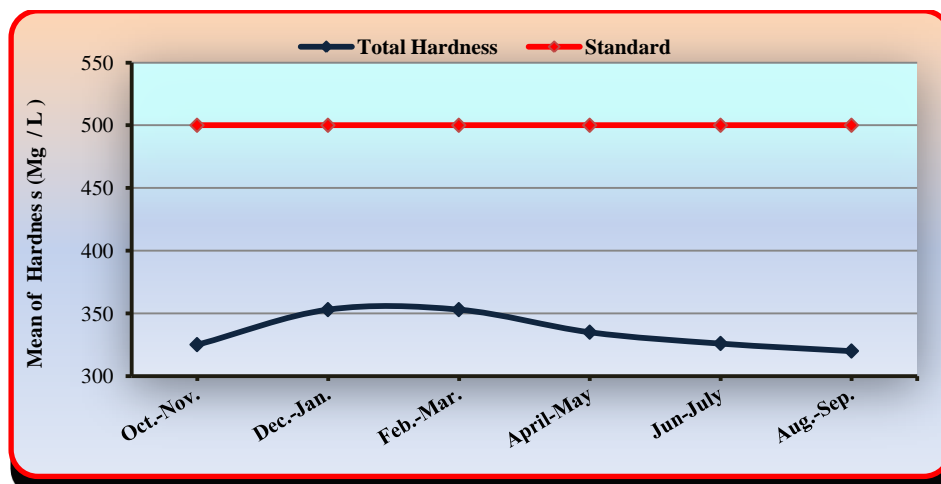


Figure 3: The variations of Total Hardness (TH) values in Central Karbala drinking water treatment station during study period.

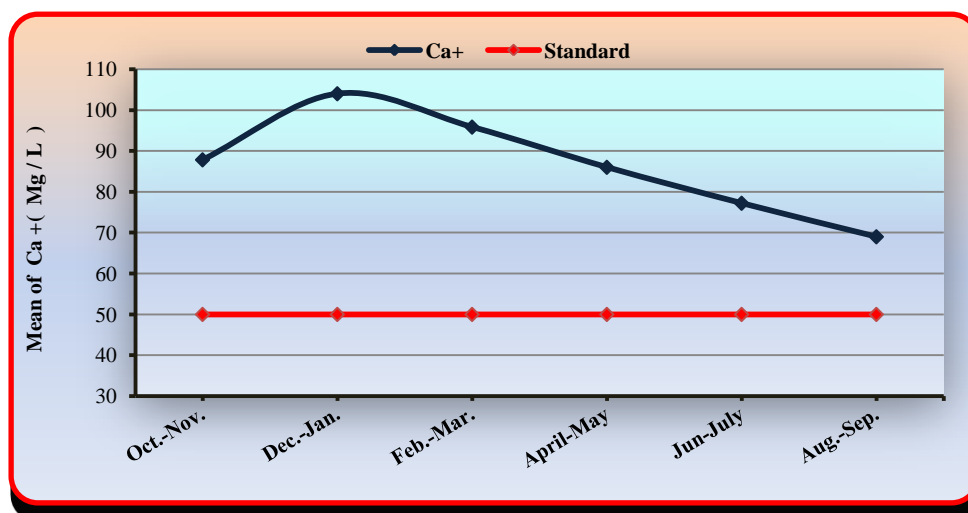
Table 1- Total Hardness Analysis of Variance among Al-Hussainia River, central Karbala drinking water treatment station and Karbala city areas

Analysis of Variance Table					
S.O.V.	D.F	S.S	M.S.S.	F.Cal.	F.table0.05
Treat.	14	226126.9	16151.92	7.314432	1.885
Error	75	165617	2208.226		
Total	89	391743.9			
L.S.D. 0.05 =54.12577					
Location		L.S.D.	Differences between means		
Location	Means	at $\alpha=0.05$	S1	S2	
S2	335.35	54.12577	76.79667		
S1	258.55333				
		Significant Difference at $p \leq 0.05$			
		Non Significant Difference			

Calcium and Magnesium ion

Study results showed that the highest value for Ca^{+2} was 96.8 and 104 mg/L in winter (December-January) 2014 at S1 and S2 respectively, while the lowest value was 69 and 74 mg/L in (August-September) 2014 at S1 and S2 figure.4 and 5. The statistical analysis showed a significant difference among months for Ca^{+2} and a significant difference among stations at ($P < 0.05$) table 2. The positive correlation found with TH, Sulphates (SO_4), Chloride ion (Cl^-), Calcium ion (Ca^{+2}), and Magnesium ion (Mg^{+2}) Ca^{+2} respectively in present study table 2.

