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Evaluation of Groundwater Hydrochemistry in Altun Kopri Basin, NE Iraq

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Abstract

The study area is located in the northeastern part of Kirkuk Governorate, Iraq, and its goal is to assess the hydrochemical characteristics of groundwater, identify contamination levels and sources, and determine groundwater suitability for drinking. The water quality index (WQI) and heavy metals pollution index (HPI) were used to assess groundwater contamination levels of major elements and heavy metals. The results showed that all groundwater samples were alkaline and weakly mineralized water. The total dissolved solids in the groundwater were less than the maximum accepted limit for palatable water. Groundwater was classified as excellent to good water and does not exceed the critical drinking water value. Chemically, All indices indicate that the groundwater in the study area is suitable for drinking water. Finally, the authors recommend that groundwater needs a biological assessment to make a relevant decision about water suitability for drinking.

Keywords: Groundwater, Water Quality Index, hydrochemistry, Altun Kopri, Iraq

تقييم هيدروكيميائي للمياه الجوفية في حوض التون كوبري، شمال الشرقي العراق

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الخلاصة

منطقة الدراسة تقع في الجزء الشمالي الشرقي من محافظة كركوك، العراق. يهدف البحث الحالي الى تقييم الخصائص الهيدروكيميائي للمياه الجوفية، تحديد مستوى التلوث و مصادره في المياه الحوفية، و تقييم مدى صلاحية المياه الجوفية للشرب. استخدمت مؤشر نوعية المياه و مؤشر تلوث العناصر الثقيلة لتقييم مستويات التلوث المياه الجوفية بالعناصر الرئيسية و العناصر الثقيلة. أظهرت النتائج ان جميع المياه الجوفية هي قلوية. و ان مجموع الاملاح الذائبة في المياه الجوفية اقل من اعلى قيمة مقبولة للمياه الشرب. و كذلك صنفت المياه الجوفية انه مياه ممتازة او جيدة جداً و لم تتجاوز القيمة الحرجة للمياه الشرب. كل المؤشرات تدل ان المياه الجوفية في منطقة الدراسة صالحة للشرب. يوصي الباحثين ان المياه الجوفية في منطقة الدراسة يحتاج الى بايولوجي ايضاً من اجل اتخاذ قرار مناسب حول صلاحية المياه لاغراض الشرب.

1. Introduction

Hydrochemistry is an essential part of hydrogeological studies. In the last decades, the

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results of water scarcity and the absence of surface water have increased water demand for different purposes. Groundwater plays a key role in supplying life requirements for different purposes such as drinking water, irrigation, and industrial, so assessing groundwater quality is more important than quantity. All groundwater contains minerals in solution; the type and concentration depend on the surface and subsurface environment, the groundwater movement rate, and the groundwater source. [1-4].

Anthropogenic activities have seriously affected the biogeochemical cycles of trace metals and have caused. Precipitation is relatively free of minerals until it comes in contact with various constituents in the soil. As a result of the solvent power of water, minerals are dissolved and carried into solution when the water moves through the aquifer. The cation and anion concentration depends upon the solubility of the minerals present in the formation, the time duration of water in contact with the rocks, and the amount of dissolved CO_2 in the water. Water pollution can be defined as excessive levels of chemical, physical, biological, and radiological substances capable of causing harmful effects on living organisms [5-8]. One of the most serious environmental issues today is heavy metal pollution in water because these metals are non-biodegradable and are considered the most sustainable pollutants. They can survive in the aquatic environment for a long time and must be monitored on a regular basis [9-11]. Some heavy metals are necessary for life and play an important role in the functioning of organisms; however, different organisms require different amounts of metals, which become toxic at higher concentrations [12]. Also, some metals, such as mercury, lead, and arsenic, are harmful to humans and can be toxic even at low levels of exposure [13].

