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Statistical characterization of the hydrochemical data's of groundwater in the arid land of Wadi AdDawasir area, Saudi Arabia: A probabilistic assessment

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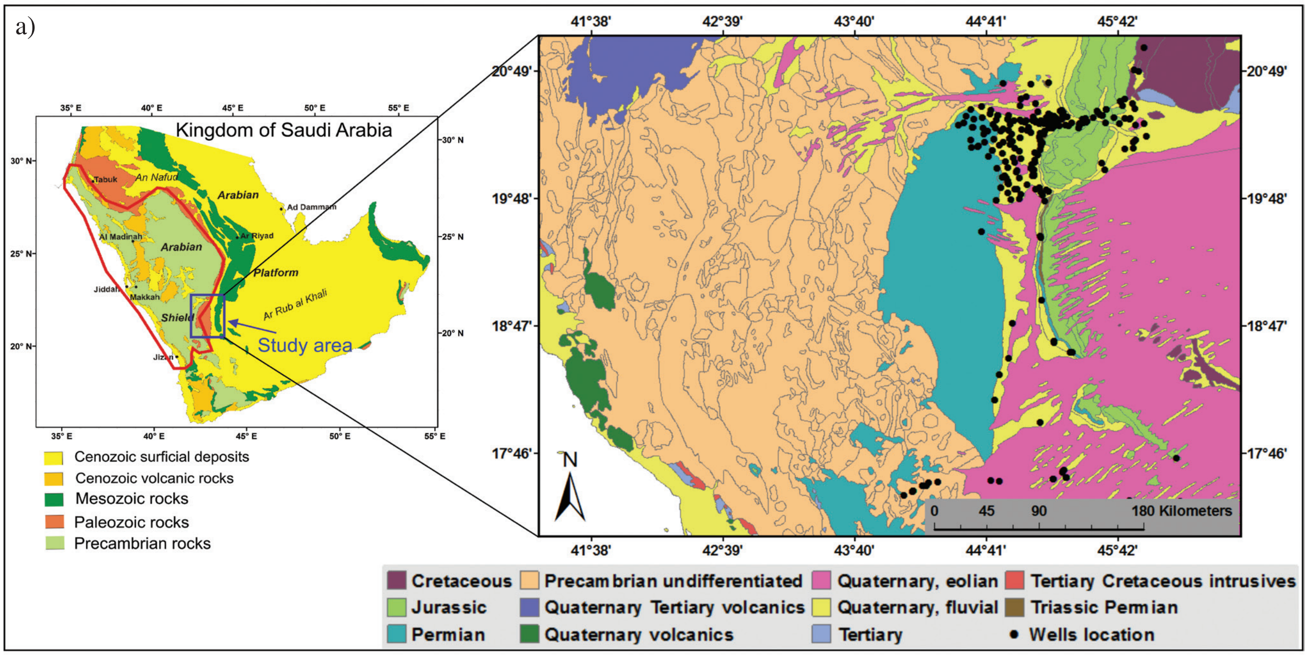
ABSTRACT

The main purpose of this research is to determine the quality of ground water in Wadi AdDawasir by the assessment of 12 chemical parameters: pH, EC, Eh, TDS, TH, Ca^{2+}, Cl^-, HCO_3^-, Mg^{2+}, Na^+, NO_3^-, and SO_4^{2-}. Statistical analyses were carried out using descriptive statistics, histograms, and normal quantile plots. The SPSS 15 software package (SPSS Inc. 2006) and JMPIN (version 4.0.4) were used as the main statistical software. Many locations within the study area show thatf pH, EC, HCO_3^- and Na^+ values exceed permissible limits. The concentration of anions is in the order SO_4^{2-}>Cl^->HCO_3^-. Some of the analyzed parameters approach a normal distribution, as both their skewness and kurtoses are close to zero. However, skewness for some parameters such as Mg^{2+} and HCO_3^- is high. Kurtosis for most of the elements varies from moderate to low. Only pH, HCO_3^- and SO_4^{2-} have kurtoses. Both the results of cluster tree and geochemical features of variables could be generally classified into three main groups. Group 1 is comprised of Na and SO_4^{2-}. The relationships within this group are strong. Group 2 consisted of Mg^{2+}, NO_3^-, pH, HCO_3^-, and Ca^{2+}. The fact that this group has a close relationship with group 1 demonstrates that the increase in the concentration of some elements could be the same. Group 3 is comprised of TH, Cl^-, Eh, and EC.

Keywords: Hydrochemistry, geostatistics, histograms, normal quantile plots, Wadi AdDawasir, Saudi Arabia

1. INTRODUCTION

The chemical composition of water is an important factor in determining its healthy condition for the various applications that support human life. The quality of groundwater is governed by many factors, such as soil characteristics, circulation pattern of groundwater through different rock types, topography of the region, saline water intrusion in coastal areas, and finally human activities, REGHUNATH et al. (2002). In many countries, for instance Saudi Arabia, groundwater is the unique source of freshwater to satisfy domestic uses as well as industrial and agricultural demands HAKEN (2013). When limited trace element data are available, geochemical environmental scientists are often requested to evaluate the character and quality of groundwater. If the distribution of trace elements in groundwater is known, then observed data could be used to easily differentiate between representative or anomalous groundwater compositions. However, because characterizing a groundwater system is difficult and expensive, a representative benchmark of known element distributions to categorize observed data is rarely available. As a result, effective evaluation of concentrations of observed trace elements might be challenging



and require further investigation, NEWCOMB, W.D. & RIMSTIDT, J.D. (2002).

