EVALUATION OF GROUNDWATER QUALITY IN AL-WAFFA AND KUBAYSA AREAS USING MULTIVARIATE STATISTICAL ANALYSIS, AL-ANBAR, WESTERN IRAQ

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ABSTRACT

The groundwater is a substantial source of fresh water and has been used for various anthropogenic uses. The aim of this work is to investigate groundwater quality and type in kubaysa and AL-Waffa areas, Anbar, Iraq using multivariate statistics approach. The groundwater was sampled from ten wells for each region during the period from October 2018 to March 2019. The levels of T, TUR, pH, EC, TDS, DO, COD, TH, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, F^-, SO_4^{2-},, NO_3^-, HCO_3^-, S^{-2} and SiO_2, were measured. The majority of the physicochemical parameters exceed the permissible guidelines. Pearson's Correlation technique, multivariate statistical tools such as cluster analysis and principle component analysis were applied to determine the groundwater type. For Al –Waffa area, the EC had a positive strong correlation with TDS, Na^+, Cl^-. The TDS had positive strong correlations with NO_3^-. TH and Ca^{2+} possess a very good positive correlation between each other and positive strong correlations with SO_4^{2-}. Sodium has positive strong correlations with k^+ and Cl^-. For the kubaysa area, the EC has positive strong correlations with TDS, Na^+, K^+ and Cl^-. The TDS have positive strong correlations with TH, Ca^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}. The piper diagram indicates that the groundwater types in AL-Waffa and kubaysa regions are Ca^{2+}, Mg^{2+}, SO_4^{2-} and Ca^{2+}, Mg^{2+}, Cl^-, SO_4^2 respectively. The results showed unsuitable water for drinking purposes and need to be treated. The main finding of the current study is a suggestion to use the multivariate statistics technique in determining the groundwater classification type as an alternative method for the piper diagram.

Keywords: Groundwater quality; Multivariate statistical; Al-Waffa and Kubaysa

INTRODUCTION

The groundwater might be considered as one of the most valuable and one of the essential prerequisites for human presence and the endurance of humankind giving him the extravagances and solaces notwithstanding satisfying his necessities of life and furthermore

for industrial and agricultural development, in this manner, it is a significant constituent of our eco-systems (Sarala and Ravi Babu, 2012). Jumaah and Al-Shammaa (2020) mentioned that the groundwater in the study area is believed to be affected by the Euphrates river level, therefore, the salinity during the low river level season is greater than during the high river level season. Groundwater quality is affected by natural and anthropic factors. The anthropogenic activities have played a major in the deterioration of groundwater quality as pollution sources. The groundwater pollution sources include agricultural practice (use of fertilizers and pesticides) in addition to liquids pollutants resulting from industrial activities (Fryar et al., 2000). Generally, the climate of Iraq is arid. During the past few decades, water tables of the prime fresh aquifers in Iraq have been dropping because of the high extraction rates. The fast rise of population related to lifestyle changes, particularly next 2003, has likewise expanded the human uses of groundwater in whole Iraq (Al-Abadi, 2012). Awadh, 2018 mentioned that the connate spring waters in the study area are impermissible for use due to its high salinity. In general, springs typically contain more than 1000 ppm sulfate which is harmful to plants. Awadh et al., 2016. Mentioned that ground Water in Al-Hawija area is poor, very poor and unsuitable for human drinking are distributed in wells that are nearby the discharge channel carrying deteriorated water. The hydrogeological, hydrogeochemical and Balneological studies of the groundwater in the study area were investigated by several authors (Hussien and Gharbi, 2010; Al Dulaymie et al., 2010; Awadh and Abdul Al-Ghani, 2013). Recently, the geochemical classification of groundwater and hydrogeochemical assessment of groundwater was studied using multivariate statistics approach in different regions (Bodrud-Doza et al., 2016; Retike et al., 2016; Gulgundi and Shetty 2018; El-Baghdadi et al., 2019; Celestino et al., 2019; Bouteraa et al., 2019 and Molekoa et al., 2019). In Iraq, few studies employed multivariate statistical analysis to assess groundwater quality, in Makhmor plain (Shihab and Abdul Baqi, 2010), Baghdad City (Ismail et al., 2015), Erbil City (Issa 2018), and Halabja Saidsadiq Basin (Abdullah et al., 2019). The aims of this study are evaluation groundwater quality in Al -Waffa and Kubayasa regions and determination of groundwater type using a multivariate statistics approach.

STUDY AREA DESCRIPTION

The study area, which includes the Al-Waffa and Kubayasa regions, is located in Anbar, Iraq (Fig. 1). It is characterized by simple slope, non-rugged terrain and spread of the seasonal valleys, such as Al-Marij and Al-Asel valleys (Al Dulaymie et al., 2013). The study area is affected by the Abu-Jir Fault zone which is described as a right lateral strike slip fault

(Fouad, 2004). The tar and sulfate springs spread in the study area are one of the evidence of the presence of this fault. The climate of the study area is described as a dry desert with minimal effect of the Mediterranean climate (Hussien and Gharbi., 2010).

Fig. 1. Location map of the study area

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The subsurface geological section of the study area is revealed in Fig. 2. The hydrogeologic conditions and the hydraulic characteristics of the water-behavior layers within the hydrogeologic system of the study area are explained in details by Hussien and Gharbi (2010). The local depositional basin of upper oligocene-quaternary sediments is defined as the hydrogeologic system. According to the properties of the formation sediments, there are three hydrogeologic units: first hydrogeologic unit is water-behavior layers of Quaternary sediments. This Unit is mainly composed of gravel, sandy gravel, sand and silt. It is characterized by unconfined local expansion of bank loading status, which exists along the right side bank of the Euphrates River. The second hydrogeologic unit is water-bearing layers of the Fatha Formation, these layers are formed from porous limestone and fractured gypsum, which characterized by semi-confined to the finite setting of low extension. Third hydrogeologic unit is water-bearing horizons of the Euphrates Formation. The aquifers are consisted of limestone rich in fossils, fractures and dolomitic Limestone.These layers are distinctive by the unconfined and semi-confined to confined conditions in recharge and discharge zones, respectively.
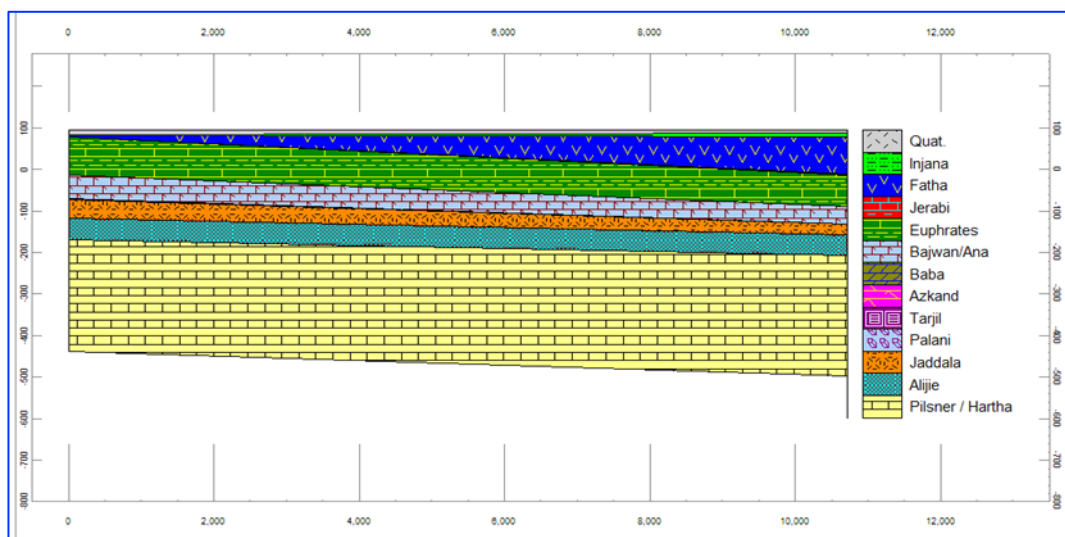
Fig. 2. Geological section of the study area (After Hussien and Gharbi., 2010)

