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A combined hydrochemical-statistical analysis of Saq aquifer, northwestern part of the Kingdom of Saudi Arabia

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ABSTRACT: The present study includes detailed hydrochemical assessment of groundwater resources of Saq aquifer. The Saq aquifer covers a large area (about 375,000 km²) and lies in the arid region with low annual rainfall and extremely high evaporation. In the study area, groundwater serves as the major source for agricultural activity and for domestic usages. A total of 295 groundwater samples collected and were analyzed for physico-chemical parameters such as hydrogen ion concentration (pH), total dissolved solids (TDS) and electrical conductivity (EC) , sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) ,bicarbonate (HCO_3) chloride (Cl^-), sulfate (SO_4^{2-}) and nitrate (NO_3). The goal and challenge for the statistical overview was to delineate chemical distributions in a complex, heterogeneous set of data spanning over a large geographic range. After de-clustering to create a uniform spatial sample distribution with 295 samples, histograms and quantile-quantile (Q-Q) plots were employed to delineate subpopulations that have coherent chemical affinities. The elements showing significantly higher positive correlation are: TDS with EC; Ca with EC, TDS; Mg and EC, TDS, Ca, K; Cl and EC, TDS, Mg, Na, Ca; SO_4 and EC, TDS, Ca, Cl, Na, Mg. The distribution of major ions in the groundwater is $Na^+ > Ca^{++} > Mg^{++} > K^+$ and $Cl^- > SO_4^{-2} > HCO_3^- > NO_3^-$. Ionic abundance plot of alkalis with Ca and Mg is suggestive of mix type trends of concentrations as evident by moderate correlation (r = 0.57). About 60% of the total samples have alkalis abundance and rests have more Ca + Mg concentrations than alkalis. Taking both results of cluster tree and geochemical features of variables into consideration, the authors classify the elements into two major groups, the first includes TDS, Na, EC, Cl, Ca, SO_4, and Mg, where the relationship within the group are strong. The second group includes K, HCO_3, pH, and NO_3. This group has close relationship with group 1 demonstrate that, the increase in the concentration to some elements could be the same. Some of the analyzed parameters approach a normal distribution, as both their skewnesses and kurtoses reach close to "0". The study revealed that, all of the element pairs exhibit positive relations.

Key words: hydrochemistry, statistical analysis, Histograms, normal quantile plots, Saq aquifer, Saudi Arabia

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1. INTRODUCTION

Ground water is the major source of water supply for drinking, irrigation, and industrial purposes. Groundwater contamination includes natural sources or anthropogenic influences. The quality of groundwater is affected by residential, municipal, commercial, industrial, and agricultural activities. Contamination of groundwater results in poor groundwater quality, loss of water supply, high cleanup costs, high costs for alternative water supplies, and/or potential health problems, (Bilgehan et al., 2010). The selected study area is Saq aquifer area is located in the northwestern part of the Kingdom of Saudi Arabia. Focusing on the Saq aquifer which is covering vast area in the northwestern part of the Kingdom of Saudi Arabia, this research works attempts to study the hydrochemical properties and quality of groundwater. Statistical techniques applied to help in data interpretations, (MWE, 2008).

The groundwater resources of the Saq study area, covering 375,000 km^2 in the northern part of the Kingdom of Saudi Arabia (Fig. 1) are intensively exploited. The current rate of groundwater abstraction by far exceeds the rate of groundwater recharge. As the wells tapping the various aquifers of the region are unevenly distributed, the consequences of this unbalanced groundwater exploitation vary from one part of the Saq study area to another. Schematically, water levels of the main aquifers have dropped sharply over the past three decades in areas where groundwater abstractions are concentrated, but show little or no decline elsewhere.

The absence of a declining trend in a specific aquifer or a specific area is not an indicator of groundwater sustainability. Due to its very large lateral and vertical extent, the multi-layer aquifer system of the Saq study area reacts slowly to any stresses imposed on it, and declining trends expand only gradually outside the abstraction areas and towards overlying or underlying aquifers, (MWE, 2008).