Probabilistic methods are well suited for describing the complex distributions of trace elements in groundwater. These techniques rely on large sample populations which can satisfactorily represent the system of groundwater to be studied. The costs associated with sample collection and laboratory analyses to establish large sample populations may impose a barrier to the application of probabilistic methods. Public domain data resources, such as STORET, are appropriate databases where large environmental data can be accessed at low cost, EPA (2001). However, little or no data analysis capabilities are provided in the public domain sources. Moreover, trace element sample populations are often censored at multiple reporting limits (RLs), depending upon variations in laboratory analysis methodology and techniques. The use of data analysis techniques, as described by HELSEL (1990), and HELSEL, D.R. & HIRSCH, R.M. (1992), for multiple-censored sample populations can be used to extract salient information from raw trace element data.

The present study deals with the assessment of the major groundwater parameters data. To achieve this, histograms and normal quantile plots were used to define subpopulations in the water samples. This work provides a rapid, cost-effective screening tool for evaluating groundwater quality based on the observed element concentration data. Normal quantile plots yield significant detail on the behavior of subpopulations at both the high and low end of the frequency spectrum, as well as those having a central tendency. Having been utilized in data mining in space research, normal quantile plots demonstrate their strong capability in explaining clustered properties even in very large data sets (e.g., MANKU et al., 1999). NEWCOMB, W.D. & RIMSTIDT, J.D. (2002) used the probability distribution of trace elements in very large numbers of ground water samples in the STORET da-

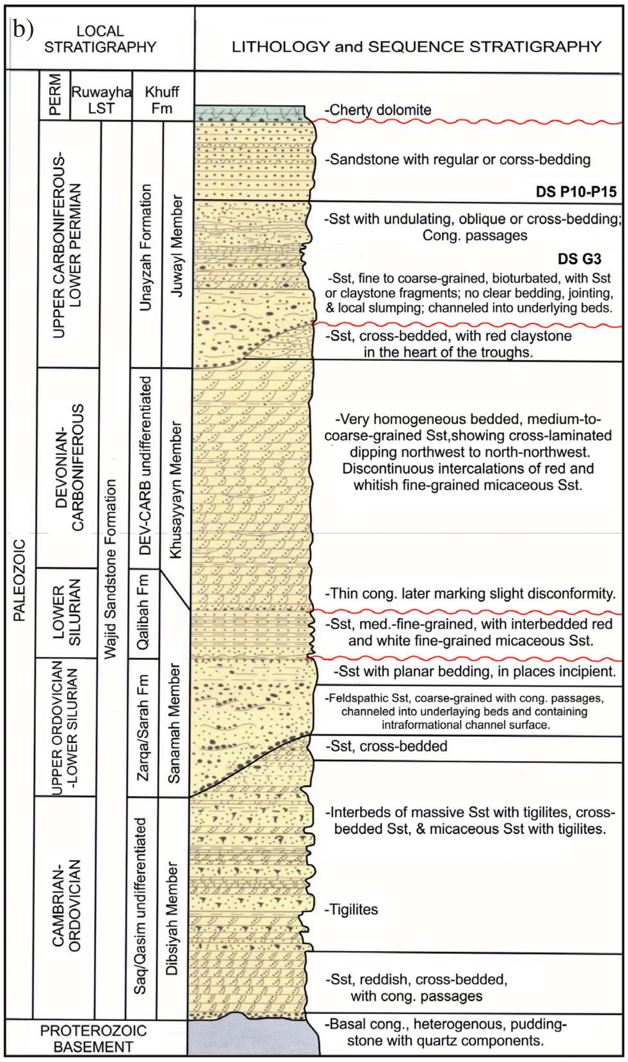


Figure 1: a – Sampling locations and geological map of Wadi AdDawasir in Saudi Arabia; b – Summary stratigraphic succession of the Wajid Sandstone in the Region (after KELLONG et al., 1986).

tabase, U.S. ENVIRONMENTAL PROTECTION AGENCY (2002).

Major research and discoveries related to Wajid sandstone hydrogeology, geology, and hydrochemistry of the study area have been published by DABBAG (1981), DABBAG, M.E & ROGERS, J.J.W. (1983), MOSHARIF (1989), MOSHARIF & EL-HITTI, A. (1989), STUMP, T.E.& VON der EEM, J.G.(1994), ITALCONSULT (1969), and AL-FAIFI, H.J.A. (2005).

2. STUDY AREA

2.1. Descriptions of the study area

The study area is situated within Wadi AdDawasir. It is located between latitudes 19° 30′ 00″ N, 21° 00′ 00″ and longitudes 44° 00′ 00″ E, 46° 30′ 00″ 650 km south of Riyadh (Fig. 1a).The study area is very important in Saudi Arabia from an agricultural point of view. The Annual average temperature in the area is about 29 °C, the maximum average temperature is 43 °C, and the minimum average temperature is 6 °C. The mean temperature during summer is 35 °C and June is the hottest month of the year. The annual average relative humidity is about 24% and it is more than 70% during winter. The average rainfall is 37.6 mm/year. Maximum rainfall in March includes the Mediterranean storm effect on winter rainfall, AL-FAIFI, H.J.A. (2005).