MATERIALS AND METHODS

Water Sampling and Collection

Twenty sampling sites were selected to collect the groundwater samples (Fig. 3). The assortment of each site has been exactly determined using a GPS device (model etrex). The groundwater samples were collected monthly from twenty active wells evenly distributed in kubaysa and Al -Waffa areas, during the period from October 2018 to March 2019. Samples were collected by the plastic bottles which have been prewashed with acid and soaked in deionized water. Three types of sampling plastic bottles were used: 1.5 L for physicochemical parameters, 0.5 L for chemical oxygen demand COD, ammonium NH_4, Nitrate NO_3^- analysis, treated with con. $\leq$ 2 using con. H_2SO_4 and 0.25 L Suphide S^{-2} sample treated with zinc acetate. The water samples are carried to the laboratory at 4 °C in the sampling box. The pH, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and temperature (T) were measured in the field using the portable meter (HANNA). Major cations such as calcium (Ca^{2+}), magnisum (Mg^{2+}) and anions, bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed by titration, sodium (Na^+) and potassium (K^+) by flame photometer BWB XP and SO_4^{2-} by precipitation method. F^- was estimated by using an ion-selective electrode (ISE) with a pH/ISE Mettler toledo meter. S^{2-} was evaluated by using an ion- selective electrode (ISE) with a pH/ISE HANNA combined electrode. Nitrate and ammonium are measured by using kits by multi direct spectrometer. Silica is estimated by UV/ visible spectrophotometer jenway 6045. The accuracy of major ions was estimated from ionic balance differences percentage (IB %) (UN / ECE 2002).
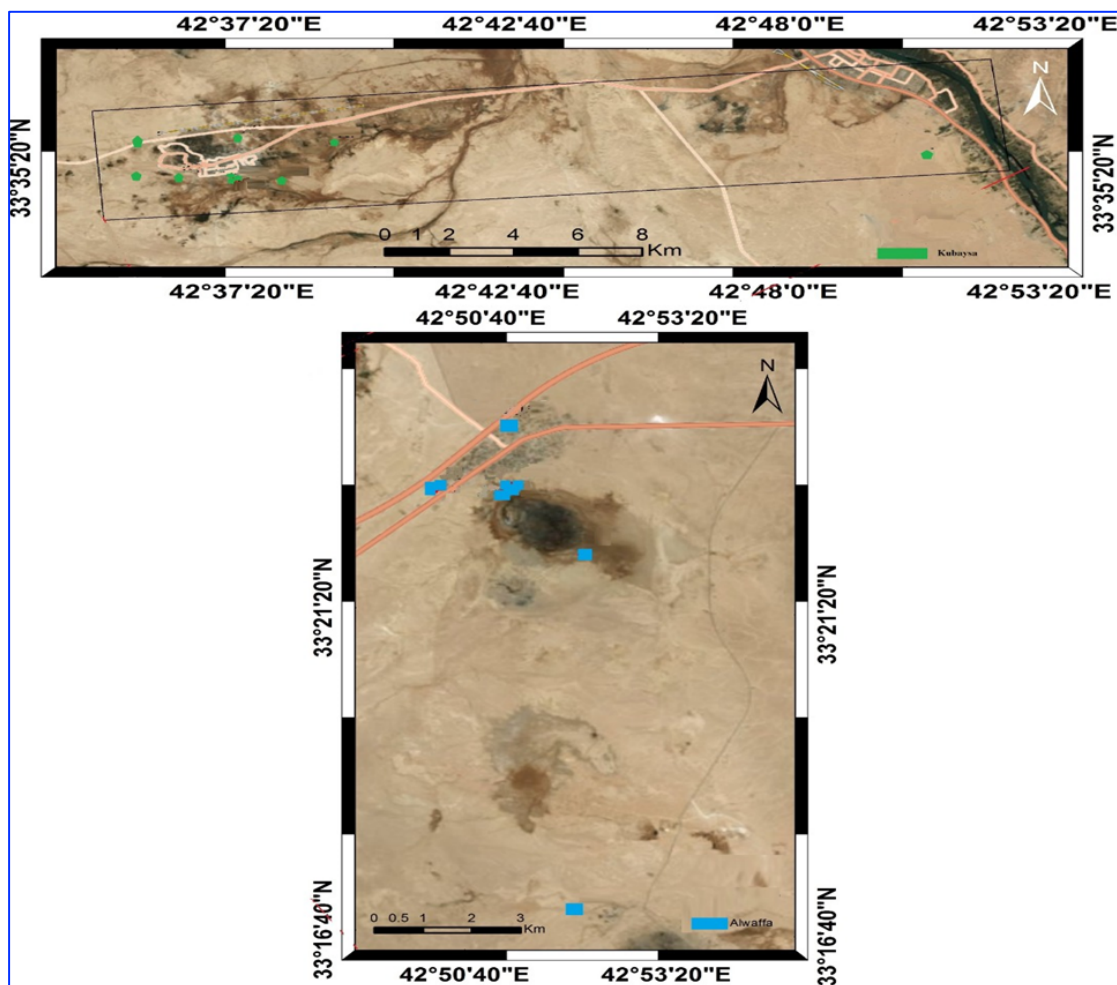
Fig. 2 . Location map of groundwater sampling sites in Al-Waffa and Kubaysa areas

It is calculated from the equation under where r RC at and r RA ni are the amount of cations and anions (EPM), respectively. The accepted limit of or ionic balance (IB) relative differences is between (0 and 5 %).

$$EBI\% = \frac{(\sum Cat - \sum Ani)}{(\sum Cat + \sum Ani)} \, X \, 100 \tag{1}$$

Quality Assurance and Quality Control QA/QC

It included the technical blank, duplicate Analysis, and standard reference solutions. The standard solutions of $AgNO_3$, EDTA, and NaOH are from FLUKA, BDH, and MERK, respectively. Recoveries for $AgNO_3$, EDTA, and NaOH, are 98.77%, 99,81%, and 98,86%, respectively.