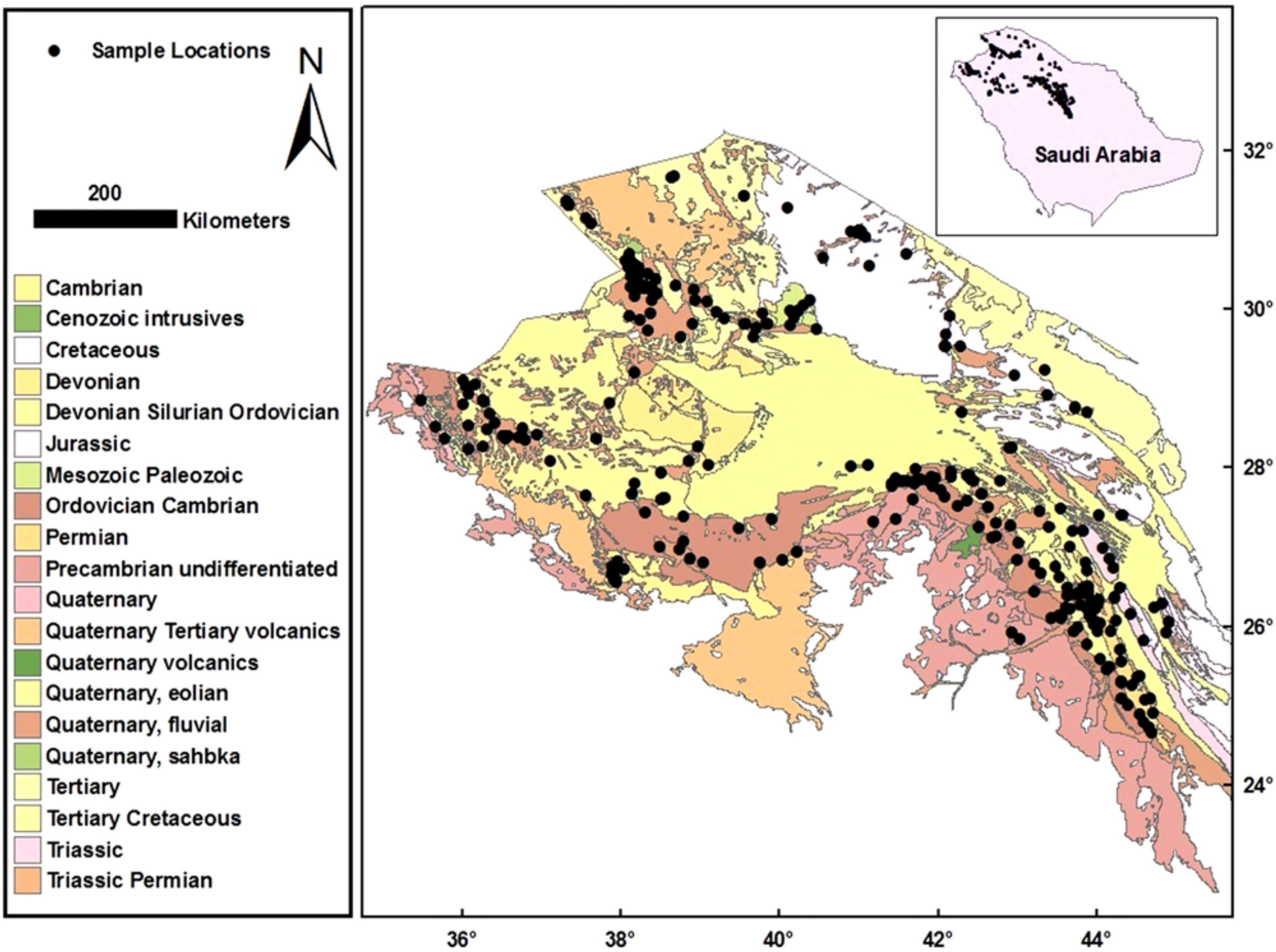

Fig. 1. Location, Sampling locations and geological map of Saq aquifer in Northwestern part of Saudi Arabia.

Statistical applications in hydrochemical studies weres carried out by many researches e.g., Zang et al. (2008), Cloutier et al. (2008), and Garcia et al. (2001). All those studies applied the statistical methods to link between the chemical elements and sources of pollutions. In the present study the statistical methods such as histograms used to analyze the data distribution, while quantile plot used for each interval variable for visualizing the extent to which variables is normally distributed. Also Kolmogorov-Smirnov (K-S) test used to measure the degree to which a given data set follows a specific theoretical distribution. So far the technology here is not employed to characterize Saq aquifer chemistry which will further help in decision making plans.

Considering the complexity of the water balance in the Saq multi-layer aquifer system, with water leakage between the various aquifers and the relatively large de-stockage of the aquifer and aquitard water, accurate long-term predictions on the evolution of the aquifer system require a groundwater mathematical model covering the full extent of the Saq system. Impact of human interactions on the Saq aquifer is posing serious threats for groundwater sustainability. Beside excessive abstraction, groundwater quality is being deteriorating day by day. The present study main aim is to deal with detailed hydrochemical characterization of the Saq aquifer using classical and statistical methods.

2. STUDY AREA DESCRIPTIONS

2.1. Study Area

The selected study area in the present research proposal is Saq aquifer area is located in the northwestern part of the Kingdom of Saudi Arabia. The Saq Sandstones in Saudi Arabia are separated by the vast aeolian Nafud Desert and can be divided into the eastern Qassim-Ha'il region1 with natural groundwater flow towards the north-east, and the western Tabuk-Tayma region where the flow direction is generally northward (BRGM, 1985).The groundwater resources of the Saq study area, covering 375,000 km^2 in the northern part of the Kingdom of Saudi Arabia (Fig. 1).

2.2. Geology

The Arabian Peninsula can be divided into two main geological units. The western part is occupied by Precambrian rocks of the Arabian Shield. In the central and eastern part of the peninsula, a succession of continental and shallow-marine sedimentary rocks of the Arabian Shelf overlies the Precambrian basement. This succession consists mainly of sandstone and limestone that are exposed in a great curved belt along the eastern margin of the Shield. The western boundary of the area is marked by the contact between Precambrian basement and the overlying sedimentary rocks of the Arabian Shelf. The sedimentary cover is composed of a thick succession of formations ranging in age from Cambrian-Ordovician to Quaternary. Tilting of the Precambrian basement resulted in a gentle dip of the sedimentary strata to the east. The Saq Sandstone is found at the base of the sedimentary sequence and crops out in a strip adjacent to the basement, following the S-shape of the Arabian Shield (Fig. 1). Moving away from the contact with the basement towards the east, the overlying formations appear one after the other in chronological order, (MWE, 2008).

2.3. Topography

Among the sedimentary formations, the less resistant strata have been eroded into a series of lowland strips and the more resistant sedimentary strata form escarpments. The highest elevations are encountered in the mountains along the western boundary, from the border with Jordan down to Al Ula, where harrats (basalt plateau) form the crest line at elevations above 1,800 m above mean sea level (msl) with Jabal al Juhayyir (36°43′20″E / 27°38′40″N) reaching 2,111 m msl. The boundary of Saq area, defined by the contact between Saq Sandstone and basement rocks, does not coincide with the crest line as Saq Sandstone is exposed west of the harrats. As a result, along the western boundary of the Saq area the surface-water drainage basins do not match with the groundwater basin.

The mountains along the western boundary of Saq area are bordered to the east by the Tabuk and Al Ula valleys with flat valley-bottoms at an elevation around 800 m msl. Farther to the east a second ridge stretches from the Jordanian border southward, passing east of Tabuk and then between Al Ula and Tayma, reaching elevations slightly above 1,000 m in the central part with peaks above 1,200 m msl in the northern and southern part. The area to the east of this second ridge, representing 85% of the Saq aquifer's area and is characterized by a flat topography gently dipping eastward from elevations near 900 m msl in the west to below 400 m msl along the eastern boundary (MWE, 2008).

2.4. Climate and Hydrogeological Setting

The climate in the entire Saq area is arid with low annual rainfall. Nevertheless some local differences exist, with the lowest mean annual rainfall (less than 30 mm/year) being encountered in the western part of the area (Tabuk region) and the highest rainfall in the southeastern part (170 mm/year). With such a low rainfall and extremely high potential evapotranspiration of approximately 2,400 mm/year, groundwater recharge can only occur where concentration of runoff waters coincides with favourable infiltration characteristics of the surface layers.