The hydrochemistry study emphasizes the assessment of water quality by analysis the water samples for major elements (Ca, Mg, Na, K, HCO_3, SO_4, and Cl), minor elements (PO_4 and NO_3), and heavy metals (AS, Pb, Cd, Cr, Ni, and Zn), also measurement of other some physiochemical properties (pH, EC, TDS, Temperature, Turbidity, TH, SAR, and NA%). Then, compare analyzed concentrations with standard values of physiochemical properties for suitability assessment of drinking water, irrigation, livestock, industrial, and other purposes [14-15]. However, the previous study [16] studied the hydraulic characteristics of the aquifers, classified the soil type, and assessed the quality of groundwater and Lesser Zab water. Also [17] studied the vulnerability assessment and wellhead protection zones of the Alton Kopri basin, where she divided the area into three zones according to their contaminants vulnerability and designed a model for initiating protection zones around the wells. The main reasons for this study are population extension, increased water demand, increased agricultural and industrial activities, and the residents' complete dependence on groundwater for different purposes. The current research aims to evaluate hydrochemical characteristics, identify the contamination level and its sources in the groundwater, and assess groundwater suitability for a drink.

2. Materials and Methods

2.1. Study Area

The study area is located in the northeastern part of Kirkuk, Iraq. Apart from about 6.5 km to the north of Kirkuk City, it covers about 826.4 km^2 (**Figure 1).** Tectonically, the study area is located in the Outer Platform of the Arabian Plate within the western Zagros Fold Thrust Belt in the Low Folded Zone [18]. It looks like an asymmetric syncline, with a gentle slope limb from east and southeast and a steep slope from west and northwest. The exposed formations in the study area extend from the oldest (Pliocene) up to the youngest (Holocene): 1) Bai-Hassan Formation and 2) Quaternary Deposits [19, 20]. Hydrogeologically, The study area is situated in the foothill aquifer system within the Chamchamal-Klar sub-system [20].

The two aquifers exist in the study area; the upper unconfined aquifer represents the quaternary deposits in the basin's cente, consisting of gravel, sand, silt, and clay. Meanwhile, clay layers interposed between the lower semi-confined aquifer of the Bai-Hassan Formation, composed of gravel, sand, and conglomerate.

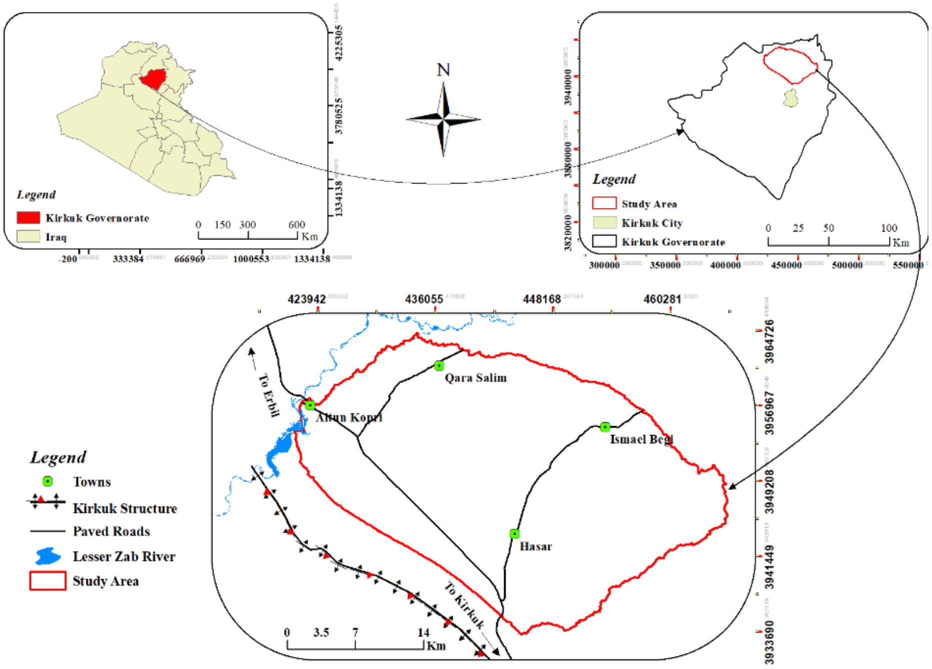

Figure 1: Location map of the study area.