The results showed that there is an increase in calcium values during winter this may be because the increase of rain rate that transfers the agricultural wastes to the river because of washing soil, also the decrease of temperature helps in CO_2 decreasing in the water and forming carbonic acid that helps in dissolution the salts of calcium and magnesium [19]. The obtained results of this study near to Al-Fatlawy [11] found that the values of calcium were ranged between 58.5 and 109.3 mg/L and Ahmed [20] found that the values of calcium were ranged between 54 and 185 mg/L.

**Figure 4-**The variations of Calcium Ca^{+2} values in Al- Hussainia River during study period.

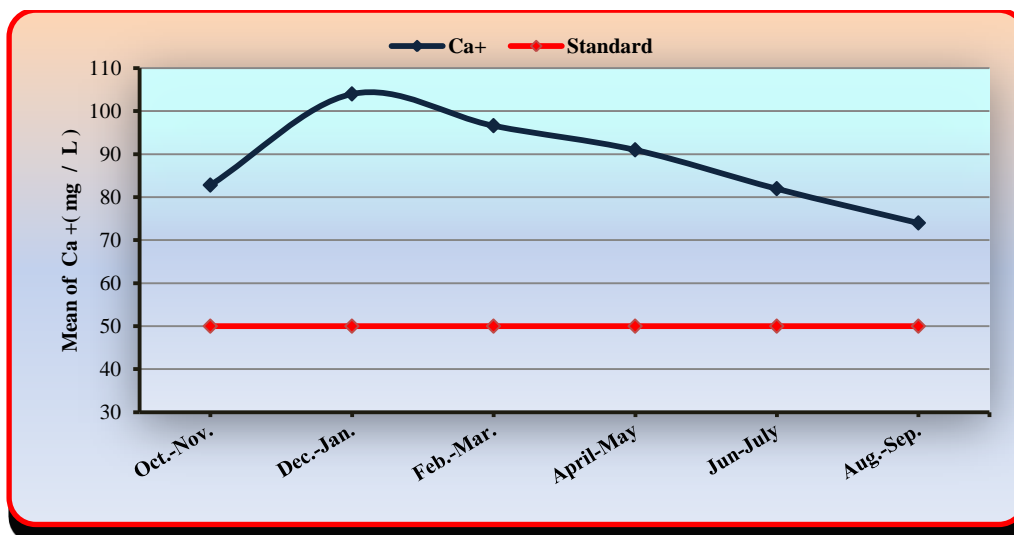


Figure 5-The variations of Calcium Ca²⁺ values in Central Karbala drinking water treatment station during study period.

Table 2- Ca²⁺ Analysis of Variance among Al-Hussainia River, central Karbala drinking water treatment station and Karbala city areas

Analysis of Variance Table					
S.O.V.	D.F	S.S	M.S.S.	F.Cal.	F.table0.05
Treat.	14	10325.86	737.5615	3.444247	1.885
Error	75	16060.73	214.143		
Total	89	26386.59			
L.S.D. 0.05 =16.85521					
Location		L.S.D.		Differences between means	
Location	Means	at α=0.05		S1	S2
S2	87.195667	16.85521		0.550833	
S1	86.644833	16.85521			
L.S.D. Least Significant Difference					
	Significant Difference at p ≤ 0.05				
	Non Significant Difference				

The concentrations of Ca²⁺ in both S1 and S2 were out of the permissible limit for Iraqi standard specification for drinking water 2001 No. (417), and WHO standards (2004) [18], which was 50 mg/L Appendix 2.