At a regional level, groundwater recharge has been assessed at 2.5 mm/year for the Saq Sandstone outcrops south of Tayma (MWE, 2008). At the scale of the entire Saq area, groundwater recharge most probably does not exceed 5 mm/year (MWE, 2008).

Historical data on groundwater use are provided by BRGM (1985). An updated evaluation of groundwater abstractions for the year 2005 has been realized as part of this study. The total groundwater volume abstracted in the Saq area in 2005 (8,727 Mm^3/year) equals a water column of 24 mm covering the entire Saq area (~370,000 km^2). This is 5 to 10 times higher than the recharge occurring during the same period and is therefore it is not accorded with sustainable development (MWE, 2008).

Hydrogeologically, there are seven aquifers or aquifer groups, from bottom to top:

- Saq Sandstone
- Kahfah sandstone
- Quwarah - Sarah sandstones
- Sharawra and Tawil sandstones
- Jubah sandstone
- Khuff limestone
- Secondary (Mesozoic)-Tertiary-Quaternary (STQ) sandstone and limestone.

Two layers act regionally as aquitards but they contain units that are locally exploited as aquifer:

- Jauf limestone and sandstone;
- Unayzah and Berwath sandstones.

3. METHODS

A total of 283 samples of groundwater were collected for chemical analysis from different boreholes in the Saq aquifer area, Saudi Arabia (Fig. 1). Samples were collected in polyethylene bottles of one-liter capacity. Prior to their filling with sampled water, these bottles were rinsed to minimize the chance of any contamination. The samples preservation and the used of analytical techniques were in accordance with the standard methods from American Public Health Association (APHA, 1995). Unstable parameters such as hydrogen ion concentration (pH), total dissolved solids (TDS) and electrical conductivity (EC) were determined at the sampling sites with the help of a pH-meter, a portable EC-meter and a TDS-meter (Hanna Instruments, Michigan, USA). The Sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) ions were determined by atomic absorption spectrophotometer (AAS). Bicarbonate (HCO_3^-) and chloride

(Cl^-) were analyzed by volumetric methods. Sulfate (SO_4^{2-}) was estimated by the colorimetric and turbidimetric methods. Silicon dioxide (SiO_2) was calorimetrically analyzed by ammonium molibdate method. Nitrate (NO_3^-) was measured by ionic chromatography. A statistical of physco-chemical parameters was presented and explained in relation to human consumption criteria (WHO, 2011). Groundwater genesis was explained using various bi-variate plots.

For present study statistical analyses were carried out using descriptive statistics, histograms and normal quantile plots. The main statistical software in use was SPSS 15 software package (SPSS Inc., 2006) and JMPIN (version 4.0.4).

Histograms are used to analyze the data distribution; they are tools for displaying frequency distributions and rely on dividing the data into classes (or bins). The data following a normal distribution will show a symmetric bell-shaped histogram, where a tail towards high values implies that the data are positively skewed. Histograms provide visual approximations to distributions like the bell shape of a normal distribution, but they have some limitations. The number of bins affects the shape of the curve and this number can be determined by the software. A curve representing the normal distribution corresponding to the mean and standard deviation of the data set is superimposed on the histogram for the purpose of comparison. Extreme values occur at the high end, and they are separated and identified as outliers in order to show the major tendency of the data. The limitations of the histograms are offset by normal quantile plots.

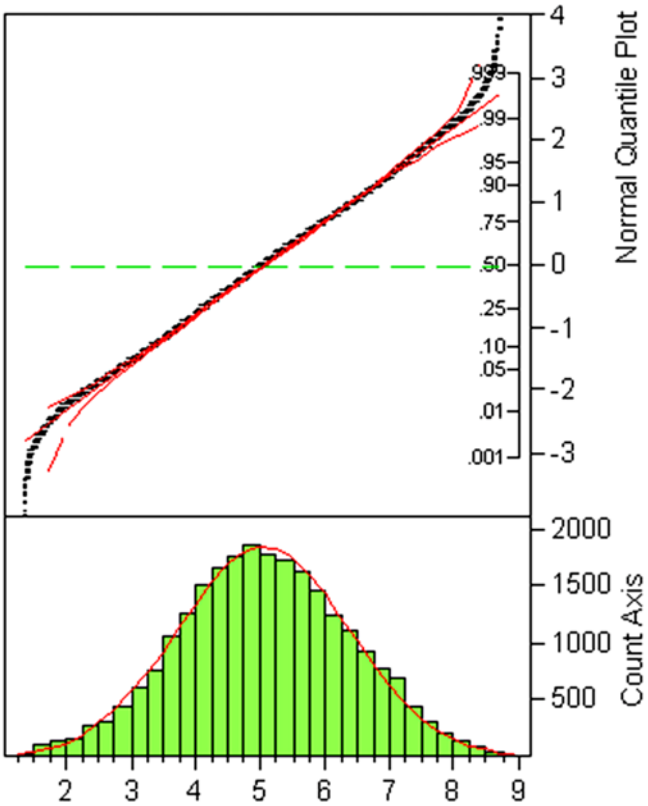

Fig. 2. Histogram and normal quantile diagram.

The normal quantile plot is graph for each interval variable, which is useful for visualizing the extent to which the variable is normally distributed. If a variable is normal, the normal quantile plot is a diagonal straight line. This plot is also referred to as a theoretical quantile-quantile plot or Q-Q plot. Normal quantile-quantile (Q-Q) plots are created by plotting observed values of a variable against the corresponding normal quantiles. Display of data is done by plotting the normal quantiles (or scores) of the standard normal distribution on the y-axis with values usually between –4 to 4, and the variable under study on the x-axis (Fig. 2).

The Kolmogorov-Smirnov (K-S) test measures the degree to which a given data set follows a specific theoretical distribution (such as normal, uniform, or Poisson). The statistical test of K-S is based on the largest absolute difference between the observed and the theoretical cumulative distribution functions. The K-S test assumes that the parameters (e.g., mean and standard deviation) of the test distribution are specified in advance, whereas the Lilliefors correction for the K-S test is applied when means and variances are not known and must be estimated from the data.