2.2 Water Quality Index (WQI)

The assessment of groundwater quality is frequently required because the chemical parameters are spatially and time-changeable. WQI is the best index of a single value that expresses the composite effects of the most important physiochemical parameters (i.e. pH, EC, TDS, TH, Turbidity, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, SO$_4^{=}$, Cl^{-}, NO$_3^{-}$, and PO$_4^{\equiv}$) on the overall water quality [21-26]. Therefore, the water quality index is an important and widely used indicator for evaluating groundwater quality, especially its suitability for drinking purposes [27-34]. The current index is computed as follows [35] **Table 1**:

$$W_i = \frac{K}{S_i} \tag{1}$$

$$K = \frac{1}{\sum_{i=1}^{n} \frac{1}{S_i}} \tag{2}$$

$$Q_i = \left[\frac{V(-)V_i}{S_i - V_i}\right] * 100 \tag{3}$$

$$WQI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{4}$$

Table 1: Classification of Water Quality Index (WQI) [35].

WQI	*Water Quality*
< 25	Excellent
26-50	Good
51-75	Poor
76-100	Very poor
>100	Unsuitable for drinking purposes

Where: W_i is the unit weightage for the ith parameter, K is the proportionality constant, S_i is the standard value for *i*th parameter **Table 2**, Q_i is the sub-index of the *i*th parameter, V and V_i are the observed value and the ideal value (ideal values are equal to zero, except V_i for pH is 7) for *i*th parameters Error! Reference source not found. The negative sign (-) indicates the numerical difference between two values, ignoring the algebraic sign.

Table 2: Standard and weightage values of the physiochemical parameters used to compute the WQI of groundwater samples [14].

Parameter	S_i	$1/S_i$	K	W_i
pH	8.5	0.118	0.3376	0.04
TH	425	0.002		0.001
TDS	1000	0.001		0.0003
Turbidity	5	0.2		0.068
Ca^{++}	100	0.01		0.003
Mg^{++}	70	0.014		0.005
Na^{+}	200	0.005		0.002
K^{+}	12	0.083		0.028
$SO_4^{=}$	250	0.004		0.001
Cl^{-}	250	0.004		0.001
NO_3^{-}	50	0.02		0.007
$PO_4^{\equiv}$	0.4	2.5		0.844

Table 3: Major and Minor elements concentration in groundwater samples (all in ppm unit).

Name	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	$SO_4^{=}$	Cl^{-}	$PO_4^{\equiv}$	NO_3^{-}
GW1	28	34	15	2.9	191	36.6	21.3	0.08	12.57
GW2	32	36	23	3.8	215	45.1	25.1	0.13	34.5
GW3	19	33	12	2	168	38.4	20.3	0.09	25.6
GW4	22	43	15	3.1	210	33.2	23.7	0.1	44.7
GW5	24	31	14	2.8	169	41.1	21.5	0.11	30.8
GW6	28	33	17	3.3	200	42.4	17.3	0.1	35
GW7	30	37	15	3.6	217	36.5	21.1	0.09	31
GW8	25	44	13	2.4	223	39.9	22.5	0.11	17.78
GW9	42	32	18	4.1	208	41.6	26.2	0.1	31.12
GW10	26	40	23	2.5	211	40.5	28.3	0.12	18.16
GW11	36.1	27	28.5	6.4	195	45.4	29.8	0.1	24.3
GW12	25	23	33	4.1	192	38.5	26.3	0.09	29.75
GW13	32	35.5	24	9	202	51.2	32.9	0.09	28.6
GW14	37.9	32	27	4.1	211	48	25.6	0.12	23.8
GW15	31	27.5	19	5.2	172	32.4	29.5	0.11	15.3
GW16	24	38	21	4.5	217	34.2	21.3	0.09	20.67
GW17	36.5	29	23	4.1	192	48.2	26.5	0.11	38
GW18	35	25	21	3.6	210	35.6	15.9	0.1	21.77
GW19	38	30	25	3.8	199	44.1	27.2	0.08	33.1
GW20	33	28.3	18	2.2	189	38.1	22.3	0.13	22.56
WHO, 2021	100	70	200	12	-	250	250	0.4	50
U.S. EPA, 2017	-	-	-	-	-	250	250	-	10
Max	42	44	33	9	223	51.2	32.9	0.13	44.7
Min	19	25	12	2	168	32.4	15.9	0.08	12.57
Ave.	30	33	20	4	200	40.8	24.2	0.1	26.95