2.2. Geological setting

The study area lies within the Wadi Tathlith Quadrangle, which covers a surface area of 8902 km^2 of the southern Najd Province of Saudi Arabia. About two thirds of the quadrangle is underlain by an assemblage of stratified rock overlying the oldest crystalline, metamorphosed, Precambrian basement rocks of the Arabian shield, much of it comprising an almost flat pediment surface. Almost horizontally bedded Phanerozoic sedimentary rocks underlie the remaining part of the Wadi Tathlith Quadrangle in the southwest. In the study area, the Phanerozoic rocks lie unconformably on the Proterozoic of the Arabian shield. The contact is not clearly exposed anywhere in the Wadi Tathlith Quadrangle, and is commonly concealed by debris from the poorly consolidated basal conglomerate of the Wajid Sandstone. The Wajid Formation, which is one of the important geological formations in the study area, is divided into four members from bottom to top: Dibsiyah member, Sanamah member, Khusayyan member, and Juwayl member (Fig. 1a, and b), AL-FAIFI, H.J.A. (2005).

2.3. Hydrogeological setting

The Wjid aquifer is considered to be one of the most important hydrostratigraphic units in the Kingdom of Saudi Arabia. It is only to the east that there remain any doubts as to its extent. The depth of the aquifer, which reaches 480 metres, has made it impossible to detect the aquifer east of longitude 45 35 00 E. The unconfined part of the aquifer, in and near the outcrop zone of the Wajid formation, is very extensive. It can be followed from the south bank of Wadi AdDawasir to the Yemen border in the south. The unconfined part of the aquifer seems to be absent to the north of Wadi AdDawasir. The confined part of the aquifer is more extensive. The border between the unconfined and confined conditions roughly coincides with the western limit of the Khuff formation at outcrop. The presence of the confined Wajid Aquifer has been confirmed over an area of 12000 km^2 in the Wadi AdDawasir region. However, it is reasonable to suppose that it continues for a considerable distance to the east of the Sulayyil-Wadi Hinw, AL-FAIFI, H.J.A. (2005).

3. MATERIALS AND METHODS

A total of 253 samples of groundwater were collected (each from a different water well location) in the Wadi AdDawasir, Saudi Arabia, in the period between January to June 2013 (Fig. 1). These wells are used for irrigation and public supply purposes. Water depth ranges between 450–472 m, well casing is 269–278 m, screen is open.The pumps are installed in the wells and the samples collected directly from the well during pumping, AL-FAIFI, H.J.A. (2005). Samples were collected in 1 litre capacity polyethylene bottles, which were rinsed with well water prior to filling in order to minimize the chance of contamination. The sample preservation and applied analytical techniques were in accordance with the standard methods from the 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 by means 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 an 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^{2-}) was calorimetrically analyzed by the ammonium molybdate method. Nitrate (NO_3^-) was measured by ionic chromatography.

For the present study, statistical analyses were carried out using descriptive statistics, histograms, and normal quantile plots. The SPSS 15 packages (SPSS Inc. 2006) and JMPIN (version 4.0.4) were used as the main statistical software.

Histograms were used to analyze the data distribution. They are the appropriate 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 such as the bell shape of a normal distribution, but they have some limitations. The number of bins affects the shape of the curve where 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, which 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.

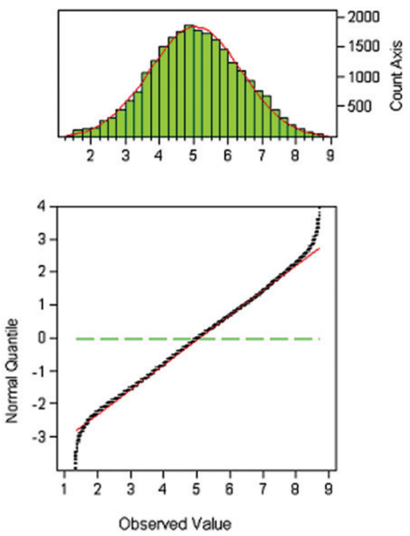


Figure 2: Histogram and normal quantile diagram of study area.

The normal quantile plot is a 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 by the SPSS statistical software, which automatically utilized the Lilliefors correction. If the p-value reported is less than 0.05 (or some other alpha), then the distribution is not normal, SALL, J. & LEHMAN, A. (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 was 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), while sampling location maps were produced with ArcView GIS software (version 3.3).