The highest value for Mg²⁺ was 42.3 and 44mg/L in winter (December- January) 2014 at S1 and S2, while the lowest value was 25 and 32 mg/L in (August-September) 2014 at S1 and S2 figure 6 and 7. The statistical analysis showed significant differences among months for Mg²⁺ in (P<0.05), and significant differences among stations were observed table 3

Generally, calcium ion was more than magnesium ion concentration at the most of the study period this agree with [21,22], when the carbon dioxide reacts with calcium ion more than its reaction with magnesium ion, so that amount of calcium more than magnesium, that convert to dissolved bicarbonate [23]. This agrees with many studies about Iraqi water quality [24, 25].

The concentrations of Mg²⁺ were within the permissible limit for Iraqi standard specification for drinking water 2001 No. (417), and WHO standards (2004) [18], which was 50 mg/L Appendix 2.

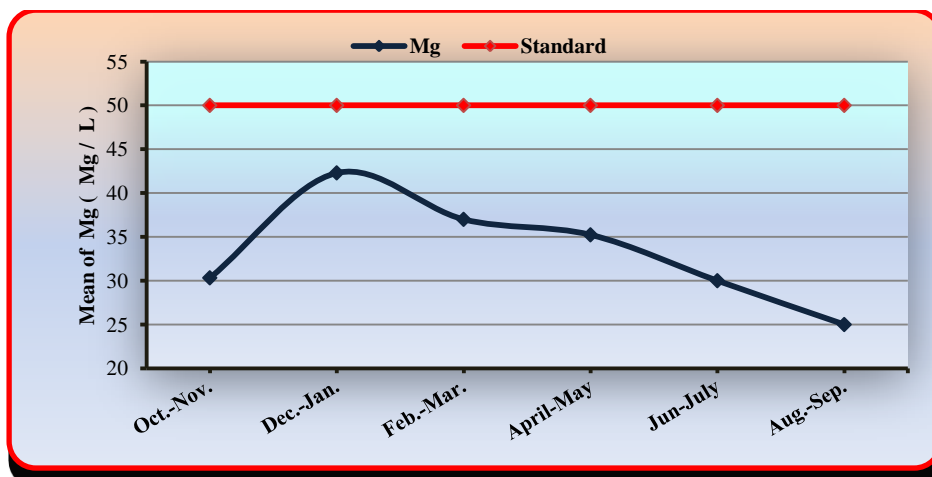


Figure 6-The variations of Magnesium Mg⁺² values in Al- Hussainia River during study period.

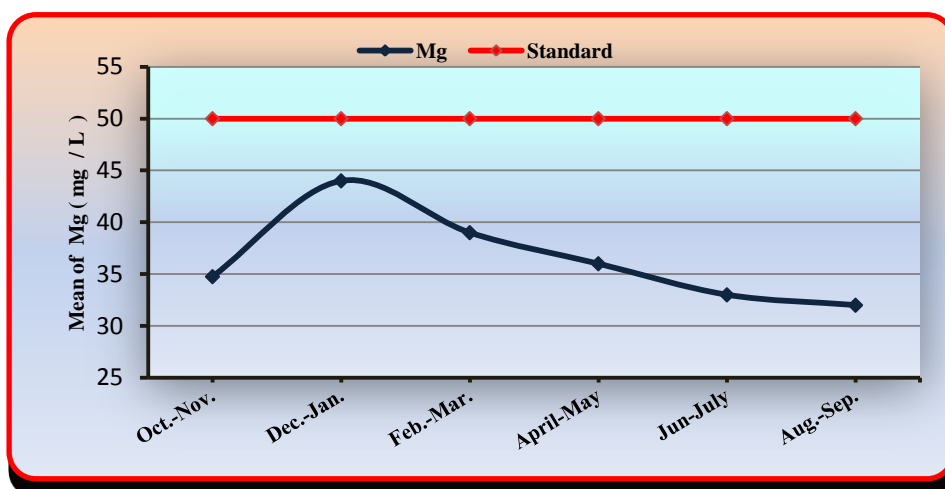


Figure 7-The variations of Magnesium Mg⁺² values in Central Karbala drinking water treatment station during study period

Table 3- Mg⁺² Analysis of Variance among Al-Hussainia River, central Karbala drinking water treatment station and Karbala city areas