2.3 Heavy Metal Pollution Index (HPI)

Heavy metals are a type of trace element with a specific gravity over five and an atomic mass greater than sodium. These metals are very toxic, harmful, and hazardous [32, 36, 37]. The main sources of contaminants are: 1) natural sources (e.g. deposition of atmospheric salts, leaching of soil, lithogenic source, and mixing of two groundwater with different chemical characteristics), 2) anthropogenic sources (e.g. industrialization, urbanization, and agricultural activities) [38]. Heavy metals are the most continual pollutants in aquatic environments because these metals are nondegradable and can remain in the water for a long time. They should be monitored periodically [9, 10]. Heavy metals can accumulate in the human body within vital organs such as the kidneys, liver, and bones, so they cause non-carcinogenic adverse impacts and carcinogenic impacts [39].

The Heavy Metal Pollution Index (HPI) is an effective index for evaluating temporal and spatial changes in water quality; it refers to the extent to which groundwater is polluted with heavy metals and provides an overview of these metals' impacts on water quality [40]. Thus, the heavy metal pollution index (HPI) was calculated as follows [41, 42]:

$$W_i = \frac{K}{S_i} \tag{5}$$

$$K = \frac{1}{\sum_{i=1}^{n} \frac{1}{S_i}} \tag{6}$$

$$Q_i = \sum_{n=1}^{n} \frac{(M_i(-)I_i)}{(S_i - I_i)} \tag{7}$$

$$PI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{8}$$

Where: W_i is the unit weightage for *i*th heavy metal, K is the proportionality constant, n is the number of heavy metals considered, Q_i is the sub-index, M_i is the monitored value, I_i is the ideal value, and S_i is the standard value of *i*th heavy metal (**Tables 4 and 5**). The sign (-) indicates the numerical difference between two values, ignoring the algebraic sign. So, the critical value of *HPI* is (100) proposed for drinking water [41-43].

Table 4: Standard and weightage values of heavy metals used to compute the HPI of groundwater samples [14].

Parameter	S_i	*1/*S_i	*K*	W_i
As	10	0.1	2.1245	0.21245
Pb	10	0.1		0.21245
Cd	5	0.2		0.424899
Cr	50	0.0005		0.001062
Cu	2000	0.02		0.04249
Ni	20	0.05		0.106225
Zn	5000	0.0002		0.000425
total		0.4707		1

Table 5: Heavy metals concentrations in the groundwater samples (all in ppb unit).