Statistical analysis

The descriptive statistical and multivariate statistics are calculated using statistical software version 13.3 (www.tibco software.com).

RESULTS AND DISCUSSION

Physico-Chemical Parameters

The descriptive statistics results for the physical and chemical variables of groundwater of the study area are listed in Tables 1. The obtained values of physic-chemical groundwater parameters were compared with WHO guidelines. The levels of most physical and chemical parameters exceeded the quidelines except for pH and HCO_3^- were within the permissible limits. When comparing the results of our study with the results of Hussien and Gharbie (2010), it was found that there is a consistency in the values of T, pH and TDS and inconsistency with levels of Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, NO_3^- and Th. This inconsistency may be interpreted in terms of the groundwater sampling . In our study, the water samples were collected from wells, while in the previous study from the springs, and the groundwater in the current study were sampled after ten years from the previous study.

The mean and range of water samples temperature in Al-Waffa region are 22°C and from 18 to 33°C, respectively, while in Kubaysa, it ranges from 19 to 32 with a mean of 22°C. The water temperature is described as being cold (< 20°C), tepid (25-34°C), warm (34-42°C). The turbidity of water samples in the Waffa region ranges from 0.2 to 8 NTU with a mean value of 1.6 NTU while in the Kubaysa region ranges from 0.1 to 117 NTU with mean value 9.3 NTU. Increasing turbidity in the kubaysa region is interpreted in the terms of crushing wells and erosion of the lining pipes and non-develop and clean the well as well depends on the location of the pump from the bottom of the well. The range of pH value of Al-Waffa water samples was from 6.71 to 7.71 with a mean value of 7.12 while kubaysa ranged from 6.72 to 7.5 with a mean of 7.05. It is classified as slightly alkaline to slightly acidic water.

The EC values in water samples of Al-Waffa range between 2702 to 6512 µS/cm at 25°C with mean value of 4479 and for kubaysa 3270 to 10011 with an mean 5818 µS/cm at 25°C. The high value of EC indicates the existence of inorganic material in groundwater.The variation of EC values of two areas refers to the high dissolution concentration of cations and anions in the kubaysa area compared with Al-Waffa. EC is an indicator of the suitability of water for irrigation purposes and salinity hazards. The range of TDS in water samples of Al – Waffa was from 2430 to 5310 mg/L with a mean value of 3604 mg/L whereas in Kubaysa from 2412 to 7246 with a mean 4013 mg/L. The high level of salts in groundwater samples is due to the ooze of salts from the soil and also by anthropogenic activities (Selvam et al., 2014).

Table 1. Descriptive statistics of physic-chemical parameters of groundwater in Al-affa and Kubaysa areas

Variable	Al-Waffa				Kubaysa				WHO Guidelines
	Mean	Min.	Max.	Std.Dev.	Mean	Min.	Max.	Std.Dev.	(2011)
Tem (^{0}C)	22	18	33	3	22	19	32	2	-
Turb (NTU)	1.6	0.2	8.0	1.6	9.3	0.1	117.0	20.0	5
pH	7.12	6.71	7.71	0.22	7.05	6.72	7.50	0.16	6.5–8.5
EC (μS/cm)	4479	2702	6512	839	5818	3270	10011	1451	2500
TDS (mg/l)	3604	2430	5310	624	4013	2412	7246	956	500
TSS(mg/l)	5	1	15.0	3	26	3	288	52	-
TH(mg/l)	1851	990	2411	319	1571	1107	2818	345	100
Ca^{2+}(mg/l)	473	188	616	111	346	200	667	103	75
Mg^{2+}(mg/l)	162	102	239	33	168	105	280	35	50
Na^+(mg/l)	344	134	680	135	666	129	1050	205	200
K^+(mg/l)	26	11	54	10.16	48	12	88	18	10
F^-(mg/l)	2.2	0.7	6.5	1.2	0.67	0.13	1.22	0.26	1
HCO_3^-(mg/l)	204	108	309	57	1.8	0.5	6.1	0.9	500
Cl^-(mg/l)	676	397	1213	171	229	135	311	37	250
SO_4^{2-}(mg/l)	954	576	1061	100	1545	438	2603	457	250
NO_3^-(mg/l)	368	30	730	196	551	222	1033	220	45
(SiO_2 (mg/l	20.1	11.1	28.7	3.5	19.3	11.3	42.2	6.4	-
(S^{-2} (mg/l					23	2	45	10	-

The high levels of TDS refer to the high concentration of cation Na^+, K^+,Ca^{2+},,Mg^{2+}, and anions SO_4^{-2} and Cl^- in kubaysa samples while the concentrations of Na^+, $K^{+,}$ and Cl^- are much less in Al-Waffa samples. The high levels of these anions and cations and in turn TDS recorded in the current study depend upon soluble products of rock weathering and decomposition through the trip of groundwater from recharge area to discharge area, in addition to water interactions with the limestone, dolomitic limestone and gypsum. The TSS levels ranged from 1 to 15 mg/l with a mean value of 5 mg/l in water samples of Al-Waffa and kubaysa samples from 3 to 288 mg/l with mean 26 mg/l. The high value of TSS in the kubaysa area due to crushing wells and corrosion of the lining pipes and non-develop. The monthly means of DO and COD of kubaysa and ALWaffa are listed in Table 2. The DO level in water samples ranges from 4.3 to 11.6 mg/l with a mean of 7.6 mg/l in Al-Waffa and the kubaysa from 2.1 to 13.7mg/l with mean of 7.1 mg/L. This may due to leaching dissolved oxygen from rains to groundwater and contributed in oxidation NH_4^+ to NO_3^-. The COD level in the groundwater samples of Al-Waffa ranges from 4 to 351 mg/l with mean of 33 mg/L,whears in Kubaysa from 11 to 714 mg with mean of 226 mg/L. The high level of COD in water samples in kubaysa is interpreted in terms of availability of hydrocarbons compounds result from limestone, nitrogen compounds inorganic compounds, CH_4, H_2S gases and NH_4^+ that's result by anaerobic bacteria.