4. RESULTS AND DISCUSSION

4.1. General Chemistry

Table 1 shows the statistical summary of selected physicochemical parameters. The pH values obtained from the analytical procedures indicates an alkaline nature for some of the studied water samples, where the maximum value of 9.08 and a minimum value of 5.56 have been recorded, with a mean value of 7.4. Higher electric conductivity (EC) values (i. e., between 577.7 to 12170 µs/cm) have been observed in the study area, whereas the HCO_3^- values ranged between 0.11 to 339 mg/l. Many locations show higher than the permissible values of 22–26 mg/l, (GULF COUNTRIES COMMITTEE STANDARDIZATION ORGANIZATION GUIDELINES 2008). Mg^{2+} values range between 0.16–1359 mg/l, TDS between 17.8–7880 mg/l, NO_3^- 6.04–2016 mg/l, and Ca^{2+} 6.3–979.5 mg/l. As a dominant constituent, the anion concentration pattern is in the order of $SO_4^{2-}>Cl^-$ $>HCO_3^-$. In the case of cations, the observed range of Na^+ has been placed between 0.21 to 1648.4 mg/l, which shows 12 locations in the northeastern part of the study area exceed the permissible limit of 200 mg/l, GCCSOG (2008). The possible sources of Mg in the study area are igneous rocks, primarily ferromagnesian minerals like olivine, pyroxenes, amphiboles, and dark colored micas. Also within metamorphic rocks, magnesium occurs in minerals such as chlorite, montmorillonite, and serpentine. In sedimentary environments, magnesium occurs as magnesite, dolomite and other carbonates, sometimes mixed with calcium carbonate. Dolomite contains calcium and magnesium in equal amounts. Most groundwater contains relatively small amounts of Mg^{2+}, except where they have been in contact with dolomite (amounts of Ca^{2+} and Mg^{2+} about the same), or with Mg^{2+} – rich evaporates that could cause Mg^{2+} to become the dominant cation in the groundwater.

Sodium is primarily derived from feldspars in igneous rock and its weathering products (clay minerals) in other material. Shale and clay layers often yield water with relatively high sodium contents. Other sources of sodium are leachate and deep percolation water from the upper soil layers (including atmospheric precipitation that has been subject to concentration effects), and contamination of groundwater by salty connate water or water of marine origin. Brines and other salty waters which usually occur at great depths contain large amounts of sodium. Primary sources of chloride in groundwater are evaporites, salty connate water, and marine water. Igneous rock materials contribute little chloride. Groundwaters containing significant amounts of chloride also tend to have high amounts of sodium, indicating the possibility of contact with water of marine origin. Leaching of chlorides that have accumulated in upper soil layers may be a significant chloride source in dry climates. The recommended maximum concentration for chloride in drinking water is 250 mg/1, primarily for reasons of taste. Sulfate is formed by oxidation of pyrite and other sulfides widely distributed in igneous and sedimentary rocks. The most important sulfate deposits are found in evaporite sediments (gypsum, anhydrite, sodium sulfate). In arid regions, leaching of sulfate from the upper soil layers may also be significant, causing sulfate to be the principal anion of the underlying groundwater. Sulfate concentrations in drinking water should not exceed 250 mg/1 because the water will have a bitter taste and can produce laxative effects at higher levels.

Factors that govern the concentration of various elements in the groundwater of the study area are the climate of the area, chemical composition of the water and the presence of accessory minerals in the rocks through which the groundwater is circulating. The high salinity particularly within agricultural areas envisages anthropogenic influence. A variety of chemical fertilizers used for agricultural growth may enter into the groundwater system through return water. Over exploitation of groundwater in the study area causes groundwater decline which may also affect its quality, AL-FAIFI, H.J.A. (2005). Thus, anthropogenic activities in the study area are also considered as potential factors in groundwater quality. Industrial sources, including for example the production of glass, ceramics, electronics, steel and aluminum, processing pesticide and fertilizers and untreated waste water, together with agricultural activities are all considered as important anthropogenic sources for various elements in the study area. Agricultural and industrial developments place huge demands on precious water resources. There has been significant over-exploitation of water resources resulting in large cones of depression. With the Pumping rate of 1800 USG/min, drawdown after 20 years equals 43m. The predicted drawdown after 40 years and 60 years may reach to 90 m and 141m, respectively, AL-FAIFI, H.J.A. (2005).

4.2. Basic statistics

The basic statistics (maximum, minimum, percentiles, mean, median, and standard deviation) for the data are shown in Table 1. Percentages are variable for all of the parameters in the study area; e.g., Mg^{2+} varies between 0.16 and 1359.9 mg/l. The shape parameters (skewness and kurtosis) are also calculated and listed in Table 2. Some of the analyzed parameters approach a normal distribution, as both their skewness and kurtosis reach close to 0. Skewness for some elements is high; e.g., Mg^{2+} shows a high value of 4.51. Others such as HCO_3^- have a much lower level of skewness. Some parameters are characterized by high kurtosis values; Mg^{2+} shows a high value of 29.02, which may be due to a large number of low value samples compared to the wide data range associated with the outliers. Parameters such as HCO_3^- also have fairly low kurtosis, with the fact that these values are more evenly distributed within the data ranges.

Skewness measures the presence of a tail deviating from a normal distribution (0) toward lower values (negative skewness) or higher values (positive skewness). For the raw data sets, the skewness for the other parameters are positive, many of which are high (Mg^{2+}).This confirms the strongly skewed distributions displayed in the histograms and normal Q–Q plots. Kurtosis refers to the "fatness" of the tails in statistical plots, where positive kurtosis denotes peakedness while a negative value represents a "flat" distribution. The kurtosis for most parameters is moderate to low. High positive kurtosis shows that very high values in the data are rare, presumably associated with rare processes such as mineralization. Only pH, HCO_3^- and SO_4^{2+} have a fairly small kurtosis, showing that these values are more evenly distributed within the data ranges, and that special concentration of these parameters is rare.

Logarithmic transformation tends to move both skewness and kurtosis for most parameters towards normality, i.e., closer to 0. Another feature of the logarithmic transformation is that most of the transformed data sets have negative skewness values showing that the log-transformation has over-transformed the data.