Name	*As*	*Pb*	*Cd*	*Cr*	*Cu*	*Ni*	*Zn*
GW1	1.2	7	0.61	7.2	4.4	0.2	3971
GW2	0.9	7.3	0.67	5.3	1.7	0.5	4159
GW3	0.7	9.4	0.73	8.4	1.2	0.3	2911
GW4	0.9	9	0.77	8	18	0.2	2487
GW5	1	6.5	0.82	6.1	13.1	0.9	3179
GW6	0.8	5.4	0.66	6.4	2	0.8	1960
GW7	0.8	6.1	0.59	8	0.8	0.67	3570
GW8	0.6	8.9	0.74	7.5	1.6	0.4	2522
GW9	1.2	6.3	0.81	7.5	2.4	0.3	2800
GW10	0.6	6.7	0.85	6.1	0.9	0.6	2672
GW11	0.8	8	0.93	7.3	0.6	0.4	1833
GW12	0.4	9.1	1.1	9.2	1.8	0.2	3801
GW13	0.7	7.7	1.7	4	2.4	0.4	2361
GW14	0.6	6.5	0.74	1.1	0.8	0.5	2722
GW15	0.7	7.2	0.95	1.7	10.1	0.5	4563
GW16	0.8	6.5	1.3	3.4	10.1	0.8	4408
GW17	0.4	3.8	0.62	2	0.9	0.7	4673
GW18	0.6	8.5	0.45	2.5	4.5	1.6	2891
GW19	0.7	9.1	0.57	1.1	1.1	0.4	2753
GW20	0.7	8.6	0.55	2.1	8	0.8	2172
WHO, 2021	10	10	5	50	2000	20	5000
U.S. EPA, 2017	10	15	5	100	1300	-	-
Max	1.2	9.4	1.7	9.2	18	1.6	2971
Min	0.4	3.8	0.45	1.1	0.6	0.2	833
Ave.	0.7	7.4	0.8	5.1	4.3	0.6	1707.6

3. Results and Discussions

3.1. Physiochemical Properties

The results of analysis and measurements of physiochemical parameters in the groundwater samples GW1 - GW20 are exhibited in **Table 6**.

Concentration of Hydrogen Ion (pH)

pH is the negative logarithm with base 10 of the hydrogen ion concentration [44]. It is considered one of the essential chemical parameters in the assessment of groundwater quality [14]. According to [1], pH is the best indicator for alkalinity and acidity, where pH > 7 is alkaline, pH < 7 is acidic, and pH = 7 is neutral. The water or solution with pH = 4 tends to dissolve trace elements and other substances that can be harmful and toxic to humans, animals, and plants, and pH number affects the physical, chemical and biological processes [45]. Also, it influences and controls heavy metal mobility [2]. The in-situ measured pH values refer to all groundwater samples as alkaline water and within the allowable range for drinking purposes **Table 6**.

Table 6: Physiochemical characteristics, SAR, and Na% in the groundwater samples.

Name	*pH*	*EC µs/cm*	*TDS ppm*	*Temp. ℃*	*Turbidity NTU*	*TH ppm*	*SAR*	*Na%*
GW1	7.79	419	274	19	0.63	210	2.7	13.3
GW2	7.44	520	340	20	0.7	228	3.9	17.7
GW3	7.76	335	219	21	1.16	183	2.4	12.3
GW4	7.8	485	317	19.4	1.65	232	2.6	12.2
GW5	7.64	406	266	21	1.42	187	2.7	13.7
GW6	7.81	457	299	21	1	206	3.1	15.0
GW7	7.63	477	312	20	0.8	227	2.6	12.3
GW8	7.92	395	258	22	0.91	243	2.2	10.3
GW9	8.08	701	458	23	1.74	237	3.0	13.9
GW10	7.91	397	260	21.5	1.32	230	4.0	17.7
GW11	7.93	857	560	23	2.1	203	5.1	22.7
GW12	7.88	610	399	21.8	1.32	165	6.6	29.6
GW13	7.69	1210	791	22	1.81	226	4.1	18.0
GW14	7.92	546	357	21.8	1.24	226	4.6	20.2
GW15	7.86	418	273	22.8	0.67	191	3.5	17.3
GW16	7.91	284	186	21	1.09	216	3.8	17.1
GW17	7.89	607	397	21.5	1.09	210	4	18.8
GW18	7.79	640	419	21	0.58	190	3.8	19.0
GW19	7.66	584	382	23	0.74	218	4.3	19.6
GW20	8.28	369	241	23	0.77	199	3.3	16.3
WHO, 2021	6.5-8.5	-	1000	-	5	425	-	-
U.S. EPA, 2017	6.5-8.5	-	500	-	-	-	-	-
Max	8.28	1210	791	23	2.1	243	6.6	29.6
Min	7.44	284	186	19	0.58	165	2.2	10.3
Ave.	7.82	535.9	350.4	21.4	1.14	211.4	3.6	16.9