Table 2. The monthly variation of DO and COD levels in groundwater samples of the study area

No	Data	AL-Waffa		Kubaysa	
		DO mg/l	COD mg/l	DO mg/l	COD mg/l
1	October 2018	7.2	119	5.8	135
2	November 2018	7.5	27	5.9	236
3	December 2018	7.1	17	5.7	334
4	January 2019	8.7	14	9.8	190
5	February 2019	7.8	13	7.9	231
6	March2019	7.5	11	7.4	340
Standard limits		5>	10>	5>	10>

The TH (as $CaCO_3$) values in the water sample of the study area ranged from 990 to 2411 mg/L with a mean of 1851 mg/L in Al-Wafa region and from 1107 to 2818 mg/l with a mean of 1571 mg/L in kubaysa. This means that the groundwater in the study area is classified as very hard water. The Euphrates Formation within the study area could have contributed to the high value of hardness. The Ca^{2+} ion concentrations in the collected water samples in the study area ranged from 188 to 616 mg/Lwith a mean of 473mg/L in Al-Waffa, while that of Kubaysa is 200 to 667 mg/L with a mean of 346 mg/L. The partial dissolution of limestone, dolomitic limestone and dolomite of Baba, Anah, and Euphrates formations have been contributed in providing the aquifer with Ca^{2+} and Mg^{2+}, and dissolution of gypsum and anhydrite of the Fatah Formation also contribute to provides Ca^{2+}. The presence of Ca and Mg ions in the groundwater of study regions may be due to excess dissolution of Ca^{2+} from gypsum and carbonate rocks by rainwater in Al -Waffa while in kubaysa the Ca^{2+} results from ion exchange with Na^+ which forms aquifer sediments. The range of Mg^{2+} in the water samples of Al-Waffa is from 102 to 239mg/L with a mean of the value of 162 mg/L, while that of Kubaysa is 105 to 280 mg/L with a mean value of 168 mg/L. The limited dissolution of dolostone determines Mg^{2+} concentration in groundwater (Vasanthavigar et al., 2010). The presence of a small difference in the concentration of Mg^{2+} refers to the finite dissolution of dolomite in the study area.

Na$^+$concentration in the water samples collected from Al –Waffa areas ranged from 134 to 680 mg/L with a mean value of 344 mg/L, while that of Kubaysa is 129 to 1050 mg/L with an average value of 666 mg/L. The spatial variation of the sodium ion concentration can be interpreted in terms of localized high dissolution results from rainwater and halite dissolution (Anantha and Chandrakanta, 2014). A high concentration of Na^+ ion is observed

in groundwater samples of kubaysa than Al-Waffa due to juvenile intruded water of deep source throughout Abu-Jir fault. The high concentration of Na^+ than that Ca^{2+} and Mg^{2+} is expected due to the effect of ion exchange which is low in Al-Waffa region. The K^+ concentration in water samples of Al-Waffa ranges from 11 to 54 mg/L with mean of 26 mg/L while that of Kubaysa is 12 to 88 mg/l with mean value of 48 mg/L. Weathering and dissolution of the K-feldspars may be the cause of increased potassium ion concentration (Srivastava et al., 2015). The high concentration of K^+ is expected due to the effect of ion exchange with Ca^{2+} and Mg^{2+} (Vasanthavigar et al., 2010). The ion exchange between K^+ dissolved in water with Ca^{2+} and Mg^{2+} in limestone and dolomitic limestone prevalent in the study area may be the source for high concentration of K^+ recorded in groundwater samples of the current study. The Ammonium concentration NH_4^+ in the water samples of Kubaysa region ranged from 0.13 to 1.22 mg/L with a mean of 0.67 mg/L. Ammonium may originate from differently NO_3^- reduction under highly reducing conditions (Arumugam et al., 2009). The emergence of NH_4^+ in kubaysa water and it's missing in Al-Waffa area is interpreted in terms of availability of the reduction anaerobic bacteria that reduce NO_3^- to NH_4^+, while in Al –Waffa, the aerobic bacteria is available which in turn oxidize NH_4^+ to NO_3.

The F^- concentrations in the water samples of Al-Waffa area ranges from 0.7 to 6.5 mg/L with a mean of 2.2 mg/L while that of Kubaysa is 0.5 to 6.1 mg/L with a mean of 1.8 mg/L. The enrichment sources of F^- in groundwater are from weathering of the minerals and the interaction of water with rocks and associated minerals present in the granite and gneissic (Narsimha et al., 2017). The averages of F^- content in sedimentary rocks are 200, 220, 260, and 940 mg/kg for sandstone, limestone, dolomite, and shale, respectively (Fleischer and Robinson., 1963). Because of predominance of limestone and dolomitic rocks in the study area, the high concentration of F^- may be interpreted in terms of the interaction between water and these rocks.

The range and mean values of HCO_3^- concentration in the groundwater samples are from 108 to 309 mg/L and 204 mg/L in Al-Waffa, from 135 to 311 mg/L and 229 mg/L in Kubaysa. The silica rocks weathering, carbonates dissolution processes and soil and atmospheric CO_2 are the potential sources of HCO_3^- in the groundwater (Boateng et al., 2016). The hydrogeological units in the study area are characterized by the presence of the carbonates formations represented by the Fatha and Euphrates formations. The HCO_3^- levels in the groundwater can be interpreted in terms of dissolution of the limestone rocks.

In Al-Waffa, Cl^- concentrations in the water samples ranged from 397 to 1213 mg/L with a mean of 676 mg/L while that of Kubaysa is 438 to 2603 mg/L with mean of 1545mg/L. Chloride in groundwater originates from the dissolution of disseminated halite. The concentration of Cl^- ion in Kubaysa area is higher than Al-Waffa. The high concentration of Cl^- is the result of evaporation, which can be used as an indicator to detect the mineralization degree of groundwater (Yang et al., 2016). The SO_4^{2-} concentrations in the water samples of Al -Waffa range from 576 to 1061 mg/L with a mean of 954 mg/L while that of Kubaysa is 222 to 1033 mg/L with a mean of 551 mg/L. The oxidative weathering of pyrite and the dissolution of the gypsum contribute an increase in SO_4^{2-} concentration. The excessive saturation condition related to dolomite and calcite of most samples may be due to gypsum dissolution (Tiwari et al., 2016). The dissolution of gypsum of the Fatah Formation in the study area contributes to a high concentration of SO_4^{2-} in the groundwater samples of the study area. The difference of SO_4^{2-} concentration in two areas is attributed to the availability of reduction anaerobic bacteria in kubaysa that reduce the large amount SO_4^{2-} to H_2S gas. The range and mean value of NO_3^- concentration in Al-Waffa water samples are from 30 to 730 mg/L and a mean of 368 mg/L. The excess amount of NO_3^- may be of geogenic origin. The nitrification of the aquifer materials containing the nitrogenous compound, such as ammonia results in the nitrate by interaction with water. Ammonia is oxidized to nitrate by ammonia-oxidizing bacteria (Stadler et al., 2008). The lack of nitrate in the groundwater in Kubaysa is due to the absence of this type of bacteria.