Results were obtained for K-S test values performed by SPSS statistical software which utilized the Lillierfos correction automatically. If the p-value reported is less than 0.05 (or some other alpha), then the distribution is not normal (Sall and Lehman, 1996). Therefore it is useful to use the normal quantile plot to help assess the lack of normality in the distribution.

The authors therefore used the K-S test to minimize the effect of outlier populations for many of the elements. During comparison studies, discrepant results were obtained for K-S test values performed by SPSS and S-Plus statistical software. The problem was resolved when it was found that the K-S results obtained with the S-Plus application automatically utilized the Lilliefors correction. For comparison, the Lilliefors significance correction for the K-S test using SPSS was also applied. This method best applied by Zhang et al. (2008). The raw data were stored in a dBASE file (dbf format), and basic calculations were performed using Microsoft Excel. Most of the statistical calculations were accomplished with SPSS software (version 11.0). The sampling location maps were produced with ArcView GIS software (version 3.3).

4. RESULTS AND DISCUSSIONS

4.1. Hydrochemistry

The waters are slightly acidic to alkaline with pH values ranging from 6.4 to 9.6. Electrical conductivity (EC) ranges from 284 to 9902 μS/cm, with an average of 1599.4 μS/cm. About 31% of the samples are crossing the maximum permissible limit of EC (1,500 μS/cm). The large variation in EC values is attributed to geochemical evolution of groundwater through rock-water interaction during long resident time period and the anthropogenic influences. The total dissolved solids (TDS) were measured through summing up all major ions concentrations which range of 195.5–6771.7 mg/L with an average value of 1072 mg/L. Only 27% sample has TDS value <500 mg/L. As per TDS classification, 29% of the wells are brackish (TDS > 1,000) water type and 44% wells are fresh (TDS < 1,000) water (Freeze and Cherry, 1979).

The distribution of major ions in the groundwater is $Na^+ > Ca^{++} > Mg^{++} > K^+$ and $Cl^- > SO_4^{-2} > HCO_3 > NO_3$. The concentration of Na^+ shows a large variation from 3.8 to 1640 mg/L, averaging 177.4 mg/L. About 23% of samples have Na values greater than permissible limit of 200 mg/L. The concentration of Ca^{2+} in the study area ranges from 17 to 820 mg/L with an average of 111.4 mg/L. As per WHO (2011) standards, 45% of the samples from this study exceed the permissible limit of 75 mg/L, The major source of Ca^{2+} in the groundwater is due to ion exchange of minerals from rocks of this area. Further, this may also be due to the presence of $CaCO_3$ and $CaSO_4$ minerals present in the soil horizon, Gypsum, anhydrite, dolomite etc. The concentration of Mg^{2+} ranges from 1.1 to 335.5 mg/L with an average value of 36.5 mg/L. Most of the Mg^{2+} concentrations (81%) are within the desirable limit of 50 mg/L. The concentration of K^+ ranges from 0.9 to 91 mg/L with an average value of 15 mg/L.

The Cl^- concentration ranges from 12.9 to 2622 mg/L, averaging 295.9 mg/L. About 45% sample has Cl^- concentration more than the permissible limit of 200 mg/L. The

