



Hydrochemistry of Groundwater in Dibdibba Aquifer Between Karbala and Najaf, Central Iraq

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ABSTRACT

Thirty-seven water samples are collected from the study area between Karbala and Najaf between longitudes (43°90′-44°25′) and latitudes (31°95′-32°40′) to study the physicochemical properties including concentrations of the major and minor ions and heavy metals. The electrical conductivity range between (2670-13270 μ/cm), total dissolved solids (1709-8489 ppm), calcium (188-798 ppm), magnesium (81-563 ppm), potassium (3-128 ppm), sodium (235-1200 ppm), chloride (355-1710 ppm), sulphate (582-2740 ppm), bicarbonate (114-1358 ppm), nitrates (0.2-2.1 ppm), the concentration of iron, lead, and cobalt are less than (0.05 ppm), manganese (0.05-0.23 ppm), copper (0.143-0.157 ppm), and nickel (0-0.21 ppm). The hydrochemical variables show that salinity concentrations and the major ions increase in the direction of groundwater flow. The water type in the study area is sulphate. The groundwater is polluted with heavy metals in some places of the study area, as it is higher than the permissible standard limits, especially for (Mn, Ni, Pb). As for the evaluation of groundwater in the study area for human drinking purposes, it is found that it is not suitable in most of the wells. With regard to its use for animals, it is suitable for livestock and unsuitable for poultry. Indicators (SAR, Na%, PI, KI) are used to evaluate water for irrigation purposes and it is found to be good.

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هيدروكيميائية المياه الجوفية في خزان دبدبة الجوفي بين كربلاء والنجف، وسط العراق

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الملخص

جمعت سبعة وثلاثون عينة ماء من منطقة الدراسة الواقعة بين كربلاء والنجف بين خطي طول (43 ° 90' - 44 ° 25') وخطي عرض (31 ° 95' - 32 ° 40') لدراسة الخصائص الفيزيوكيميائية وتركيز الأيونات الرئيسية والأيونات الثانوية والمعادن الثقيلة. تراوحت التوصيلية الكهربائية بين (13270-2670 μ/cm)، المواد الصلبة الذائبة الكلية (563-81 ppm)، البوتاسيوم (3-128 ppm)، الصوديوم (235-1200 ppm)، كلوريد (355-1710 ppm)، كبريتات (2740-582 ppm)، بيكربونات (114-1358 ppm)، نترات (0.2-2.1 ppm)، تراكيز الحديد والرصاص والكوبلت كانت أقل من (50 ppb)، والمنغنيز (50 - 230 ppb)، والنحاس (143 - 157 ppb)، والنيكل (0-210 ppb). أظهرت المتغيرات الهيدروكيميائية أن تراكيز الملوحة والأيونات الرئيسية تزداد في اتجاه جريان المياه الجوفية، كما استنتج ان المياه الجوفية ملوثة في بعض الأماكن من منطقة الدراسة بالمعادن الثقيلة حيث كانت تراكيزها اعلى من الحدود المسموح فيها مقارنة مع المواصفات القياسية لاستعمالات المياه حسب منظمة الأمم المتحدة والمواصفات القياسية العراقية خصوصا تركيز ايونات (Pb، Ni، Mn). قيمت المياه الجوفية في منطقة الدراسة لأغراض شرب الانسان من خلال مؤشر جودة المياه ووجدت أنها غير مناسبة في معظم الآبار، أما بالنسبة لشرب الحيوان فهو مناسب للماشية وغير مناسب للدواجن، واستخدمت مؤشرات (SAR، Na، PI، KI) لتقييم المياه لأغراض الري ووجدت أنها جيدة حسب هذه المؤشرات في جميع الآبار لمنطقة الدراسة.

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Introduction

The groundwater contains variable concentrations of dissolved chemical elements as well as organic components. That may have negative or positive effects on the water quality for various uses. Water is a solvent dissolving mineral from the rocks which it comes in contact with.

Groundwater investment decisions concentrate frequently on the quantitative side, but the qualitative side is critical since it affects its suitability for various uses (Tood, 2007) and it is also affected by geological layers more than surface water, so it contains a variety of total dissolved substances (Zoran and Adrian, 2008). Groundwater quality means determining special criteria for assessing water's physical, chemical, and biological properties. The most common of these criteria is the quality of drinking water for humans and animals (Nah et al., 2017). There are many previous hydrochemical studies conducted on the current Dibdibba plateau in Karbala and Najaf. Al-Ghanimy (2018) assessed the hydrogeology of the Karbala-Najaf Plateau in Iraq, and the groundwater quality using chemical analyses and physical

properties of the aquifers at Dibdibba and Dammam. His findings revealed that the groundwater TDS and EC values increased in accordance with the groundwater's flow direction from west to east. According to TDS values, groundwater samples taken from the Dibdibba aquifer in the research area are classed as brackish type water based on classification systems.

By evaluating the physical, hydraulic, and hydrochemical characteristics of the Dibdibba and Dammam aquifers, Al-Sudani (2018) explained good sites for groundwater exploitation in the Dibdibba aquifer.

However, due to the significant population growth as well as the investment of groundwater for significant agricultural and industrial projects in the study area over the past few years, the study area needs to be periodically monitored and complementary studies in terms of hydrochemical developments and the suitability of water for life uses. The purpose of the study is evaluation and interpretation of the physicochemical and hydro-chemical properties of the Dibdibba aquifer in the study area.

Materials and Methods

Location of the study area

The study area includes (1114) km² between the Governorates of Karbala at north and Najaf at south, between longitudes (43°90′-44°25′) and latitudes (31°95′-32°40′) (Fig. 1).