The SiO_2 concentrations in the analyzed samples range from 11 to 28.7 mg/L with a mean of 20.1 mg/L in Al-Waffa, and from 11.3 to 42.2 mg/L with an average of 19.3 mg/l in Kubaysa. The origin of SiO_2 in the study area is from marl, silt and clay of Fatha and Euphrates formations, and Quaternary sediments, while some increase of SiO_2 in these sediments originated from chemical deposition in the slightly acidic water. The mean values of SiO_2 in the two areas are approximate and exceed the WHO guidelines. The concentrations of S^{2-} ranged from 2 to 45mg/L with a mean of 23.2 mg/L in the groundwater samples in Kubaysa, while it was depleted in the groundwater of Al-Waffa . The high level of Sulphide could be as a result of microbial action capable of reducing SO_4^{2-} to S^{2-} leading to Sulfate depletion in study area. S^{2-} depletion in the Al-Waffa region is due to the absence of reducing bacteria. The health hazard of hydrogen sulfide gas increases with increasing dose, ranging from the smell of rotten eggs (0.13–0.15ppm) to irritation of the respiratory system and eyes (100ppm) to Olfactory nerve paralysis (150ppm) and coma (100ppm) (Lim et al., 2016). S^{2-} ion concentration exceeds the WHO guidelines in the Kubaysa area.

Hydrochemical Facies

The groundwater samples have been classified based on their main anions and cations using the piper diagram (Tijani et al., 1994). The hydrochemical facies of groundwater samples in the study area are revealed in Figs. 4 and 5. It is evident from the piper diagram that the groundwater in the Al-Waffa region belongs to Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- (normal earth alkaline water type). The solubility of gypsum deployed in the study area is the source of excess sulfate in groundwater. The excess Ca^{2+} is interpreted in the term dissolution of gypsum and or ionic exchange process between Na^+ and Ca^{2+}. The diagram also shows the dominance of alkaline earth elements (Ca+Mg) over alkaline elements (Na+K) and strong acids (Cl^- + SO_4^{2-}) excess weak acids (HCO_3). The type of most groundwater samples in kubaysa is $Na^+ + K^+ + Cl.SO_4^{2-}$, followed by mixed Ca-Mg -Cl facies. The distribution of ions in the diagram shows that the alkalis elements (Na^+ and K^+) and strong acids (SO_4^{2-} and Cl^-) predominate over. The diagram points out that alkalis (Na^+ and K^+) and vigorous acids (Cl^- and SO_4^{2-}) dominated over the alkaline earth (Ca^{2+} and Mg^{2+}) and low acids (HCO_3^-) .The ionic exchange process between Na^+ and Ca^{2+} is a significant geochemical operation for the Na and Cl groundwater type.
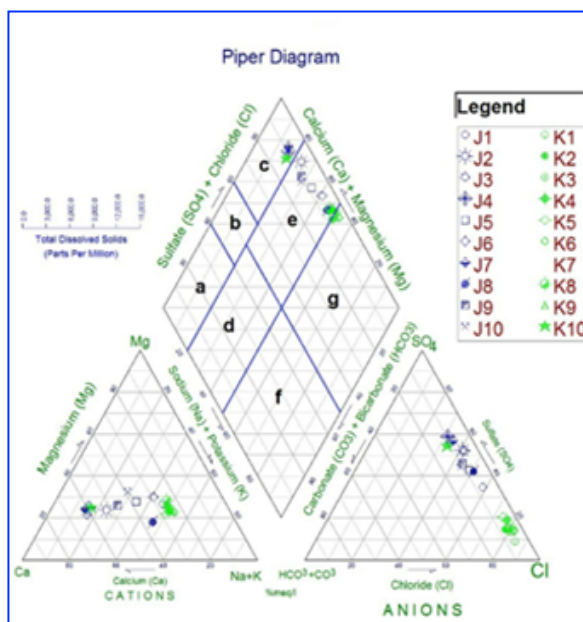

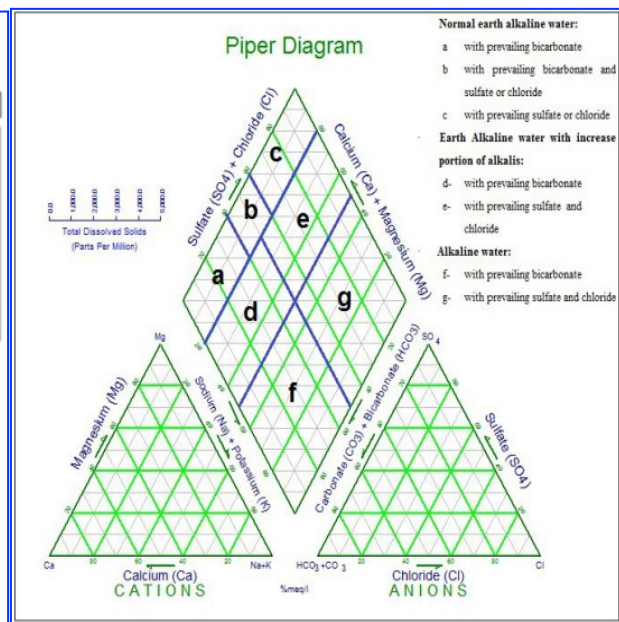**Fig. 4. Piper diagram showing the classification type**   **Fig. 5. Piper diagram depicting of water hydrochemical facies of groundwater**