Electrical Conductivity (EC)

Electrical conductivity is defined as the ability of electrical current at room temperature (25℃) and expressed by a unit of micro-siemens per centimeter (µS/ cm), its water temperature and salts concentrations dependent [1, 47, 48]. Electrical conductivity is considered an indirect index of water contamination and salinity; groundwater with high EC indicates highly mineralized groundwater [49]. The electrical conductivity of groundwater samples ranged between (284 – 1210) µS/ cm with an average value (535.9 µS/ cm) (**Table 6)**. According to EC values, the groundwater samples were classified as very weakly mineralized water, except GW13 was classified as weakly mineralized water (**Table 7)** [50].

Table 7: Classification of water depending on the electrical conductivity [50].

EC (µS/cm)	*Water Mineralization*
< 1000	Very weakly mineralized water
1000 – 2000	Weakly mineralized water
2000 – 4000	Slightly mineralized water
4000 - 6000	Moderately mineralized water
6000 - 10000	Highly mineralized water
> 10000	Excessively mineralized water

Total Dissolved Solids (TDS)

Total dissolved solids defined by [3] is the total amount of solids that remain after evaporating the water sample to dryness. The TDS is calculated by using the following equation [47]:

$$TDS_{\ (ppm)} = 0.64 \times EC_{\ (^{\mu S}/_{cm})} \qquad \textbf{(9)}$$

The maximum, minimum, and average values of TDS were (971, 186, and 350.4) ppm, respectively. According to [14], TDS values of all groundwater samples did not exceed the acceptable limit, while according to [15], all groundwater samples have TDS less than the maximum permissible limits, except GW13 and GW11 Exceeded the same limit (**Table 6)**. According to water classification by [51-53], all groundwater samples are classified as freshwater **Table 8**.

Table 8: Classification of water depending on the TDS (ppm) content.

Water Class	*[52]*	*[53]*	*[51]*
Freshwater	0 - 1000	0 - 1000	< 1000
Slightly Brackish water	-	1000 - 3000	-
Brackish water	1000 - 10000	3000 - 10000	1000 - 20000
Salty water	10000 – 100000	10000 - 100000	-
Saline water	-	-	35000
Brine water	100000	> 100000	> 35000

Total Hardness

The water hardness results from the most abundant divalent cations (Calcium and Magnesium) in the water [1]. In the current study, the total hardness in groundwater samples was determined by using the following equation [1]:

$$TH_{(ppm)} = 2.5\ Ca^{++}_{(ppm)} + 4.1\ Mg^{++}_{(ppm)} \qquad \textbf{(1)}$$

The results of TH are presented in **Table 6**. The value of all groundwater samples was less than the acceptable limit adopted by [14] for drinking water. Also, according to [1], all samples classified as hard water **Table 9**.

Table 9: Classification of water according to TH value [1].

TH (ppm)	*Water quality*
0 – 75	Soft
75 – 150	Moderate hard
150 - 300	Hard
> 300	Very hard

Turbidity

Turbidity is defined as measurements of water cloudiness caused by the presence of Chemical particles (e.g. manganese and Iron), Organic particles, and suspended particles (e.g. clay and silt). It is expressed by the nephelometric turbidity unit (NTU). The highly turbid water reduces the light passing through the water and is unsafe to drink [14]. The turbidity in all groundwater samples did not exceed the standard value recommended by [14-15] (**Table 6).**

Temperature of Groundwater

Temperature is considered an important parameter in water [6]. Cold water is more palatable and holds dissolved oxygen than warm water, while warm water increases the rate of chemical reactions and its relevant environment for the growth of microorganisms [14]. The temperature of groundwater samples ranged between (19°C – 23°C) with average value (21.4°C) **Table 6**.