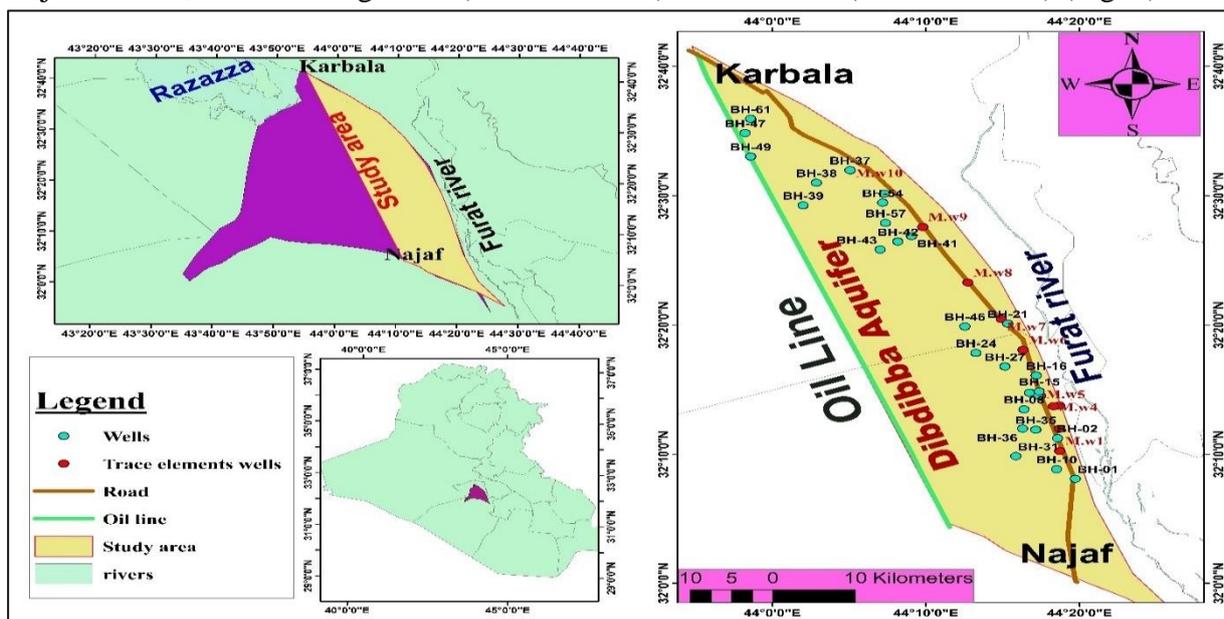


Fig.1. Location map of the study area.

Geological and hydrogeological description

The geological formation in the study area within Tertiary and Quaternary from the middle Eocene to Pleistocene, and they are from oldest to youngest (Dammam, Euphrates, Fatha, Injana, Dibdibba), whose deposits are of the Quaternary Era (Jasim and Goff, 2006) (Fig. 2). The study area is located hydro geologically within the Mesopotamia and western desert zone, within the main aquifers of groundwater of the Miocene carbonate and Mesopotamian Plain silt (Jasim and Goff, 2006).

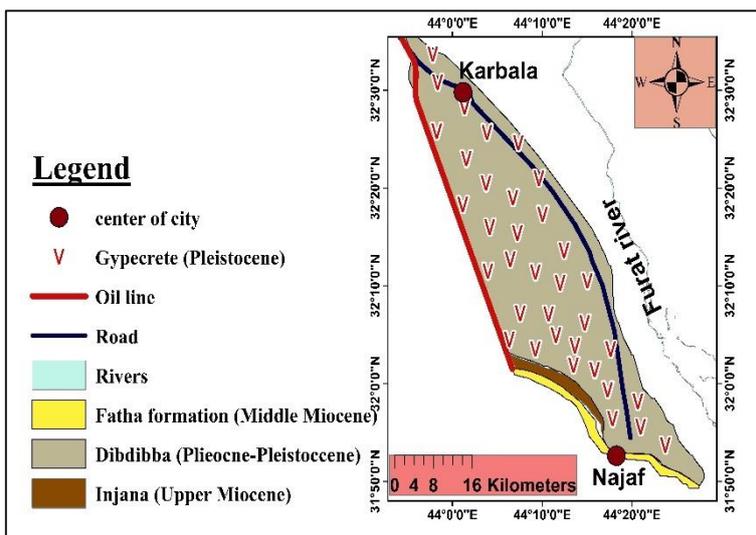


Fig.2. Geological map of the study area from Iraqi geological map, 1996

Samples collection and analysis

Wells are selected from different locations between Karbala and Najaf in the study area for sampling. The samples are filtered with 45-micron paper and acidified with nitric acid. The samples are analyzed by the central laboratory of the University of Tikrit and the laboratory of the General Authority for Ground Water in Baghdad according to the analytical methods and to the references listed in Table (1).

Table 1: summary of chemical analysis techniques according to standard methods

Parameter	unit	Method of analysis	reference
Na ⁺ ,K ⁺	ppm	Flame photometer	APHA (2012)
Ca ⁺ ,Mg ⁺²	ppm	Titration with Ethylene Diamine Tetracetic Acid, 0.2	APHA (2012)
Cl ⁻	ppm	Titration with AgNO ₃ – chromate indicator	Lind (1979)
SO ₄ ⁻²	ppm	Technecon in Ultra Violet Spectro Photometer, (U.V)	APHA (2005)
HCO ₃ ⁻	ppm	Titration with H ₂ SO ₄ using phenolphthalein + Methanol 60%	APHA (2005)
NO ₃ ⁻	ppm	Ultraviolet spectrophotometer	APHA (2005)
TDS	ppm	Drying, at 105° C	Boyd (2000)
EC	µs/cm	Conductivity Meter	Boyd (2000)
pH		Field electrode meter	APHA (2012)
Co,Cu,Fe,Ni,Mn,Pb	ppm	Atomic absorption spectrometer	Lind (1979)

Hydrochemistry evaluation

The concentrations are in (ppm), then converted to (epm) and (epm%) for use in ionic balance to show the accuracy of the results (Table 3), and in water indicators for irrigation, as well as we mapped the spatial distribution of salinity, electrical conductivity, major ions, minor ions, heavy metals, alkaline and total hardness, then the results are discussed.

Water quality index

The water quality index is calculated according to Cristina et al. (2014) as shown in the equations below (Eq.1, 2, 3, 4).

$Wi = k/Si \dots \dots \text{Eq.1}$,

$K = \frac{1}{\sum_{i=1}^n \frac{1}{si}} \dots \dots \text{Eq.2}$

$$Q_i = \left[\frac{v(-)vi}{vi-si} \right] \dots \dots \text{Eq.3}$$

$$WQI = \frac{\sum_{i=1}^n WiQi}{\sum_{i=1}^n Wi} \dots \dots \text{Eq.4}$$

Where W_i : unit weight, S_i : recommended standard for i^{th} parameter, k : proportionality constant

Q_i : sub-index of i^{th} parameter, v_i : monitored value of the i^{th} parameter, v : measured concentrations.