Correlation Matrix Analysis

The correlation matrix analysis between different variables is a very useful tool in enhancing research and opening new frontiers of science (Khelif et al., 2018). The results of the

correlation matrix analysis of groundwater physicochemical parameters are in the AL-Waffa region are listed in Table 3. In general, a correlation coefficient > 0.7 is interpreted as a strong correlation between two variables, while the coefficient values between 0.50 and 0.70 suggest moderate correlation (Nnorom et al., 2019). Electrical conductivity shows strong positive correlation with TDS (r = 0.82) and (0.71) and shows strong to moderate positive correlations with TDS (r =0.90) Cl (r =0.71) and Na (0.70) .These correlation relations show that EC and TDS are managed by concentrations of Na and Cl ions and the dominance of these ions. TDS shows strong positive correlation relation with NO_3 ion (0.76). This relation reflects NO_3 ion is an important contributor to the TDS level. TH has a strong positive correlation relations with Ca ion (r = 0.90) and SO_4 ion (r = 0.77) .These relations indicate that TH of groundwater in the AL-Waffa region is mainly due to Ca ion. The SO_4^{2-} excess in groundwater is due to the dissolution of SO_4^{2-} ion from gypsum and hexahydrite minerals (Adhikari and Mal, 2019). Cl ion shows positive strong correlation with Na ion (r = 0.88). Na ion has a positive strong with K ion (r = 0.82). SO_4^{2-} ion shows moderate and low positive correlation (r = 0.64, r = 0.48) with Ca and Mg, respectively. Cl ion shows also moderate positive correlation with Mg io (r = 0.55) and K ion (r = 0.56). Fluoride does not show correlation relation with the other physicochemical parameters. The positive correlation between Ca and Mg with SO_4 and the positive correlation between Cl and Mg, Na and K indicates a probable common origin which in turn determines the groundwater types and hydrochemical facies. In this study, the positive correlations between SO_4 and Ca and Mg, and between Cl and Mg show that the groundwater type in Al-Waffa region is Ca^{2+} - Mg^{2+} - SO_4^{2-} -Cl^-.

The result of the correlateion matrix analysis of physico-chemical parameters of groundwater in the kubaysa region is listed in Table 4. Significant correlations between the groundwater quality parameters were reported. Turbidity shows positive strong correlation with TSS (r = 0.99) .This correlation is logical and expected. EC has strong correlations with TDS (r = 0.87), SO_4^{2-} (r = 0.72) and moderate correlation with Mg^{2+}. These correlations indicate that EC is managed by these ions. TDS shows positive strong correlations with Ca^{2+} (r =0.94.), Na^+ (r = 0.88), K (r = 0.84), Mg (r = 0.77), Cl^- (r = 0.93) and SO_4^{2-} (r = 0.84) . These correlations suggest a common source of these cations and anions, and they are the largest contributor to the level of TDS in the groundwater in the kubaysa region. These ions may be due to the dissolution of evaporate minerals. The ionic strength of water increase because of the dissolution of evaporate minerals and favor the dissolution of sulfate salts which increase the concentrations of Mg and Ca groundwater. TH shows positive strong and

moderate correlations with Ca^{2+} (r = 0.98), Mg^{2+} (r = 0.84), Na (r = 0.77), K^+(r = 0.70), SO_4^{2-} (r = 0.84), and SiO_2 (r = 0.75). These correlations indicate that the $CaCl_2$ and $MgCl_2$ salts controller of groundwater chemical combination in the zone (Patel et al .2016). Ca has positive strong correlations with Mg (r = 0.78), Na (r = 0.79), Cl (r = 0.80) SO_4^{2-} (r = 0.83) and SiO_2 (r = 0.75). These correlations indicate a possible ion- exchange process in the groundwater aquifer system .Mg shows positive strong correlations with Cl^- (r = 0.72), SO_4^{2-} (r = 0.73), and moderate with SiO_2 (r = 0.70) . These correlations are interpreted in terms of the presence of Mg Cl_2 and hexahydrite as a source of Mg, Cl^- and SO_4^{2-}. Na and as strong correlated with K (r = 0.81) and Cl^- (r = 0.93) .A positive strong correlations between K and Cl^- (r = 0.76) and SO_4 (r = 0.74). SO_4^{2-} has positive strong correlation with SiO_2 (r = 0.79). This correlation is attributed to S^{2-} oxidation occurred along with silicate weathering (Nagaraju et al., 2016). SO_4^{2-} has positive moderate correlations with Cl and Na. The correlations between Cl and SO_4^{2-} with alkalis (Na and K) and earth alkaline (Ca and Mg) are interpreted in terms of the common origin, which in turn, suggests the groundwater type in kubaysa region. Based on the results of correlation matrix analysis, the groundwater type in the kubaysa region is Na-K-Cl mixed with Ca-Mg-SO_4. This result is in good agreement with that derived from the Piper diagram.

Cluster Analysis

Cluster analysis is an exploratory data analysis tool for solving a classification problem. The object of this tool is sorting the data into groups or clusters. The cluster showed high internal homogeneity and high external heterogeneity (McGarigal et al., 2013). Hierarchical CA, the most common method, starts with each object in a separate group and joins groups together step by step until there is only one group left (McKenna et al., 2003).The application of cluster analysis gives results that can be described using a dendrogram or binary tree. The dendrograms of the hierarchical cluster analysis for ten physicochemical parameters (EC, pH, TDS, Na^+ K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} HCO_3^- and Cl^-) of groundwater in AL-Waffa and Kubaysa regions are shown in Fig. 5. In the Waffa region, the groundwater parameters cluster into two major clusters I and II. The cluster II is controlled by cluster I. EC and TDS are grouped in cluster I reflecting positive strong correlation, and in turn, is interpreted in terms of common origin or source. Cluster II includes two sub-clusters: subcluster A comprises Ca^{2+}, Na^+, Cl^- and SO_4^{2-}, whereas subcluster b includes pH, K^+, Mg^{2+} and HCO_3^-. Each subcluster has a high degree of similarity and homogeneity, and the degree of heterogeneity and dissimilarity with other clusters. Grouping of subclusters in one cluster depends on the degree of similarity of parameters and in turn, reports positive good to a strong correlation between term. The

parameters in cluster III are influenced by common lithogenic origin, and in turn, result in the dominant groundwater type in the Waffa region. This type is earth alkaline (Ca and Mg) with sulfate prevalence over chloride. The dendrogram of groundwater parameters in the Kubaysa region showed two major clusters I and II. Cluster I includes EC and TDS. Cluster II consists of three subclusters 1, 2 and 3. Subcluster 1 include Cl^-, sub-cluster 2 includes Ca^{2+}, Na^+ and SO_4^{2-}, and subcluster 3 contains K^+, Mg^{2+} HCO_3^- and pH. Grouping of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (Cl^-, HCO_3^- and SO_4^{2-}) in one cluster reflects positive correlations between them which in turn suggests the common source. Due to cluster analysis, the groundwater in the Kubaysa region is of Ca^{2+} and Mg^{2+} with chloride prevalence over sulfate and increases the portion of alkalis especially, Na^+ (Fig. 6).
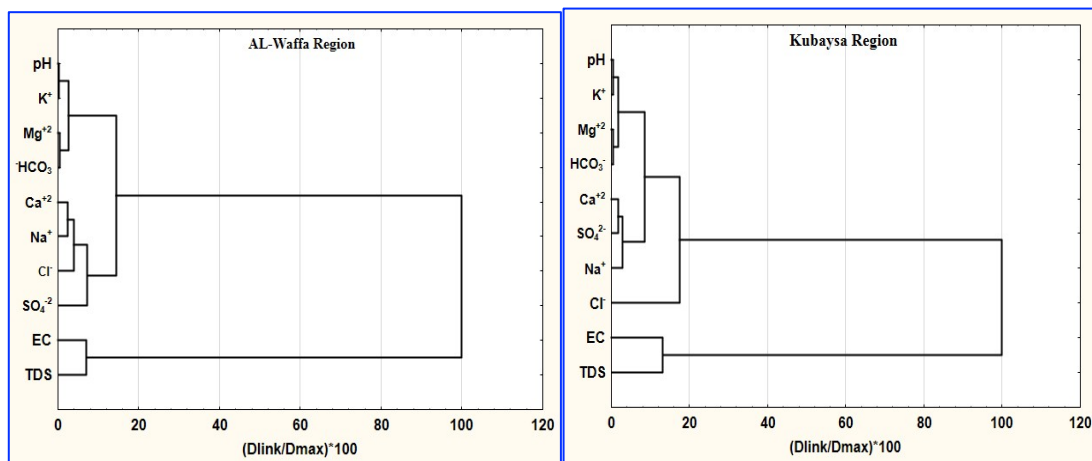
Fig. 6. Dendrogram of the cluster analysis of the groundwater in Al-Waffa and Kubaysa regions