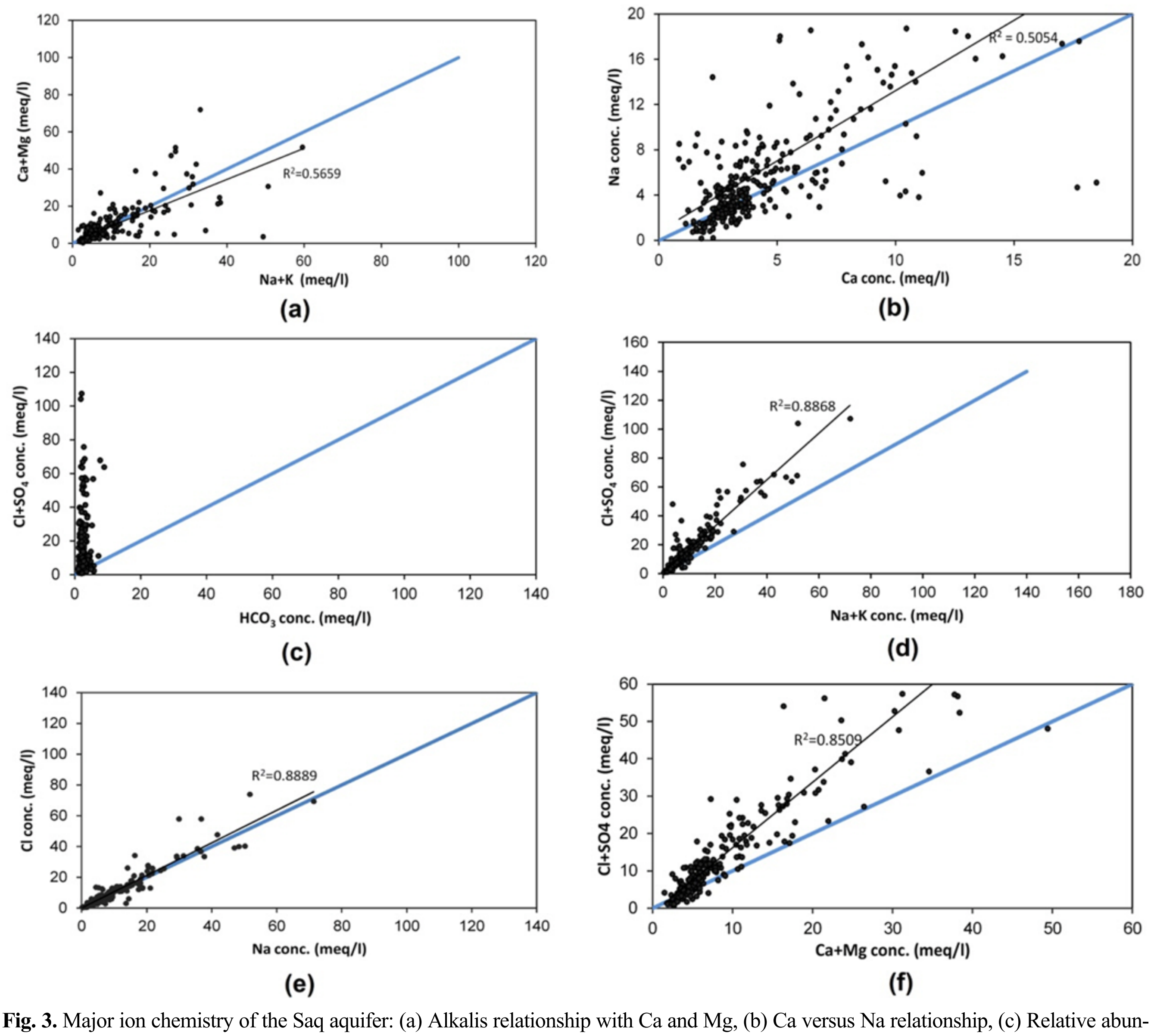

Fig. 3. Major ion chemistry of the Saq aquifer: (a) Alkalis relationship with Ca and Mg, (b) Ca versus Na relationship, (c) Relative abundance of weak (HCO_3) and strong ($Cl + SO_4$) acids, (d) Bonding affinity between Alkalis and $Cl + SO_4$, (e) Bonding relationship of Na-Cl, (f) Relationship of Ca + Mg with $Cl + SO_4$.

sulphate concentration range from 15.1 to 2120 mg/L, with an average value of 256.4 mg/L. Out of the total 32% sample has SO_4 concentration greater than the permissible limit of 200 mg/L. The HCO_3 concentration ranges from 65 to 543 mg/L with an average of 149.1 mg/L. The NO_3 concentration ranges from 0.4 to 318.2 with an average of 30.3 mg/L. As much as 19% sample has more than permissible NO_3 concentration (45 mg/L).

Hardness of groundwater results from the presence of divalent metallic cations of which concentration of Ca^{2+}, Mg^{2+}, are most abundant in groundwater. Adopting Sawyer and McCarty (1967) classification criteria, only 8% sample classified as moderately hard type. The remaining 50% and 42% samples classified to 'hard' and 'very hard' water classes.

Ionic concentrations of major elements present in groundwater were analysed for relative abundances and ionic affinity. Ionic abundance plot of alkalis with Ca + Mg is suggestive of mix type trends of concentrations as evident by moderate correlation ($r = 0.57$). About 60% of the total samples have alkalis abundance and rests have more Ca + Mg concentrations than alkalis (Fig. 3). Predominance of Ca and Mg over Na and K and abundances of Na with Ca concentration, individually (Fig. 3) are indicative of ion-exchange reactions (Subba Rao, 2012).

Relative abundance of anionic facies wase examined (Fig. 3); where Cl + SO_4 is in far more abundant than HCO_3. Ionic affinity relationships were tested first between ionic pairs having primary affinity. The plot of Cl + SO_4 concentrations against HCO_3 (Fig. 3) shows that majority of samples have excess Cl and SO_4. Cl + SO_4 ratio (<1) which can be use to present fresh recharge or meteoric nature of groundwater suggested that only 9 samples (5 Saq, 2 Jauf, 1 Tawil and 1 Kahfah) show meteoric nature. Nonetheless, predominance of Ca + Mg over HCO_3 could relate its genesis through extreme aridity and carbonate weathering (Al-Amry, 2008), ion exchange at favorable lithology (Al-Bassam et al., 1997) and lack of periodic rainfall recharge. Further, ion exchange in groundwater and host environment can be inferred through Chloro-alkaline indices (CAI) using equivalent concentrations of Cl, Na, K, SO_4, HCO_3, CO_3 and NO_3 (CAI-1 and CAI-2) (Schoeller, 1965). The positive indices (in 96% sample) decipher Base Exchange reactions i.e., exchange of Na and K in water with Mg and Ca at host environment (Shoeller, 1965; Garcia et al., 2001). The base exchange causes changes in the physical properties of soils causing deflocculating and permeability reduction (Todd, 1980).

Alkalis have bonding affinity with Cl and SO_4, show good correlation with Cl and SO_4 ($r = 0.88$) and also suggests that almost all alkalis are consumed while bonding with Cl and SO_4 (Fig. 3). A good correlation indicates that this trend evolved from a common source which is lithology of country rocks rather than anthropogenic origin (Subba Rao, 2012). The meteoric genesis index (MGI) expressed by $Na^+ + K^+ - Cl^- / SO_4^{2-}$; where all concentrations are in meq/l, helps in determining whether groundwater source is of deep meteoric water percolation type (MGI < 1) or shallow meteoric water percolation type (MGI > 1) (Soltan, 1998). The meteoric genesis indices demonstrated that most of the sample (96%) belongs to a deep meteoric water percolation type. Further, plot of Na with Cl shows a very good correlation ($r = 0.9$) indicating that halite dissolution could be the source of groundwater genesis. Besides, halite dissolution, the high Na/Cl ratios in groundwater may be explained by Na being derived predominantly from weathering of plagioclase in the overlying basaltic terrain. Samples away from 1:1 line on either sides are suggestive of excess concentrations and possibility to have secondary bonding affinity; Na with HCO_3 and Cl with Ca.

The SO_4 is showing a good correlation with Ca ($r = 0.80$) and with Mg ($r = 0.78$) suggests a possibility of originating from source rocks containing dolomites and gypsum (Table 2). Apart from natural and geogenic processes, SO_4 enrichment may enters groundwater system through different anthropogenic activity including sewage pollution, industrial wastes, specialized fertilizers etc. The spatial distribution of NO_3, further advocates the widespread anthropogenic influence on groundwater irrespective of lithology and depth.

4.2. Histograms and Normal Quantile Diagrams

Probabilistic display delineates discrete populations that have genetic or other affinities as line segments showing changes in slope (i.e., kinks). The observed distributions differ significantly from the synthetic distributions modeled by Sinclair (1974) and Zhang et al. (2008) for chemical distributions. These pioneering authors appeared to superimpose different types of distributions having the same concentration range, which yielded curved changes in slope. The present data include elemental distributions with substantial overlap and curvatures. However, notable features are, in fact, the prominent role of line segments showing sharp angular change. Such features require largely discrete chemical subpopulations.