4.3. Histograms and normal quantile diagrams

The probabilistic display delineates discrete populations that have genetic or other affinities as line segments showing changes in slope (i.e., "kinks"). The observed distributions significantly differ from the synthetic distributions modeled by SINCLAIR, A.J. (1976) and ZHANG et al. (2008) for chemical distributions. It appeared that these pioneering authors have superimposed different types of distributions having the same concentration range, which yielded curved changes in the slope. The present data include elemental distributions with substantial overlap and curvatures. In fact, notable features include the prominent role of line segments showing sharp angular change. Such features require largely discrete chemical subpopulations.

Histograms of data are shown in Figure 3. As can be seen, some parameters have high values, which are reflected in the histograms by data being located on the left of the diagram. These extreme values are well visualized on the normal quantile diagrams, and they are identified as outliers. Some parameters have values below or close to the detection limits (e.g., Na^+ and SO_4^{2+}), resulting in high frequencies for the lowest value group, near the limit of detection.

The frequency distributions of some of the parameters are positively skewed and include some very high values. Some extreme values (Eh, Cl^-, Mg^{2+}, Na^+, and NO_3^-) appear to be separated from the majority of the samples, and do not appear to be part of a continuous distribution (e.g., Figure 3, Table 1). These extreme values might be regarded as evidence of particular natural or anthropogenic processes.

The normal quantile diagrams for the data are shown in Figure 4. Straight-line segments are observed for some parameters including HCO_3^-. Samples below the detection limit form the vertical line on the left side of the diagram (e.g., Na^+ and SO_4^{2-}). Most of the parameters 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 parameters demonstrate some form of convex shapes; they are composed of multiple geochemical families and have closer to log-normal distri-

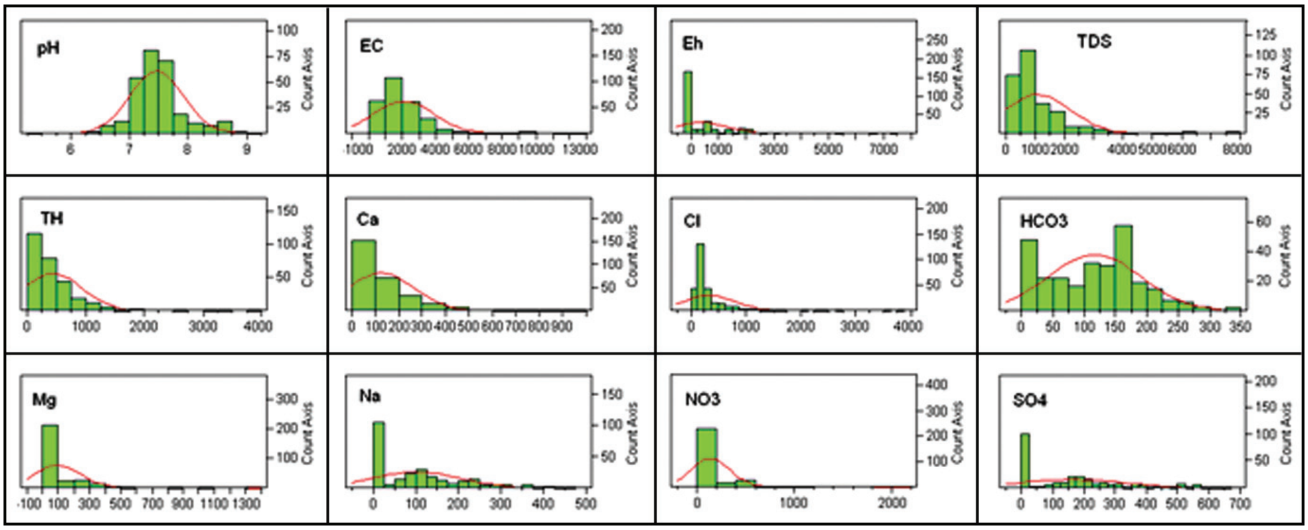


Figure 3: Histograms of the data set (a normal distribution curve for all the values is superimposed for comparison; EC in [µS/cm]; chemical parameters are in mg/L).

butions. 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 the slope for many parameters. Most elements have high values, which are well visualized in normal quantile diagrams (Fig. 4). The high concentrations for Ca^{2+}, Cl^{-}, Mg^{2+}, Na^{+}, NO_3^{-} and SO_4^{2-} show a sharp reduction in the slope at high concentration values. These samples may be influenced by natural or anthropogenic particular processes. Most parameters show 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.

4.4. Correlation Coefficient

The Correlation Coefficient is presented in matrix form in Table 3, which shows the Pearson product-moment correlation coefficients. The matrix contains 12 variables, and summarizes the strength of the linear relationships between each pair of variables. If there is an exact linear relationship between two variables then the correlation is 1 or –1 depending on whether the variables are positively or negatively related. If there is no linear relationship, the correlation tends toward zero. A finding is described as "statistically significant" when the probability is less than 0.05 ($p<0.05$) and as "highly statistically significant" when p is less than 0.01 ($p<0.01$). If the probability value is greater than 0.05 ($P > 0.05$), the coefficient of correlation is not significant.