Table 2: Summary of physico-chemical parameters (WHO, 2017) used for calculated (WQI)

Parameters	Si	Vi	1/Si	K	Wi
pH	8.5	7	0.11765	3.8613	0.45427
TH	500	0	0.002		0.00772
Alkalinity	200	0	0.005		0.01931
Ca	100	0	0.01		0.03861
Mg	125	0	0.008		0.03089
Na	200	0	0.005		0.01931
K	12	0	0.08333		0.32177
SO4	250	0	0.004		0.01545
Cl	250	0	0.004		0.01545
NO3	50	0	0.02		0.07723
			0.25898		1

Irrigation indicators

Based on their sources, the equations below (Eq.5, 6,7,8) are used to calculate the sodium adsorption rate (SAR), sodium percentage (Na%), Kelly index (KI), and permeability index (PI).

$$SAR = \frac{r(Na)}{\sqrt{r(Ca+Mg)/2}}, \text{ (Tood, 2007). Eq.5}$$

$$Na\% = \frac{rNa+rK}{rCa+rMg+rNa+rK} * 100, \text{ (Tood, 2007) } \dots \dots \text{Eq. 6}$$

$$KI = \frac{rNa}{rCa+rMg}, \text{ (Kelly, 1951) } \dots \dots \text{Eq. 7}$$

$$PI = \frac{rNa+\sqrt{rHCO3}}{rCa+rMg+rNa} * 100, \text{ (Pichaiah, 2013) } \dots \dots \text{Eq. 8}$$

Where r (Na, Ca, Mg, K, HCO_3): concentrations of ions

Result and Discussion

Hydrochemistry analysis results

The analysis results of the major ions, minor ions, salinity and electrical conductivity, water quality index, and indicator of irrigation and the balance of major ions are shown in Tables (3,4).

Table 3: (TDS, EC, major, minor ions in ppm) and indicator of groundwater

ID	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	TDS	EC	WQI	SAR	Na%	KI	PI
BH-01	705	12	213	143	648	434	1222	0.7	3377	5280	70.66	12.95	53.36	1.37	62.81
BH-02	1200	120	798	563	1710	1358	2740	1.3	8489	13270	422.99	11.24	141.44	0.61	41.13
BH-07	660	62	392	287	769	632	1263	2	4065	6360	220.20	8.73	73.51	0.66	44.41
BH-16	1104	115	691	416	1510	1137	2535	1.1	7508	11740	395.55	11.58	119.70	0.70	44.83
BH-21	515	10	305	131	697	371	1089	1.2	3118	4890	69.10	8.78	48.65	0.86	51.37
BH-24	406	3	259	132	559	338	798	1.8	2495	3900	43.53	7.24	41.52	0.74	48.28
BH-27	453	18	294	135	638	494	817	1.1	2849	4460	85.95	7.76	45.95	0.76	49.57
BH-28	618	11	352	186	725	522	1249	1.4	3663	5730	78.95	9.37	60.03	0.82	49.88
BH-31	430	128	364	218	746	478	1535	1.1	3899	6100	391.30	6.22	58.24	0.52	39.23
BH-36	624	62	346	242	726	596	1214	1.2	3810	5960	216.66	8.90	65.95	0.73	47.05
BH-49	705	12	213	143	648	434	1222	0.7	3377	5280	70.05	12.95	53.36	1.37	62.81
BH-53	874	82	421	141	936	306	1845	1.3	4605	7200	274.92	13.31	72.75	1.17	56.99
BH-46	405	16	253	96	572	437	740	0.2	2519	3940	76.73	7.77	38.56	0.86	53.20
BH-38	664	100	427	248	781	852	1605	1.1	4677	6890	323.53	8.94	73.22	0.69	46.20
BH-57	470	35	190	125	580	114	1018	2.1	2532	3940	129.61	9.19	41.14	1.03	54.23
BH-47	422	29	312	135	628	501	666	1.2	2693	4240	116.59	7.11	45.80	0.69	47.12
BH-41	695	12	203	133	641	424	1210	1.1	3318	5190	68.78	13.17	51.61	1.43	64.06
BH-39	700	14	208	138	646	429	1217	0.9	3352	5240	76.46	13.06	52.54	1.40	63.42
BH-43	235	10	277	164	563	224	816	0.3	2289	3580	63.96	3.91	37.81	0.37	32.33
BH-08	603	11	340	174	716	510	1239	1.4	3593	5620	74.99	9.38	57.79	0.84	50.63
BH-35	702	12	210	140	645	431	1217	0.7	3357	5250	71.55	13.02	52.84	1.39	63.18
BH-15	944	14	445	288	1074	594	2014	1.1	7373	8400	101.51	12.12	87.31	0.89	50.80
BH-10	483	128	413	263	788	315	1580	1.3	3970	6520	397.43	6.46	66.67	0.50	36.80
BH-61	262	9	188	81	355	230	582	0.3	1707	2670	50.54	5.69	27.68	0.71	48.60
BH-37	878	68	478	293	1168	662	1832	1.1	5379	8410	246.33	11.02	87.91	0.80	48.15
BH-42	401	3	247	129	553	332	796	0.8	2461	3850	44.39	7.28	40.45	0.76	48.96
BH-54	602	93	373	203	708	527	1452	2	3958	6190	299.08	8.81	63.95	0.74	47.35

Table 4 :Ion balance of major ions.

sample	E	A	sample	E	A	sample	E	A
BH-01	2.4	97.6	BH-36	8.6	91.4	BH-43	1.7	98.3
BH-02	5.2	94.8	BH-49	2.4	97.6	BH-08	3.1	96.9
BH-07	11.5	88.5	BH-53	2	98	BH-35	2.2	97.8
BH-16	2.4	97.6	BH-46	-0.2	100.2	BH-15	3.2	96.8
BH-21	0.2	99.8	BH-38	2.6	97.4	BH-10	4.9	95.1
BH-24	4.5	95.5	BH-57	2.1	97.9	BH-61	3.3	96.7
BH-27	3.2	96.8	BH-47	7	93	BH-37	3.5	96.5
BH-28	4.4	95.6	BH-41	1.4	98.6	BH-42	3.6	96.4
BH-31	-2.3	102.3	BH-39	1.9	98.1	BH-54	4.1	95.9

Spatial distribution maps:

The spatial distribution maps for the total dissolved solids (TDS) and electrical conductivity (EC) are drawn (Fig. 3). Their values increase towards east and southeast of the middle and go down towards west and north. There is a positive relationship between electrical conductivity and total dissolved solids ($R^2 = 0.9$) (Fig. 4).