Histograms of data are shown in (Fig. 4) some elements have high values, which are reflected in the histograms by data being located on the right of the diagram (Fig. 4). These extreme values are well visualized on the normal quantile diagrams, and they are identified as outliers. Some elements have values below or close to the detection limits (e.g., Na, K, Cl, NO_3 and SO_4) resulting in the high frequencies for the lowest value group, near that limit of detection.

The frequency distributions of some of the elements are positively skewed and include some very high values. Some extreme values appear (Cl, Mg, Na, EC, TDS, Ca, HCO_3, K, SO_4 and NO_3) to be separated from the majority of the samples, and do not appear to be part of a continuous distribution (Fig. 4, Table 1). These extreme values might be regarded as evidence of natural or anthropogenic processes.

The normal quantile diagrams for data are shown in (Fig. 4). The straight-line segments are observed for some elements

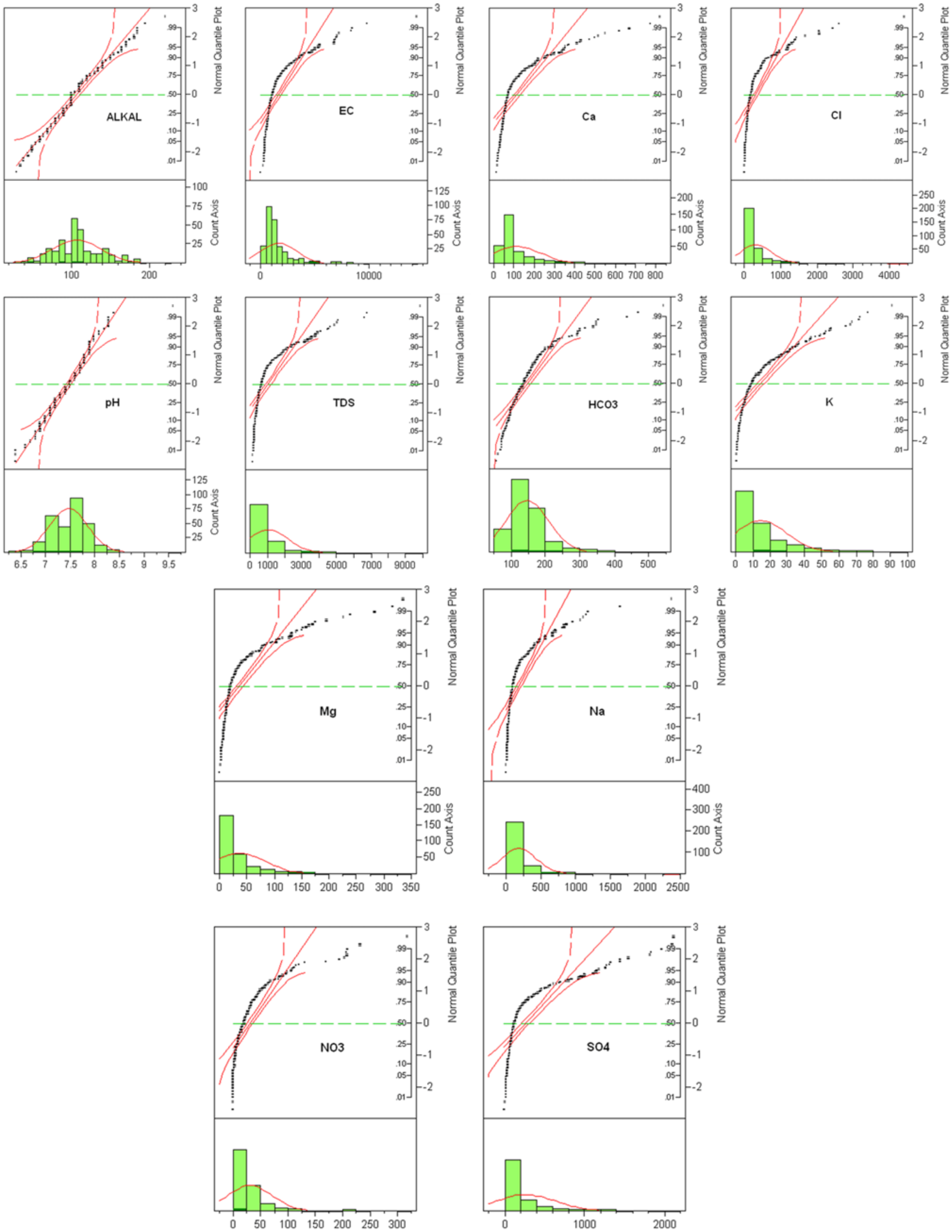

Fig. 4. Normal quantile plots (the normal quantiles are plotted on the y-axis; the observed values are plotted on the x-axis EC in [µS/cm]; chemical elements are in mg/L) and Histograms for the data set (a normal distribution curve for all the values is superimposed for comparison; EC in [µS/cm]; chemical elements are in mg/L).

Table 1. Statistical summary of groundwater quality parameters for the study area

Parameter	Min	5%	10%	25%	50%	75%	90%	95%	Max	Mean	S.D	Skewness	Kurtosis
Depth	15	57.6	80	200	350	600	850.4	1200	2400	438.63	354.98	1.73	4.20
Temp	21.6	25.42	26.3	27.7	29.4	32.9	39.76	45.16	58.1	31.39	6.14	1.83	3.71
EC	3	420.7	495.6	763	1116	1857.5	3582	5294.9	14440	1685.85	1701.18	3.20	14.27
TDS	174.7	282.175	322.03	471.85	679	1180.725	2376.56	3556.57	9861.8	1082.79	1162.53	3.32	15.18
pH	6.4	6.8	7	7.2	7.5	7.7	7.9	8	9.6	7.48	0.39	0.30	2.36
Alkal	30	60	70	90	100	125	150	165	220	107.23	31.34	0.44	0.41
Ca	17	34.41	40.78	53.8	72.7	131.2	250.6	353.99	820	116.45	116.31	2.98	10.98
Cl	0.3	38.25	61.04	102.6	184.3	314.7	663.2	1199	4420	313.69	440.92	4.55	30.13
HCO_3	59	82.3	94.2	110	138	166.5	216.6	277.2	543	148.83	61.56	2.49	9.77
K	0.9	2.11	3.22	5.6	9.7	18.75	35.1	49.12	91	15.03	14.94	2.09	4.95
Mg	1.1	7.23	9.34	13.55	21	38.9	83.68	132.82	335.5	37.80	46.73	3.32	13.70
Na	3.8	33.52	38.32	63.1	107.7	197.3	422.92	678.35	2382.9	188.83	250.64	4.15	24.96
NO_3	0.4	1.3	2.62	8	20	35.7	68	107.36	318.2	31.14	40.48	3.34	14.67
SO_4	0.2	32.18	49	81.8	130.2	267.75	705.8	1161.25	2120	272.64	369.01	2.76	8.06