Analysis of Variance Table					
S.O.V.	D.F	S.S	M.S.S.	F.Cal.	F.table0.05
Treat.	14	1182.674	84.47673	3.038867	1.885
Error	75	2084.907	27.79876		
Total	89	3267.581			
L.S.D. 0.05 =6.072884					
Location		L.S.D.		Differences between means	
Location	Means	at α=0.05		S1	S2
S2	36.459167	6.072884		3.1485	
S1	33.310667	6.072884			
Significant Difference at p ≤ 0.05					
Non Significant Difference					

Chlorides (Cl⁻)

The results of study showed that the highest value for Cl⁻ was 158.5 and 158.9 mg/L in winter (December- January) 2014 at Station 1 and 2 respectively, while the lowest value was 60 and 89 mg/L in (August-September) 2014 at Station 1 and 2 figure 8 and 9. The statistical analysis showed a significant difference among months for Cl⁻ at (P<0.05), and a significant difference among stations table 4

The increase of Cl^- value in station 1 indicates to pollution by sewage in the waters of Al-Hussainia River due to the discharged untreated sewage from the Karbala city enriched with organic matter in the river.

This phenomenon was proved by [26]. Many researchers reported that rainfall adds chloride directly. It is low in summer as compared to rainy months and occupying the intermediate position in winter [27]. This agrees with the study findings which revealed the highest value of Cl^- in winter, while lowest value in spring and summer.

The concentrations of Cl^- were within the permissible limit by Iraqi standard specification for drinking water 2001 No. (417), which was 200 mg/L, and within WHO standards (2004) [18], which was 250 mg/L Appendix 2.

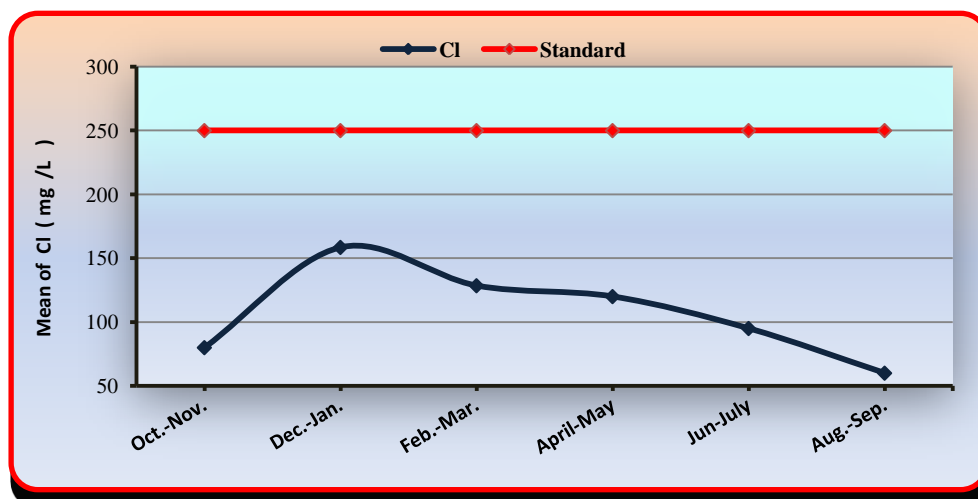


Figure 7: The variations of Chlorides Cl^- values in Al- Hussainia River during study period.