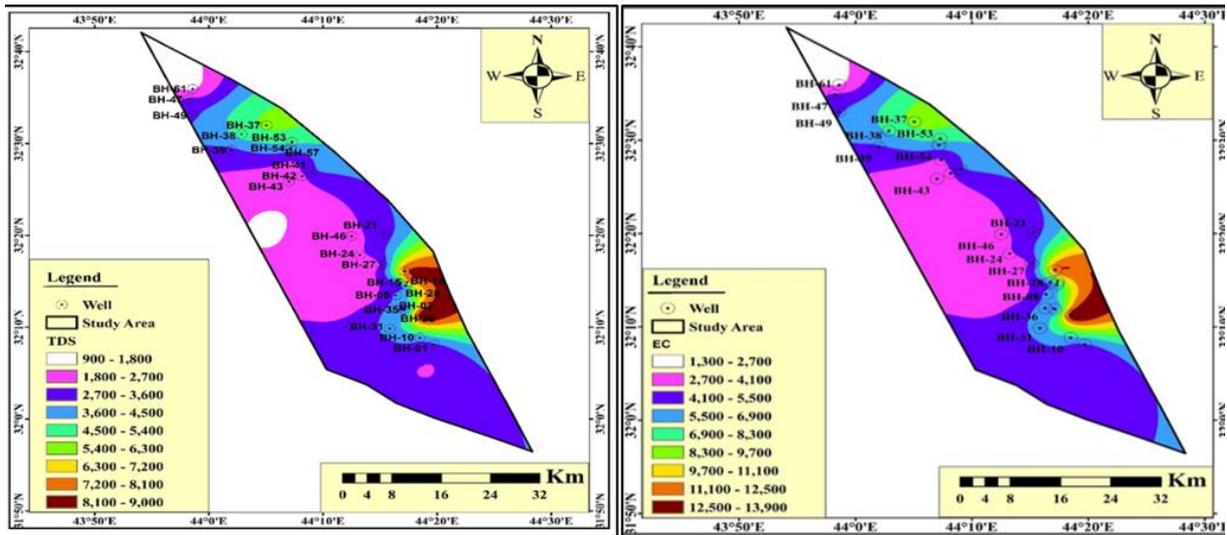


Fig. 3. Spatial distribution Maps (ppm) for TDS at left, and EC at right.

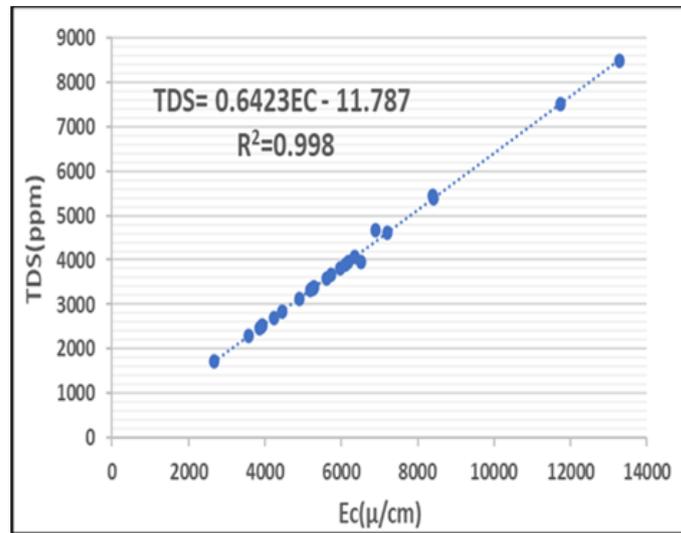


Fig.4. Relationship between EC and TDS

(Na) and (K) distribution maps (Fig. 5) show that their concentrations increase towards south and middle near the gas and fertilizer plant (BH.10) and the desert palm forests (BH.21).

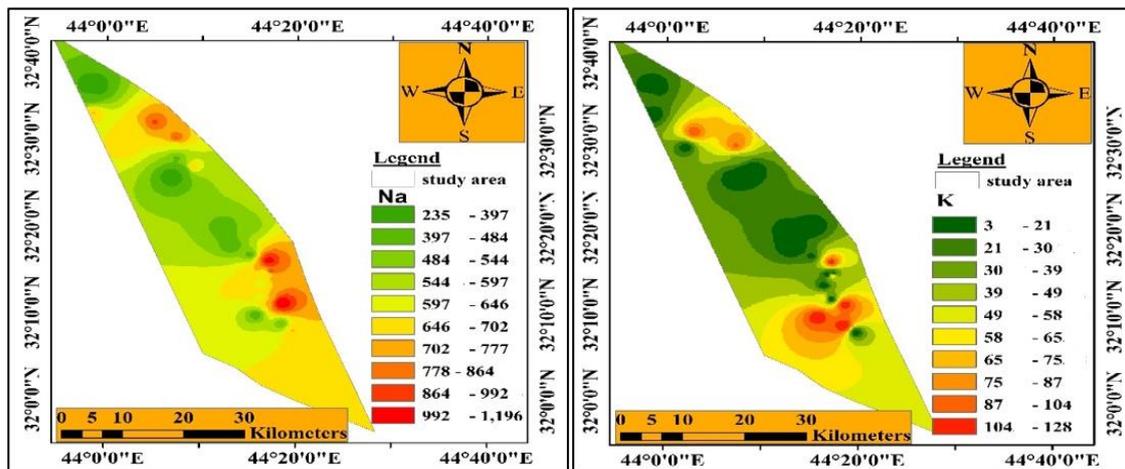


Fig.5. Concentration spatial distribution maps (ppm) for Na at left, and K at right.

Ca and Mg high concentrations (Fig. 6) are in the southeast of the middle region, while the water hardness goes in the same direction, and its water is classified as very hard according to Sawyer and MaCarty (1985) as ranges between (803-4309) ppm.