including pH and Alkalinity. Samples below the detection limit form the vertical line on the left side of the diagram (e.g., Na, Cl, NO_3 and SO_4). Most of the elements depart from normality towards the highest values, located on the right side of the straight normal distribution line. The result is referred to as the positively skewed or convex distribution feature for most elements. Most of the elements demonstrate some form of convex shapes; they are composed of multiple geochemical families and have closer to log-normal distributions. The diagrams provide useful information for outlier detection. Many single samples are separated from the distribution curve.

The diagrams indicate mixtures of populations or geochemical families by identified changes in slope for many elements. Most elements have high values, which are well visualized in normal quantile diagrams (Fig. 4). The high concentrations for Ca, Mg, K and SO_4 show a sharp reduction in slope at high concentration values. These samples may are influenced by natural or anthropogenic processes. Most elements shows a closer approach to normality with some departures from normality occurring in the highest values, located on the right side of the straight normal distribution line.

4.3. Scatter Diagrams Matrix

Correlation scatter diagrams help to visualize the correlations. Scatter diagrams of each pair of variables are displayed in a matrix arrangement. A 95% bivariate normal density ellipse is imposed on each scatter diagram. If the variables are bivariate normally distributed, this ellipse encloses approximately 95% of the points (when the number of points is large). The strong correlation of the variables is seen by the collapsing of the ellipse along the diagonal axis. If the ellipse is fairly round and is not diagonally oriented, the variables are uncorrelated (Fig. 5).

To better visualize multiple relationship between the variables, a scatter matrix plot was produced (Fig. 6) for the 12 variables showing the best relationship in the cluster tree (Fig. 5) and correlation coefficient (Table 2).On the plot each cell shows the scatter plot between the variables in the corresponding row and column, and a histogram for each variable was also provided in the diagonal cells where the variables for the corresponding row and column are the same. Upto some extent good correlation between all the 12 variables of pH, EC, TDS, Ca, Cl, HCO_3, Mg, Na, K, Alkalinity, NO_3, and SO_4 were illustrated. The best correlation existed between TDS and EC, Na-TDS, Cl-Mg, Cl-EC and Na-EC. Relatively correlations were observed for many variables (Table 2) while the scatter plots between HCO_3 and other variables were also relatively noisy. The results were in line with the cluster tree.

4.4. Hierarchical Cluster Analysis (HCA)

The hierarchical cluster analysis (HCA) seeks to identify homogeneous subgroups of cases in a population and identify a set of groups which both minimize within-group variation and maximize between-group variation. One of the general approaches to cluster analysis is hierarchical clustering. The product of this approach is dendrograms (treediagrams) (Fig. 6), show the relative size of the proximity coefficients at which cases were combined. In present study, the Euclidean distance is selected as the measured distance. The sampling sites with significant similarity are first grouped. Following this, groups of samples are joined with a linkage rule, and the steps are repeated until all observations are classified. The Ward's method has been applied successfully here to form clusters that are more or less homogenous and geochemically dis-