Most of the metal pairs exhibit positive relationships (except for Eh, EC, Mg^{2+}, and NO_3^{-}). However, only a few of these correlations are significant at the 0.05 level (2-tailed), while the majority of them are significant at the 0.01 level (2-tailed). The parameters showing significantly higher positive correlation are: TDS with EC; TH and EC, TDS; Ca^{2+} and EC, TDS, TH; Cl^{-} and EC, TDS, TH, Ca^{2+}; Mg^{2+} and EC; Na^{+} and EC, TDS, TH, Ca^{2+}, Cl^{-}; NO_3^{-} and Mg^{2+}; SO_4^{2-} and EC, TDS, TH, Ca^{2+}, Cl^{-}, Na^{+}.

Table 1: Percentiles of the variables of groundwater at Wadi AdDawasir in Saudi Arabia (EC in [µS/cm]; Eh in mV; chemical parameters are in mg/l).

	Minimum	5%	10%	25%	50%	75%	90%	95%	Maximum	Mean	S.D
pH	5.46	6.83	7.04	7.22	7.45	7.64	8.04	8.52	9.08	7.48	0.46
EC	3.5	577	828	1028	1520	2700	3672	5380	1217	2119	1830
Eh	–206	–183	–117	–42	–19	623	1850	2018	7490	424	931
TDS	17.8	172	218	464	784	1300	2282	3136	7880	1096	1119
TH	13.5	48	61	143	315	588	920	1228	3944	440	497
Ca^{2+}	6.3	14	18	30	89	172	278	366	979	127	135
Cl^{-}	5.2	94	110	151	180	356	721	1164	3793	349	464
HCO_3^{-}	0.11	6.15	13	50	128	168	203	236	339	117	73
Mg^{2+}	0.16	12	17	26	46	96	248	363	1359	97	146
Na^{+}	0.21	2.71	5.6	10	93	189	345	494	1648	149	226
NO_3^{-}	0.04	2.01	5.62	27	108	170	418.4	543	2016	147	201
SO_4^{2-}	0.01	0.1	0.19	0.43	156	272	507	633	1785	202	261

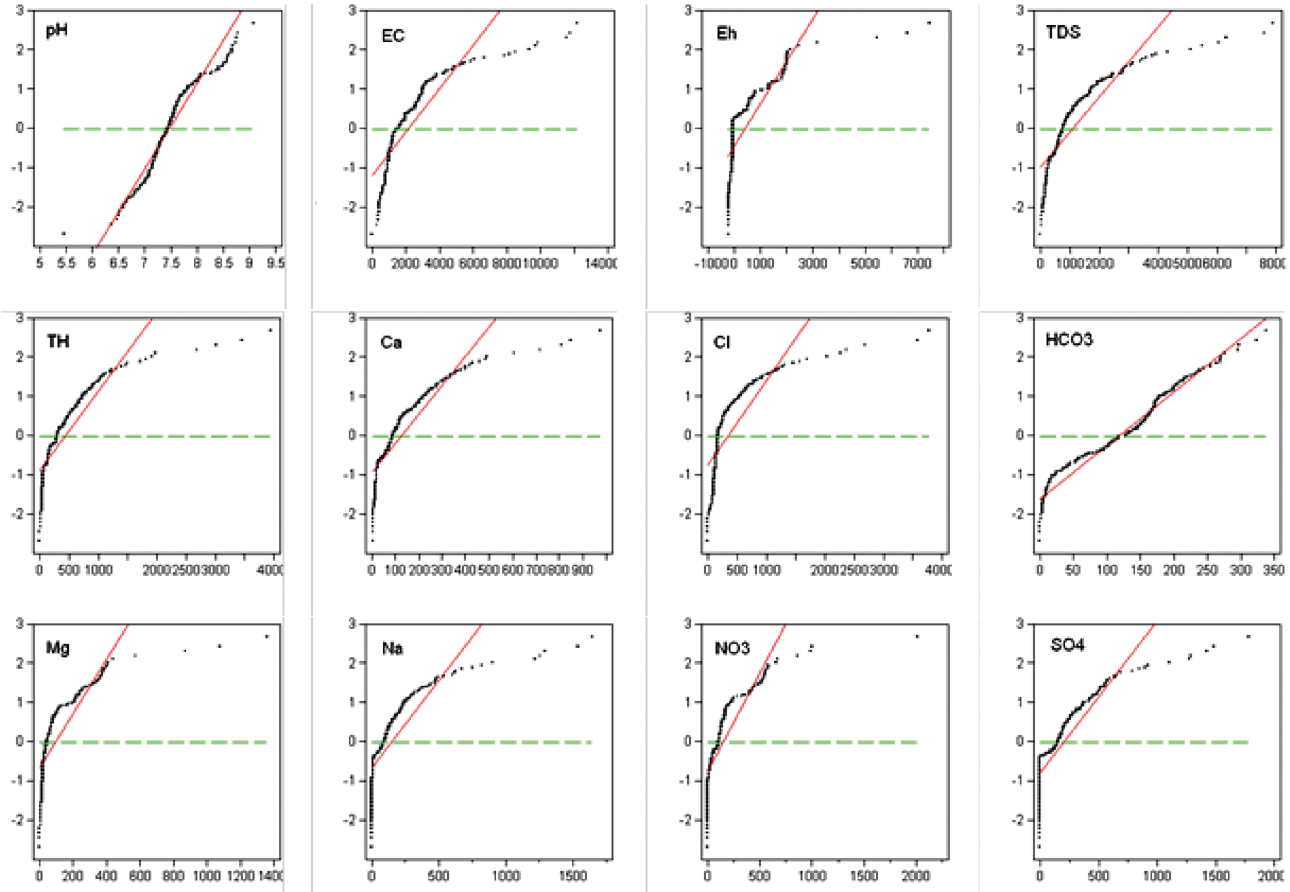


Figure 4: Normal quantile plots for the data set (the normal quantiles are plotted on the y-axis; the observed values are plotted on the x-axis EC in [µS/cm]; chemical parameters are in mg/l).