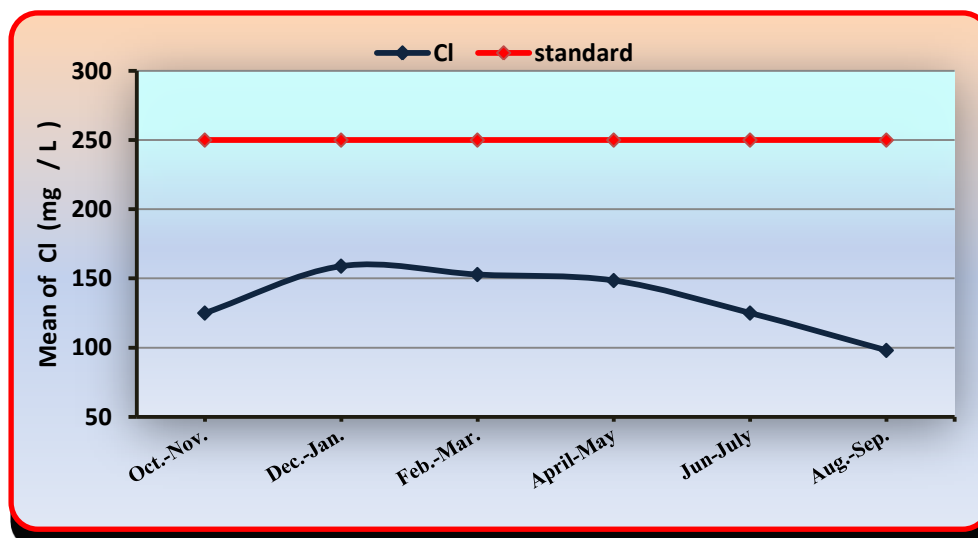


Figure 8-The variations of Chlorides Cl^- values in Central Karbala drinking water treatment station during study period.

Table 4- CI⁻ Analysis of Variance among Al-Hussainia River, central Karbala drinking water treatment station and Karbala city areas

Analysis of Variance Table					
S.O.V.	D.F	S.S	M.S.S.	F.Cal.	F.table0.05
Treat.	14	79694.32	5692.451	11.52313	1.885
Error	75	37050.15	494.002		
Total	89	116744.5			
L.S.D. 0.05 =25.60039					
Location		L.S.D.		Differences between means	
Location	Means	at $\alpha=0.05$		S1	S2
S2	134.70933	25.60039		27.70933	
S1	107				
Significant Difference at $p \leq 0.05$					
Non Significant Difference					

Sulphate (SO₄⁻²)

Al-Hussainia river stations (S1) showed variation in sulphate value. The maximum value was 340 mg/L during winter (December- January) 2014, and the minimum value was 190 mg/L during (August-September) 2014.

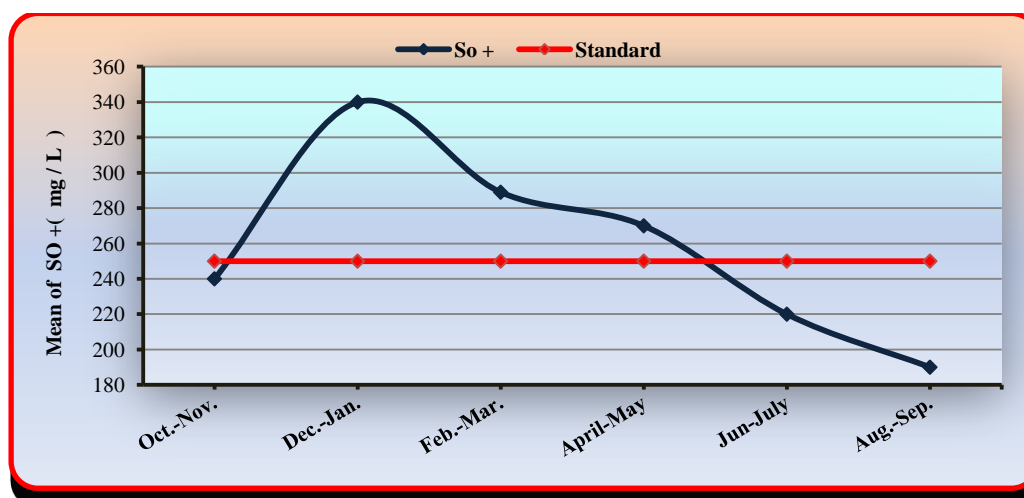
The central Karbala drinking water treatment station (S2), highest SO₄⁻² concentrations during winter (December- January) 2014 was 358 mg/L, and lowest concentration during (August-September) 2014 was 215 mg/L, figure 9 and 10. The statistical analysis showed significant differences among months at ($P<0.05$), but not any significant differences among stations table 5.

Slightly higher concentrations of sulphate were detected in study area in station 1, and this may be due to untreated domestic sewage of the Karbala city.

The increase in sulphate value in winter and decrease in hot months generally due to discharge of the untreated domestic sewage and agricultural runoff. These ions can produce from decompositions of organic matters or using chemical fertilizers in agriculture [28, 29]. Sulphates are formed due to the decomposition of various sulphur containing substances present in water bodies.

The sulphate ions SO₄⁻² occur naturally in most water supplies and hence are present in well waters [7]. The high concentrations of sulphate ions in Iraqi waters are common in southern part of Iraq because of ground water effect [30].