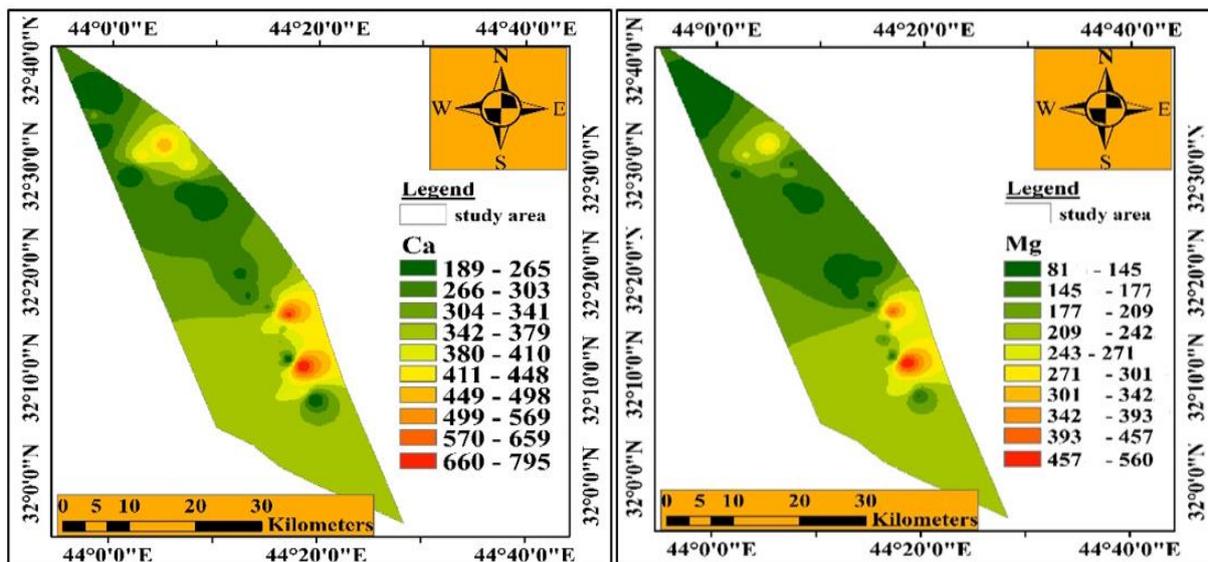


Fig. 6. Concentration spatial distribution maps (ppm) for Ca at left and Mg at right.

Cl, SO₄ and HCO₃ (Fig.7) increase towards southeast of study area near the place of population as well as agricultural areas. The increase in the concentrations of these ions is often due to geogenic reasons, especially since calcium, magnesium, and bicarbonate ions all increase almost in the same direction.

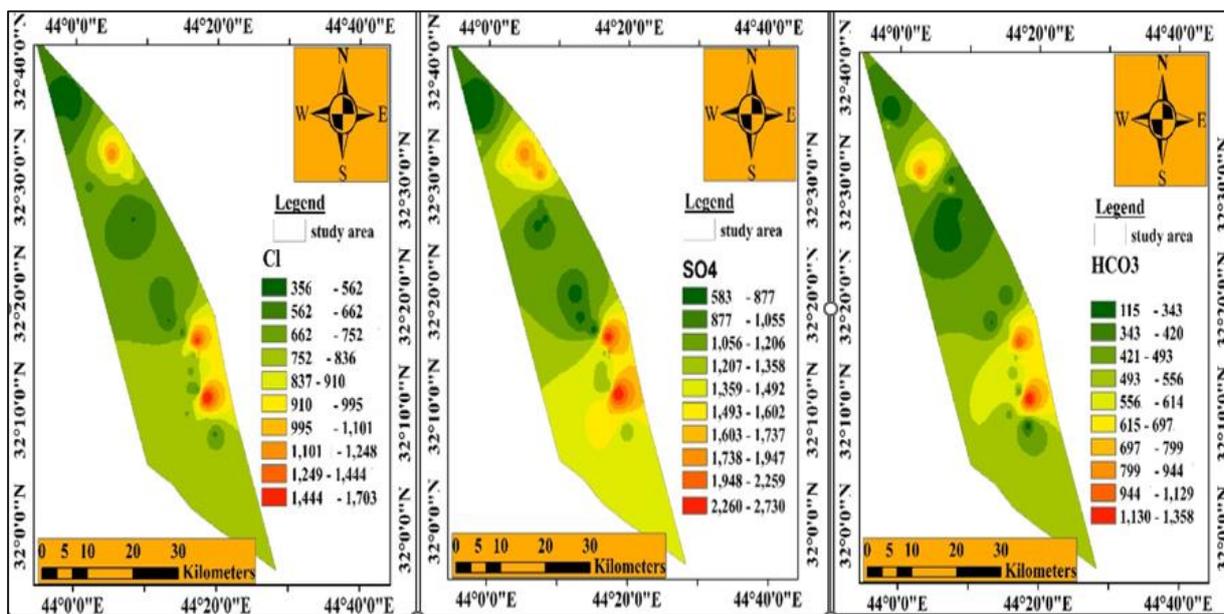


Fig. 7. Concentration spatial distribution maps (ppm) for Cl at left, SO₄ in middle, and HCO₃ at right.

The high concentrations of the minor nitrate ion (NO₃) are in the red color (Fig. 8) and their wells (BH-57,15,16) (Fig. 1). The reason for the increase is chemical or organic fertilizers.

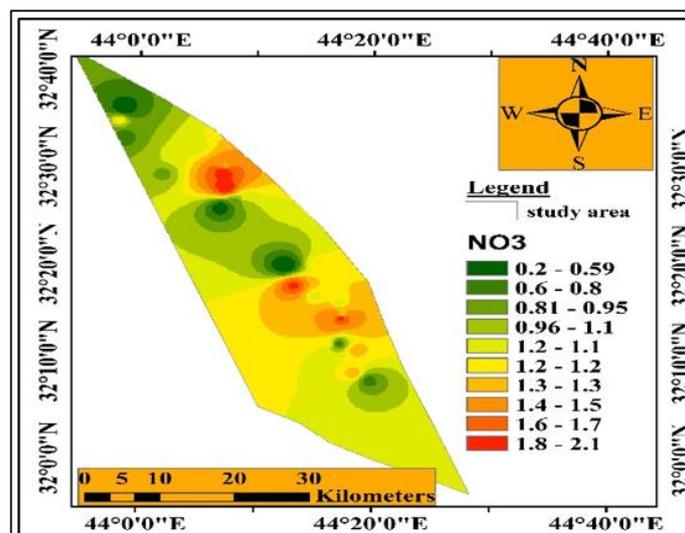


Fig. 8. Concentration spatial distribution map (ppm) for NO_3 .

The concentrations of major and minor ions increase from west to east in the study area; that is, they increase towards the groundwater flow (Al-Qaisi, 2023).

Heavy metals

The results of the heavy metals in the water samples collected from the population area within the study region (Table. 4) show that (Fe, Co, and Cu) concentrations are within the standard permissible limits in all samples, but the concentrations of (Mn) are within the standard permissible limits except (M.w2). Pb is safe in all samples except (M.w10) (very high), but most results of Ni concentrations are high and considered polluted, it is not safe of harmful effect according to the standards of WHO (2017) and IQS (2009). Figure (9) show the spatial distribution for the high concentration of (Ni, Mn).