The reason for this is the observed correlation for the various parameters based on the geochemical behaviour of the chemical species and /or the possible anthropogenic inputs to the water. Therefore, the concentration of various parameters in groundwater is related to lithology and relies on the distance from the alteration areas, climate of the area, and chemistry of the water and the presence of accessory minerals of the rocks through which the groundwater is circulating.

4.5. Scatter Diagrams Matrix

Correlation scatter diagrams help to visualize the correlations. Scatter diagrams of each pair of variables are displayed

Table 2: Skewness, Kurtosis in the data sets with results of Kolmogorov-Smirnov test.

	Raw variables			Log-Raw variables		
Parameter	Skewness	Kurtosis	K-S *p*	Skewness	Kurtosis	K-S *p*
pH	0.5	2.39	0.000	0.14	2.98	0.000
EC	2.92	10.75	0.000	–1.38	13.05	0.000
TDS	2.99	11.99	0.000	–0.37	0.91	0.000
TH	3.38	16.66	0.000	–0.21	–0.43	0.000
Ca^{2+}	2.81	11.41	0.000	–0.22	–0.56	0.000
Cl^-	4.27	23.12	0.000	–0.14	3.29	0.000
HCO_3^-	0.16	–0.52	0.000	–1.45	1.57	0.000
Mg^{2+}	4.51	29.02	0.000	0.3	0.53	0.001
Na^+	3.63	16.95	0.000	–0.3	–0.94	0.000
NO_3^-	4.14	28.47	0.000	–0.74	0.05	0.000
SO_4^{2-}	2.58	9.59	0.000	–0.46	–1.59	0.000

Table 3: Correlation coefficients between the variables of groundwater at Wadi AdDawasir in Saudi Arabia.

	pH	EC	Eh	TDS	TH	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}	Ca^{2+}
pH	1											
EC	–0.10	1										
Eh	–0.31	0.35	1									
TDS	0.03	0.89	–0.09	1								
TH	0.06	0.79	–0.21	0.94	1							
Ca^{2+}	0.00	0.79	–0.18	0.93	0.97	1						
Cl^-	0.04	0.80	–0.21	0.95	0.92	0.89	1					
HCO_3^-	0.25	0.08	–0.44	0.27	0.34	0.30	0.16	1				
Mg^{2+}	–0.21	0.61	0.92	0.21	0.11	0.11	0.08	–0.26	1			
Na^+	0.09	0.74	–0.31	0.93	0.84	0.81	0.93	0.30	–0.04	1		
NO_3^-	–0.25	0.35	0.85	0.00	–0.11	–0.06	–0.13	–0.31	0.81	–0.22	1	
SO_4^{2-}	0.09	0.66	–0.39	0.88	0.86	0.86	0.84	0.41	–0.11	0.92	–0.28	1