The values obtained for each of the locations in S1 and S2 are exceed the permissible limit for both Iraqi standards for drinking water and WHO standards drinking water (2004) which was 250 mg/L, Appendix 2, except in summer months.

**Figure 9:** The variations of Sulphate (SO₄⁻²) values in Al-Hussainia River during study period

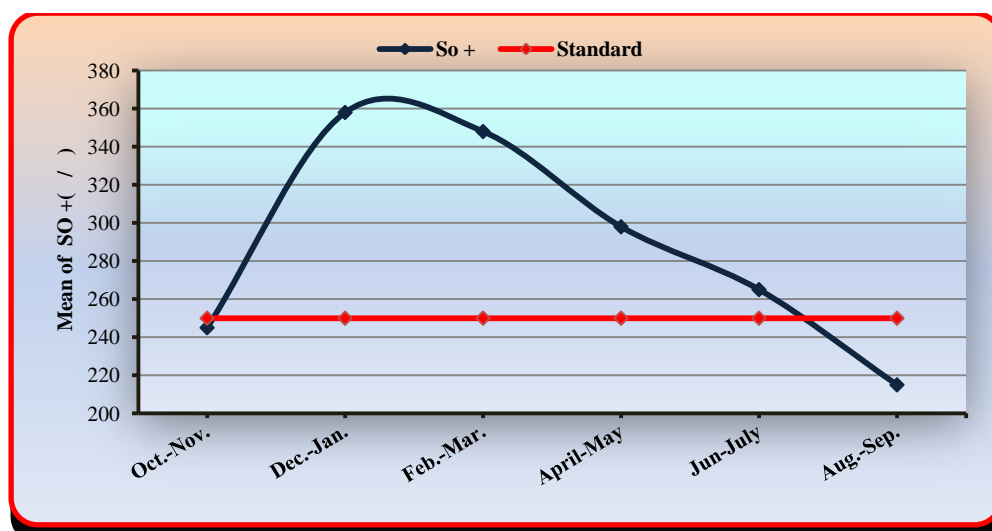


Figure 10: The variations of Sulphate (SO_4^{2-}) values in Central Karbala drinking water treatment station during study period

Table 5- SO_4^{2-} Analysis of Variance among Al-Hussainia River, central Karbala drinking water treatment station and Karbala city areas

Analysis of Variance Table					
S.O.V.	D.F	S.S	M.S.S.	F.Cal.	F.table0.05
Treat.	14	17959.59	1282.828	1.002838	1.885
Error	75	95939.81	1279.197		
Total	89	113899.4			
L.S.D. 0.05 =41.19562					
Location		L.S.D.		Differences between means	
Location	Means	at $\alpha=0.05$		S1	S2
S2	288.16667	41.19562		30	
S1	258.16667	41.19562			
Significant Difference at $p \leq 0.05$					
Non Significant Difference					

Conclusions

1. High concentrations of Total hardness (TH), Sulphates (SO_4^{2-}), Chloride ion (Cl^-), Calcium ion (Ca^{+2}), and Magnesium ion (Mg^{+2}) Ca^{+2} respectively in present study of the Al-Hussainia River in the rainy months.
2. The existence of a positive relationship between the specification and the concentrations of pollutants in the river water and drinking water.
3. Chloride, calcium and sulphate, were out of the Iraqi and the international standards water. While total hardness, magnesium, chloride and concentrated were within Iraqi and international acceptable standards.

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Appendices

Appendix 1- Correlation factor among physical and chemical tests.

	Total Hard.	Ca+	Mg	SO ₄	Cl
Ca ⁺	0.616839				
Mg	0.819815	0.886772			
SO ₄	0.755117	0.921824	0.944703		
Cl	0.750917	0.724591	0.808708	0.811565	
Significant					
Non Significant					

Appendix 2- Iraqi legislation No. (417)-2001 Standard Specification for Drinking water

Material	The Maximum allowable limit (mg/l)
Chloride (Cl)	250
Total Hardness (as CaCO ₃)	500
Sodium	200
T.D.S	1000
Sulphate (SO ₄) ⁻²	250
Calcium	50
Magnesium	50