Principle Components Analysis

The principle components analysis analyzes a data table expressive observ.ations described by several dependent variables, which are generally inter-correlated. The goal of PCA is to excerpt significant information as a set of unconcluded variables. These variables are called principle components, factors, eigenvectors, or loadings. Each unit gives a score that corresponds to its forecast on the components. The results of the analysis obtained are presented with graphs plotting the projections of the units on the components and loading the variables. The proportion of variance explained and the projection of each component express the importance of each component (Abdi, 2003).

Table 3. Correlation coefficient of groundwater quality parameters in Al-Waffa region

	Tem	Tur	pH	EC	TDS	TSS	DO	COD	TH	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	F$^-$	HCO$_3^-$	Cl$^-$	So$_4^{2-}$	No$_3^-$	SiO$_2$
Tem	1.00																		
Turb	0.12	1.00																	
pH	0.05	-0.23	1.00																
EC	-0.03	0.00	0.10	1.00															
TDS	-0.12	0.00	-0.03	**0.82***	1.00														
TSS	0.10	0.62	-0.21	-0.10	0.01	1.00													
DO	-0.28	-0.18	-0.31	-0.17	-0.09	-0.11	1.00												
COD	0.52	0.08	-0.09	-0.19	-0.16	0.24	-0.04	1.00											
TH	-0.12	0.06	-0.29	0.45	0.61	0.17	-0.14	-0.07	1.00										
Ca^{2+}	-0.13	0.05	-0.42	0.18	0.40	0.09	-0.03	-0.07	**0.90***	1.00									
Mg^{2+}	-0.01	0.03	0.17	0.69	0.60	0.20	-0.26	-0.01	0.48	0.06	1.00								
Na$^+$	0.11	-0.01	0.31	**0.70***	0.62	-0.05	-0.12	-0.01	-0.09	-0.33	0.47	1.00							
K$^+$	-0.03	-0.06	0.21	0.60	0.56	-0.05	-0.06	-0.15	-0.10	0.29-	0.36	**0.82***	1.00						
F$^-$	-0.41	-0.24	0.02	0.20	0.23	-0.16	0.34	0.19	0.22	0.13	0.24	-0.00	0.07	1.00					
HCO$_3^-$	0.00	0.11	-0.06	0.52	0.45	0.03	-0.18	-0.01	0.66	0.49	0.52	0.08	0.10	0.04	1.00				
Cl$^-$	-0.02	0.01	0.27	**0.71***	0.57	-0.00	-0.41	-0.17	0.09	-0.15	0.55	0.83	0.56	0.12	0.14	1.00			
SO$_4^{2-}$	-0.09	0.10	-0.33	0.42	0.54	0.21	-0.03	0.03	0.77*	0.64	0.48	-0.01	0.06	0.15	0.46	-0.00	1.00		
NO$_3^-$	0.04	-0.09	-0.13	0.51	0.76*	0.02	0.13-	-0.01	0.63	0.55	0.35	0.30	0.34	0.10	0.44	0.11	0.46	1.00	
SiO$_2$	-0.00	0.05	-0.09	0.07	-0.02	-0.05	-0.07	-0.09	-0.12	0.17	-0.06	-0.18	-0.16	0.19	-0.08	-0.06	0.09	-0.04	1.00

[*]Correlation is signification at the 0.01 level (1 tailed)

Table 4. Correlation coefficient of groundwater quality parameters in Kubaysa region

	Tem	Tur	pH	EC	TDS	TSS	DO	COD	TH	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	NH$_4^+$	F$^-$	HCO$_3^-$	Cl$^-$	So$_4^{2-}$	S^{2-}	SiO$_2$
Tem	1.00																			
Turb	0.00	1.00																		
pH	-0.42	0.07	1.00																	
EC	-0.35	0.15	-0.06	1.00																
TDS	-0.23	0.19	-0.08	**0.87***	1.00															
TSS	0.00	**0.99***	0.08	0.14	0.19	1.00														
DO	-0.26	0.10	0.44	-0.05	-0.06	0.09	1.00													
COD	-0.31	0.02	0.11	0.21	0.14	-0.00	-0.12	1.00												
TH	-0.10	0.19	-0.07	**0.75***	**0.93***	0.19	-0.15	0.18	1.00											
Ca^{2+}	-0.13	0.19	-0.06	**0.77***	**0.94***	0.19	-0.11	0.17	**0.98***	1.00										
Mg^{2+}	-0.09	-0.16	-0.06	0.57	**0.77***	-0.15	-0.19	0.14	**0.84***	**0.78***	1.00									
Na+	-0.17	0.21	-0.15	**0.86***	**0.88***	0.19	-0.06	0.07	**0.77***	**0.79***	0.55	1.00								
K+	0.55	0.29	0.11	**0.89***	**0.84***	0.29	0.04	0.25	**0.70***	**0.72***	0.48	**0.81***	1.00							
NH$_4^+$	0.16	-0.27	-0.28	-0.06	-0.12	-0.27	-0.13	-0.23	-0.17	-0.20	0.02	-0.01	-0.13	1.00						
F-	0.10	-0.26	-0.14	0.41	0.29	-0.26	-0.03	-0.05	0.24	0.22	0.37	0.28	0.18	0.26	1.00					
HCO$_3^-$	-0.43	0.15	0.03	0.34	0.21	0.15	-0.11	0.21	0.14	0.19	-0.03	0.26	0.41	-0.02	-0.39	1.00				
Cl$^-$	-0.12	0.09	-0.17	**0.84***	**0.93***	0.08	-0.12	0.15	**0.88***	**0.89***	**0.72***	**0.93**	**0.76***	0.00	0.28	0.24	1.00			
SO$_4^{2-}$	0.30	0.28	0.11	**0.72***	**0.84***	0.29	-0.09	0.16	**0.84***	**0.83***	**0.73***	0.63	**0.74***	-0.31	0.32	0.04	0.66	1.00		
S^{2-}	-0.22	-0.26	-0.04	-0.20	-0.41	-0.27	0.28	-0.06	-0.57	-0.53	-0.50	-0.24	-0.15	0.35	-0.10	0.17	-0.31	-0.59	1.00	
SiO$_2$	-0.45	-0.01	0.22	0.63	**0.72***	-0.00	0.06	0.29	**0.75***	**0.75***	**0.70***	0.51	0.65	-0.26	0.28	0.11	0.61	**0.79***	0.48	1.00