3.2. Water Quality Index (WQI)

The water quality index (WQI) of the groundwater samples is listed in **Table 10**, and the spatial distribution of WQI is shown in **Figure 2**. Adopted to WQI, the groundwater samples GW1, GW3, GW7, GW12, GW16, and GW19 were classified as excellent water, while the other samples as good water.

Table 10: Water quality of groundwater samples according to WQI.

Name	*WQI*	*Water quality*
GW1	21.0	Excellent
GW2	31.3	Good
GW3	23.7	Excellent
GW4	27.2	Good
GW5	28.2	Good
GW6	26.2	Good
GW7	23.4	Excellent
GW8	28.1	Good
GW9	28.1	Good
GW10	30.7	Good
GW11	28.6	Good
GW12	24.8	Excellent
GW13	26.2	Good
GW14	31.1	Good
GW15	28.1	Good
GW16	24.6	Excellent
GW17	28.9	Good
GW18	25.4	Good
GW19	21.3	Excellent
GW20	33.0	Good

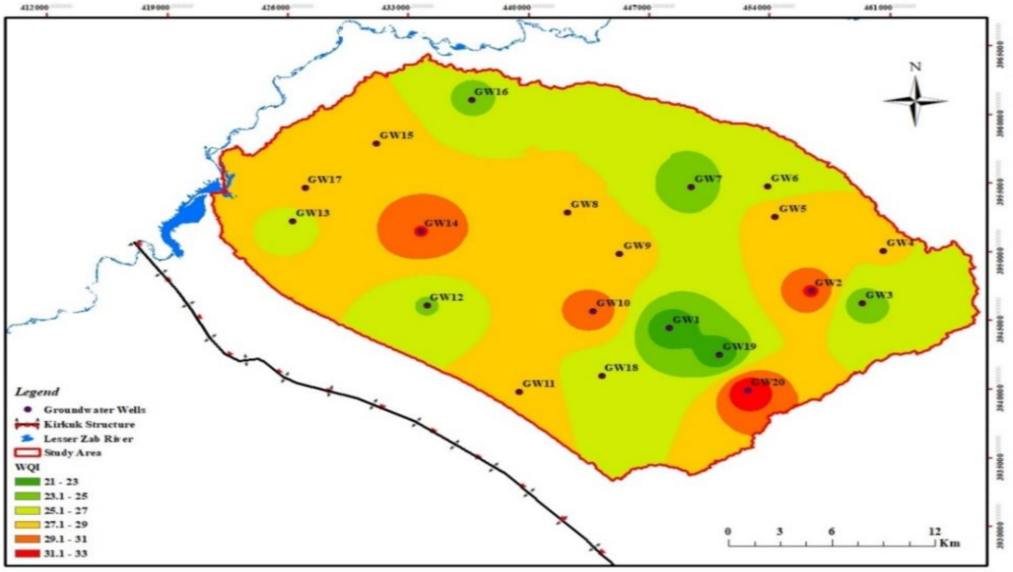

Figure 2: spatial distribution of WQI in the groundwater of study area.

3.3 Heavy Metals Pollution Index (HPI)

Table 11 lists the heavy metal pollution index (HPI) results from groundwater samples, and Figure 3 depicts their spatial distribution. According to [41-42], all groundwater samples had HPI values that did not exceed the critical value for drinking water.

Table 11: Heavy Metal Pollution Index (HPI) of groundwater samples.