Table 5: Heavy metals concentrations (ppb)

Sample	Fe	Pb	Co	Ni	Cu	Mn
M.w1	< 50	< 50	< 50	212	144	058
M.w2	< 50	< 50	< 50	159	144	236
M.w3	< 50	< 50	< 50	096	144	060
M.w4	< 50	< 50	< 50	208	157	061
M.w5	< 50	< 50	< 50	156	146	064
M.w6	< 50	< 50	< 50	100	153	052
M.w7	< 50	< 50	< 50	005	143	058
M.w8	< 50	< 50	< 50	000	146	074
M.w9	< 50	< 50	< 50	021	145	050
M.w10	< 50	0.172	< 50	127	142	060

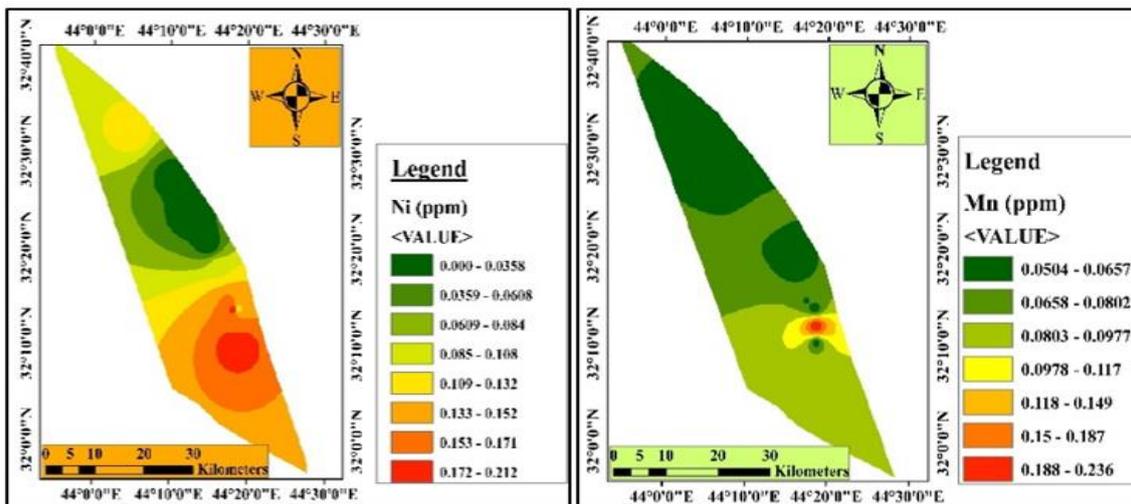


Fig. 9. Concentration spatial distribution map (ppm) for Ni at left and Mn at right.

Water quality classification

The results of the chemical analysis are represented in the Piper chart (Fig.10). The water samples are within two classes: class (g) (alkaline waters with prevailing sulphates and chlorides) and class (e) (earth alkaline water with an increase portion of alkali with prevailing sulphates and chlorides).

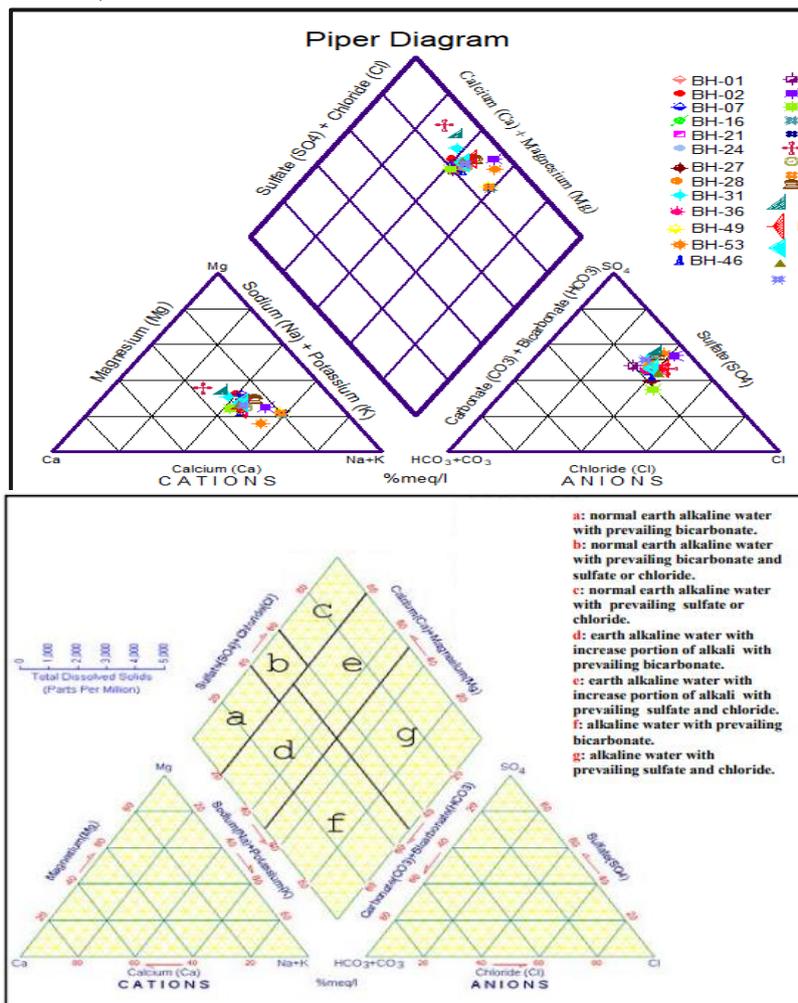


Fig.10. Piper diagram with concentrations of wells.

In Steve's chart, the water of the study area is classified as anions with prevalent sulphate, except in (6) wells; in 5 of them (BH-21, 24, 27, 43, 42), chloride and sulphate are equal, and in the 6th well (BH-47) prevailing chloride. On the other side, sodium and potassium are dominant, except in one well (BH-43) in the middle of the study area, in which magnesium predominates.