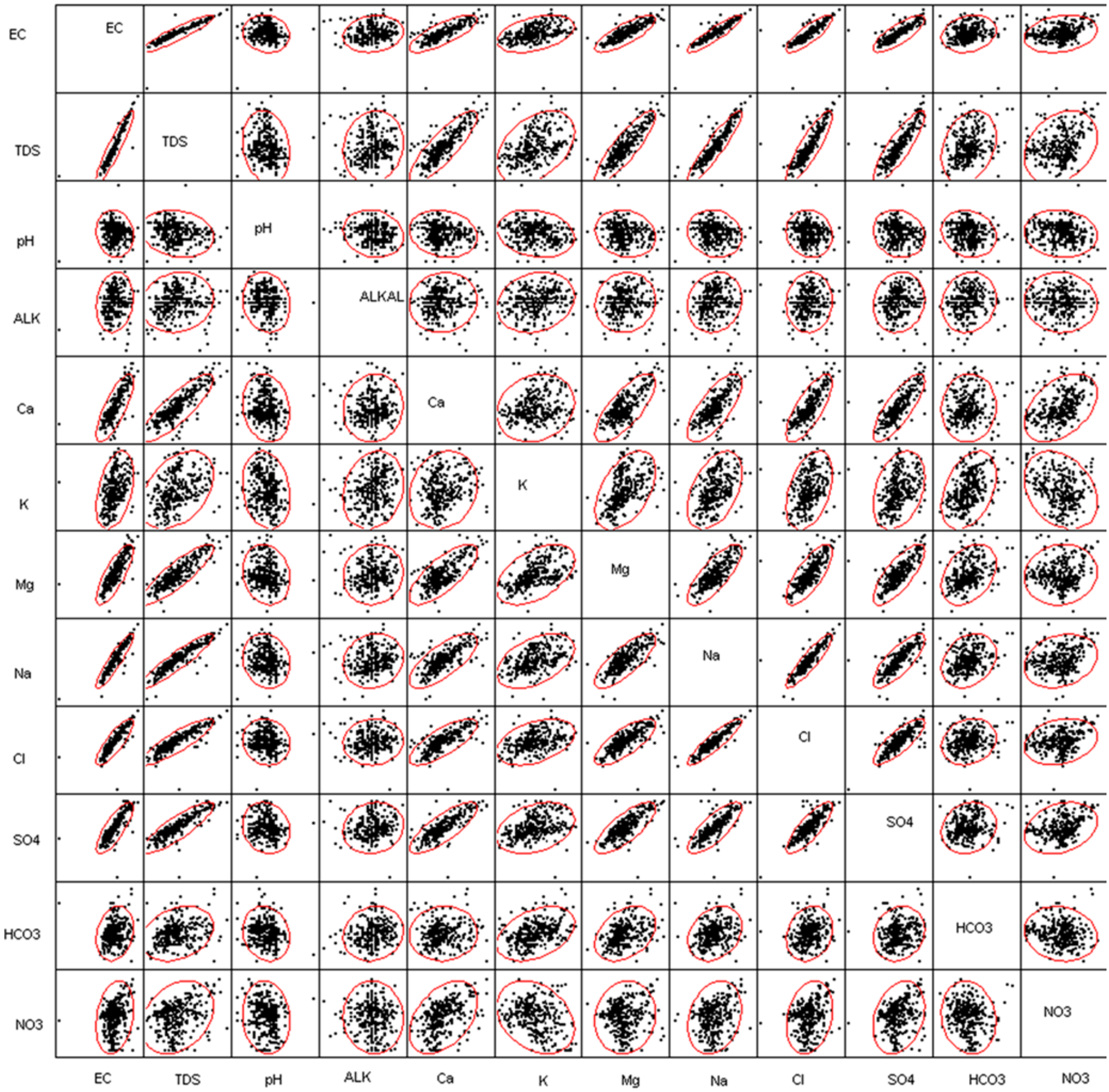

Fig. 5. Scatter Matrix plot for selected elements in study area groundwater analyzed samples.

tinct from other clusters (Cloutier et al., 2008).

Also found that using the Euclidean distance as a distance measure and Ward's method as a linkage rule produced the most distinctive groups. However, taking both the results of cluster tree and geochemical features of variables into consideration, they could be generally classified into two main groups. Group 1 comprised TDS, Na, EC, Cl, Ca, Mg and SO_4. The relationships within the group are strong. Group 2 consisted of NO_3, HCO_3, K, and pH. The fact this group has close relationship with group 1 demonstrates the increase in the concentration to some elements could be the same.

5. CONCLUSIONS

Hydrochemical variables concentrations determine in large part the overall quality and character of groundwater. Chemical elements in groundwater are derived from both natural and anthropogenic sources. Various ionic relationships are indicative of strong rock-water interaction. The present chemical characteristics of groundwater within Saq aquifer is acquired through gypsums, dolomites and halite dissolution, basalts weathering, ion exchange reaction, fertilizers and sewage pollution. The statistical analyses suggest

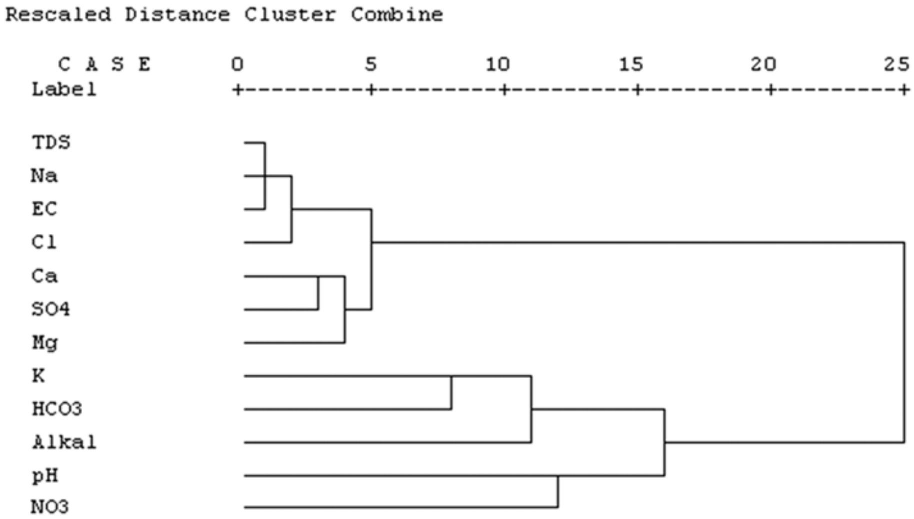

Fig. 6. Cluster tree of the variables for water samples (measure: Pearson's correlation coefficient; linkage method: furthest neighbors).

Table 2. Correlation coefficient of groundwater quality parameters for the study area

	EC	TDS	pH	ALKAL	Ca	K	Mg	Na	Cl	SO_4	HCO_3	NO_3
EC	1											
TDS	0.92	1										
pH	–0.09	–0.17	1									
ALKAL	0.15	0.12	–0.14	1								
Ca	0.78	0.85	–0.15	0.08	1							
K	0.40	0.41	–0.19	0.19	0.17	1						
Mg	0.79	0.87	–0.15	0.08	0.75	0.50	1					
Na	0.91	0.92	–0.13	0.13	0.74	0.46	0.78	1				
Cl	0.84	0.87	–0.11	0.05	0.76	0.41	0.75	0.90	1			
SO_4	0.80	0.87	–0.14	0.11	0.80	0.34	0.78	0.79	0.82	1		
HCO_3	0.20	0.28	–0.15	0.12	0.05	0.40	0.36	0.26	0.19	0.16	1	
NO_3	0.23	0.29	–0.10	–0.05	0.44	–0.30	0.09	0.24	0.24	0.28	–0.13	1

that chemical element data are approximately log-normally distributed, as both their skewnesses and kurtoses reach close to "0". The study shows that, all of the metal pairs exhibit positive relations. The elements showing significantly higher positive correlation are: The elements showing significantly higher positive correlation are: TDS with EC; Ca with EC, TDS; Mg and EC, TDS, Ca, K, Cl and EC, TDS, Mg, Na, Ca; SO_4 and EC, TDS, Ca, Cl, Na, Mg.. Cluster tree revealed that, they could be generally classified into two main groups, the first includes TDS, Na, EC, Cl, Ca, SO_4, and Mg, where the relationship within the group are strong. The second group includes K, HCO_3, pH, and NO_3. This group has close relationship with group 1 and demonstrates that the increase in the concentration to some elements could be the same.

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