*Correlation is signification at the 0.01 level (1 tailed)

Principle components analysis was carried out on the data set of 10 water quality parameters in AL-Waffa, and Kubaysa regions and factor loadings were generated (Tables 5 and 6). Both tables show the loading for varimax rotated factor matrix, the eigenvalues, the percentage of variance, and the cumulative percentage of the rotated. The variance associated with each other. Based on the eigenvalues (>1), three factors evolved and explained 81.57% and 87.28% of the total variance in the hydrochemistry of AL-Waffa and Kubaysa, respectively. In AL-Waffa region, factor 1 explains 43.75% of the total variance and has strong positive loadings on E C, TDS, Mg^{2+}, Na^+, and Cl^-. The strong positive loading indicates a strong linear correlation between factors and EC, TDS, Mg^{2+}, Na^+, and Cl^-. This factor reflects the role of geogenic processes such as the dissolution of some dolomitic and evaporates minerals in the aquifer system. Factor 2 explains 27.24% of the data set and has strong positive loadings on Ca^{2+} and SO_4^{2-}. High positive loadings indicated a strong linear correlation between the factor and Ca^{2+} and SO_4^{2-}. This factor can be interpreted in terms of the dissolution of gypsum and anhydrite in the study area as a source of 10.58% of the total variance loadings on K^+. This factor reflects the dissolution of evaporate minerals in the aquifer system as a source of K^+. The combination of factors 1 and 2 is recognized as natural factors that indicate major processes determining the groundwater type and hydrochemical facies. Based on above mentioned, the the groundwater type is alkaline earth (Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-) and alkaline earth (Ca^{2+} and Mg^{2+}) exceed alkalis (Na^+ and K^+). We suggest using principle components analysis as an alternative method to evaluate the groundwater types.

Table 5. Factor loadings of groundwater quality parameters in Al-affa region

Variable	Factor 1	Factor 2	Factor 3
pH	0.36	-0.57	0.20
EC	**0.90***	0.06	0.10
TDS	**0.82***	0.39	0.27
Ca^{2+}	0.09	**0.84***	-0.34
Mg^{2+}	**0.86***	0.18	0.24
Na^+	**0.74***	-0.29	0.53
K^+	0.27	-0.11	**0.91***
Cl^-	**0.84***	-0.39	-0.03
HCO_3^-	0.38	0.63	-0.14
SO_4^{2-}	-0.05	**0.88***	0.32
Eigenvalue	4.37	2.72	1.05
% Total variance	43.75	27.24	10.58
%Cumulative	43.75	70.99	81.57

*Marked loadings are > 0.70.

Results of the principle component analysis of groundwater parameters in the Kubaysa region (Table 5) showed three factors explaining 87.28% of the total variance. Factor 1 explains 64.93% of the total variance and has strong positive loadings on EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}. These high positive loadings reflect a strong linear correlation between factor 1 and groundwater parameters. The factor 1 reflects the role of chemical weathering processes such as the dissolution of carbonate, dolomitic and evaporitic rocks prevailing in the study region. The results of this chemical weathering influenced groundwater chemistry and its type in the Kubaysa region. Based on the high positive loadings of Ca^{2+} (0.90), Mg^{2+} (0.79), Na^+ (0.91), K^+ (0.87), Cl^- (0.94), and SO_4^{2-} (0.85), the groundwater type is alkaline earth (Ca^{2+} and Mg^{2+}) with increase portion of alkalis (Na^+ and K^+) and with chloride prevalence over sulphate. Factor 2 explains 12.31% of the total variance and has strong positive loading on HCO_3^-. Factor 3 explains 10.04% of the total variance and has strong negative loading on pH. Based on the mentioned above, we suggest using cluster and principle components analysis to determine the groundwater types and hydrochemical facies as an alternate method for the piper method.

Table 6. Factor loadings (varimax rotation) of groundwater quality parameters in the Kubaysa region

Variable	Factor 1	Factor 2	Factor 3
pH	-0.04	-0.01	**-0.98**[*]
EC	**0.83**[*]	0.43	0.06
TDS	**0.97**[*]	0.14	0.07
Ca^{2+}	**0.90**[*]	0.21	0.15
Mg^{2+}	**0.79**[*]	0.27	0.08
Na^+	**0.91**[*]	-0.08	-0.03
K^+	**0.87**[*]	-0.10	-0.25
Cl^-	**0.94**[*]	-0.05	0.08
HCO_3^-	0.07	**0.96**[*]	0.00
SO_4^{2-}	**0.85**[*]	0.18	0.03
Eigenvalue	6.49	1.23	1.00
% Total variance	64.93	12.31	10.04
% Cumulative	64.93	77.24	87.28

*Marked loadings are > 0.70

CONCLUSIONS

In the present paper, physicochemical parameters of the samples collected from 20 well points in two areas are evaluated and compared with World Health Organization standards. It is

found that the mean values of the majority of physicochemical parameters exceed the permissible limits. The high concentrations of cations and anions in the groundwater of the study area may be due to change of oxidation and reduction conditions, and also to the natural geogenic influences of infiltration and pervade. The findings obtained from this assessment have shown that the groundwater of the study area is unacceptable for drinking water. The predominant type of groundwater in Al –Waffa an Kubaysa areas is earth alkaline water with prevailing sulphate and chloride. The positive strong correlation coefficient of Ca^{2+}, Mg^{2+} with SO_4^{2-}, Cl^- of ALWafaa area and Ca^{2+}, Mg^{2+} with Cl^-, SO_4^{2-} of kubaysa agreed with the subclusters snd cluster of HCA and factors of PCA of these ions and can contribute to determining the type of groundwater as an alternative method with piper diagram.

ACKNOWLEDGMENTS

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