Name	*HPI*	*Status*
GW1	23.4	Less than the critical value
GW2	23.9	Less than the critical value
GW3	28.6	Less than the critical value
GW4	28.4	Less than the critical value
GW5	23.9	Less than the critical value
GW6	19.8	Less than the critical value
GW7	20.7	Less than the critical value
GW8	27.3	Less than the critical value
GW9	23.6	Less than the critical value
GW10	23.6	Less than the critical value
GW11	27.4	Less than the critical value
GW12	30.4	Less than the critical value
GW13	32.9	Less than the critical value
GW14	21.7	Less than the critical value
GW15	25.3	Less than the critical value
GW16	27.3	Less than the critical value
GW17	14.8	Less than the critical value
GW18	24.2	Less than the critical value
GW19	26.0	Less than the critical value
GW20	25.0	Less than the critical value

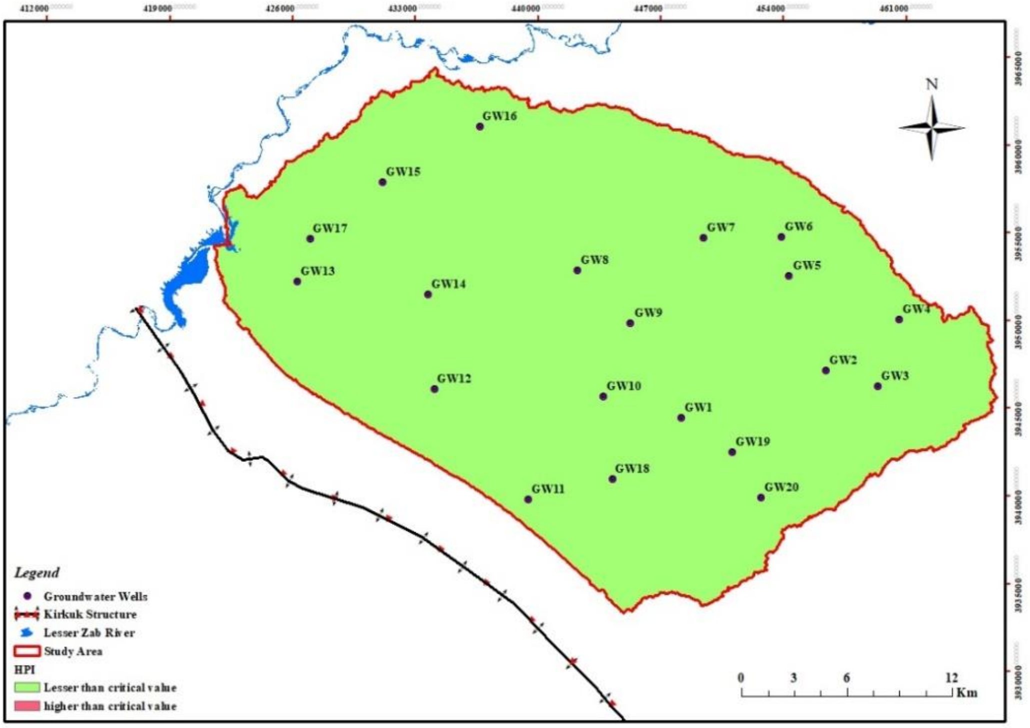

Figure 3: Spatial distribution of HPI in the groundwater of the study area.

Finally, the physiochemical parameters result of groundwater samples are not exceeded the maximum allowable values, as well as the water quality index and heavy metals pollution index indicated that the groundwater in the study area was excellent to good water type. This can be attributed to there are no directly influenced point sources of pollutant in the study area. Also the agricultural and industrial activity are specific, using relevant amounts of fertilizers and pesticides. Furthermore, the farmers focus more on poultry and livestock.

5. Conclusion

The groundwater studied is alkaline of weakly mineralized to very weakly mineralized with TDS less than the admissible limit for drinking water. It is classified as not turbid and fresh water. The water quality index and heavy metal pollution index idicates an excellent and good water, not exceeding the critical value for drinking water. Overall. measurements of parameters and calculation of indices indicate the groundwater in the study area is suitable for drinking.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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