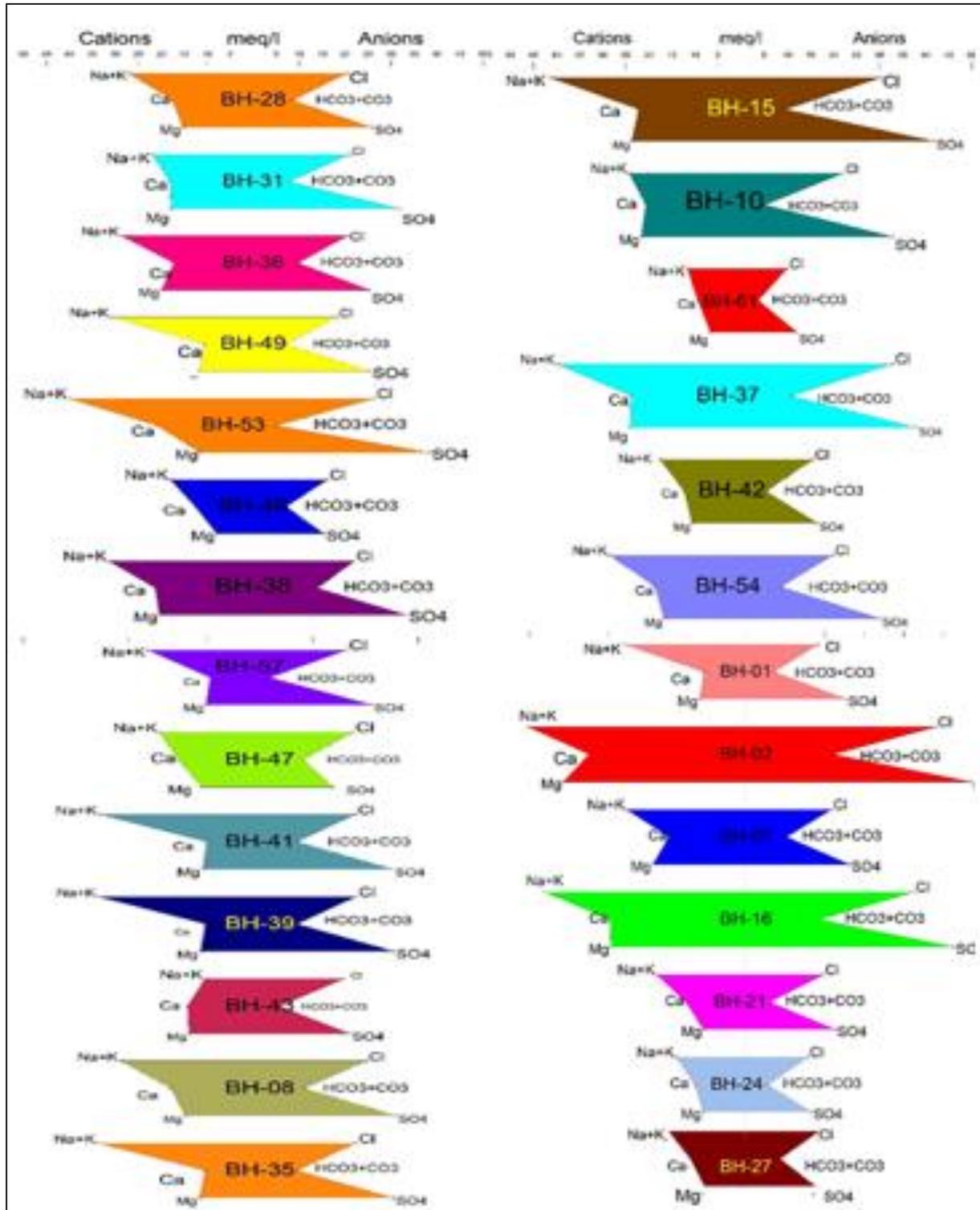


Fig. 11. Steve diagram showing the ions concentrations of wells.

Groundwater suitability index

The water quality index (WQI) provides a single number that expresses overall water quality at a certain location and time, based on several water quality parameters (Boah et al., 2015). The results of (WQI) are given in Table (3) and Figure (12) showing the spatial distribution. The results are compared with WHO standard (2006) and classified as follows:

- * Good water quality in wells (BH-24, 61, 42)
- * Poor water quality in wells (BH-1, 21, 49, 41, 43, 35)
- * Very poor water quality in wells (BH-27, 28, 46, 39, 8)
- * Unsuitable for drinking purpose in wells (BH-2, 7, 16, 31, 36, 53, 38, 57, 47, 15, 10, 37, 54)

Regarding the evaluation of animal drinking water (livestock and poultry), a comparison of the samples electrical conductivity with that of Ayers and Wescott (1989) is done, and the results are shown in figure (12).

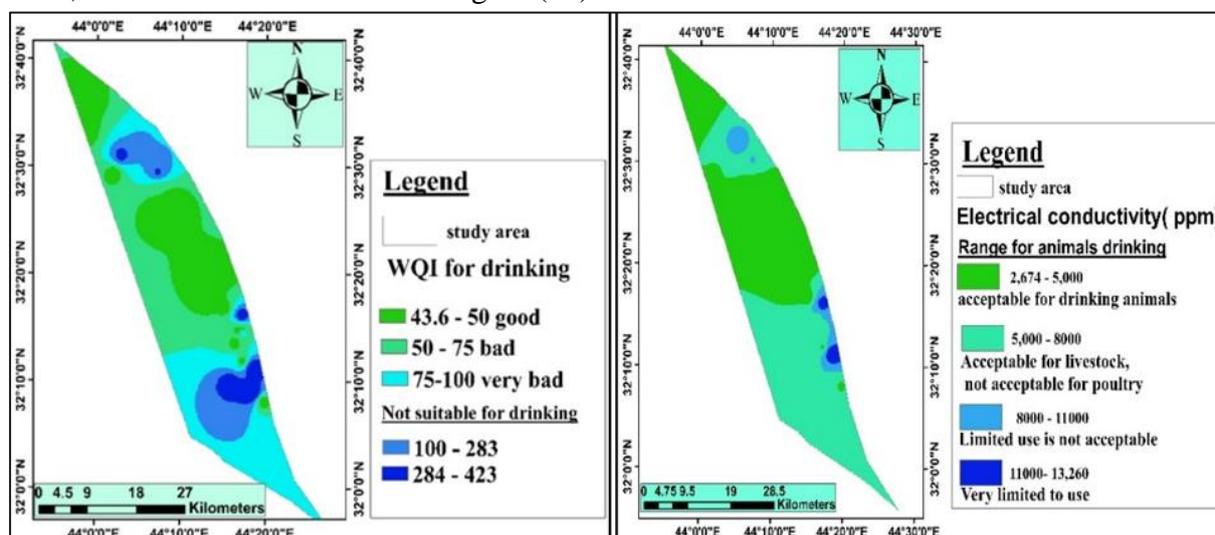


Fig. 12. Spatial distribution map of (WQI) for drinking water suitability for animals at left, and EC at right in the study area.

The standard specifications of Salvato (1982) (Table 6) are compared with the results of the current study, where he set the upper limits for the concentrations of variables in the food, chemical, cement, paper, and refining industries, and it is found that all samples are not good for these uses.

Table 6: Standard specifications for different industries (Salvato, 1982)

Elements	Food Industry	Chemical industries	cement	refineries	0.2
pH	6.5-8.5	6--9	6.5-8.5	6--9	6--9
hardness	316	1000	--	9000	475
Cl	8.46	14.1	7.05	45.13	5.6
SO4	5.2	17.69	5.2	11.86	
Ca	5.98	9.98	--	10.97	0.99
Mg	8.22	--	--	6.99	0.99
Fe	0.4	5	25	15	2.6
The current study	not good	not good	not good	not good	not good

The study area's groundwater consumption for irrigation is assessed using a number of indicators, including the sodium adsorption rate (SAR), sodium percentage (Na%), Kelly index (KI), and permeability index (PI) in table (3). Additionally, the sources for all of the standards for the aforementioned indicators are shown in table (7). The study area, according to the (SAR) indicator, is excellent for irrigation, and (Na%) is mostly good and intermediate type for irrigation, with the exception of the eastern part of the region, which is not suitable for irrigation due to the high percentage of sodium and potassium, and the (KI) considered it good for irrigation and medium. For irrigation, the (PI) is classified as intermediate. This information is discovered after the spatial distribution of the irrigation indicators in figure (13).

Table 7: Standard of (SAR, Na%, KI, PI) with references

indicator's irrigation	indicator limits for irrigation with sources			references
SAR	excellent <10	good (10-18)	Not suitable >10	Tood, 2005
Na%	good < 60	intermediate type (60-75)	Not suitable >75	Tood, 2005
KI	good < 1	intermediate type (1-2)	Not suitable >2	Kelly, 1951
PI	good >75	intermediate type (25-75)	Not suitable < 25	Nag and Suchetana, 2016

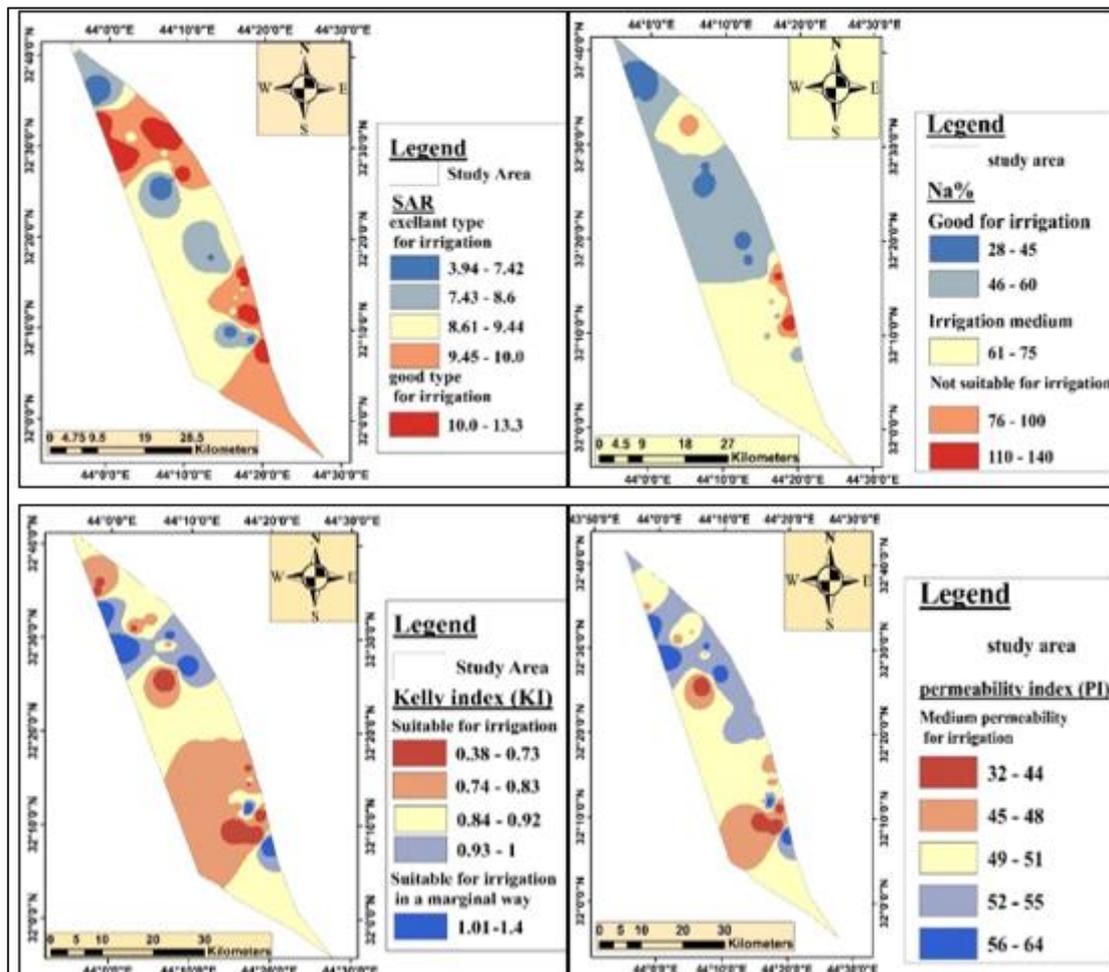


Fig.13. Spatial distribution map of irrigation indicators (SAR, Na%, KI, PI) in the study area.

Conclusion

- The potassium ion concentrations in the area are rather high, especially in Najaf Governorate near the fertilizer and gas factory and the desert palm forests, where there is heavy afforestation in the region, while the concentrations of nitrate ion range between (0.2-2.1) ppm to fertilizers chemical or organic, while the values of alkalinity are calculated for the samples of the study area between (154.2-654.4) ppm, which is identical to the bicarbonate ion in the spatial distribution map.
- There is pollution with heavy metals in the study area, especially (Ni, Pb, and Mn) according to the standard specifications of the World Health Organization (WHO, 2017) and the Iraqi Specifications (2009).
- The quality of the water is sulphate, and the reason may be due to the rocks of the Dibdibba reservoir and the covering rock of the area formed by gypsum derived from the formation itself.
- Most of the wells in the study area are not suitable for human drinking according to the World Health Organization (WHO, 2006). Based on the water quality index (WQI), it is acceptable for animals drinking and unacceptable for poultry.
- Groundwater in the study area cannot enter the food, chemical, cement, paper and refinery industries only after treatment or processing, because it is not suitable in its natural condition, due to the high concentrations of elements.
- The indicators of irrigation sodium adsorption ratio (SAR), the percentage of sodium (Na%), the Kelly index (KI) and the permeability index (PI) were showed that all wells in the study area are suitable for irrigation, but with different specifications and certain percentages after comparing it with standard specifications.

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