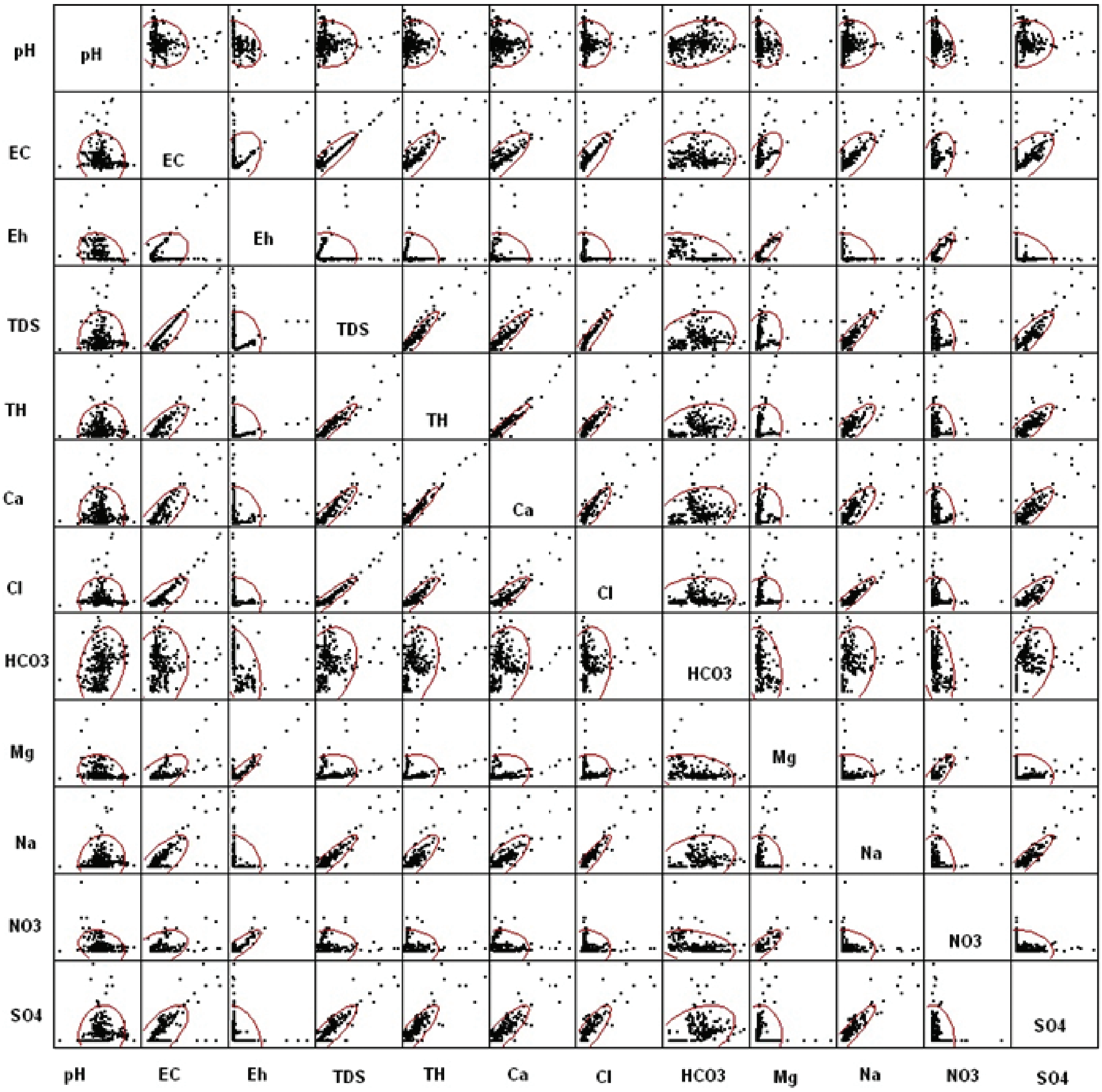


Figure 5: Scatter Matrix plot for selected elements in analysed groundwater samples from the study area.

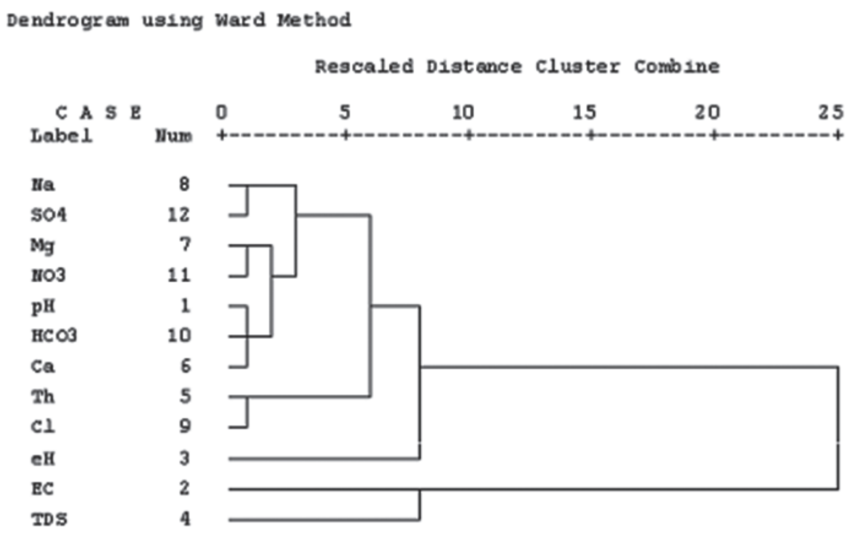


Figure 6: Dendrogram resulting from Ward's method of hierarchical cluster analysis for the 12 variables.

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 high). The strong correlation of the variables is seen by collapsing 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 relationships between the variables, a scatter matrix plot was produced (Fig. 5) for the 12 variables, showing the best relationship in the cluster tree (Fig. 6).In this plot, each cell shows the scatter between the variables in the corresponding row and column. A histogram for each variable was also provided in the diagonal cells where the variables for the corresponding row and column are the same. The histogram is shown separately in Figure 3. To some extent, a good correlation between all 12 variables of pH, EC, Eh, TDS, TH, Ca^{2+}, Cl^{-}, HCO_3^{-}, Mg^{2+}, Na^{+}, NO_3^{-}, and SO_4^{2-} was illustrated. The best correlation exists between Na and SO_4^{2-}. Relative correlations were observed for the variables TDS, TH, and Ca^{2+}, while the scatter plots between HCO_3^{-} and other variables were also relatively noisy. The results were in line with the cluster tree.

4.6. Hierarchical cluster analysis (HCA)

The hierarchical cluster analysis (HCA) seeks to identify homogeneous subgroups of cases in a population and to 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 a dendrogram (Fig. 6).Also called tree diagrams, these show the relative size of the proximity coefficients at which cases were combined. In the 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. Ward's method has been successfully applied here to form clusters that are more or less homogenous and geochemically distinct from other clusters (BATAYNEH, A. & ZUMLOT, T. 2012; CLOUTIER et al., 2008).

It was 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 the cluster tree and geochemical features of variables into consideration, they could be generally classified into three main groups. Group 1 comprised Na^{+} and SO_4^{2-}. The relationship within this group is strong. Group 2 consisted of Mg^{2+}, NO_3^{-}, pH, HCO_3^{-}, and Ca^{2+}. The fact that this group has a close relationship with group 1 demonstrates that the increase in the concentration of some elements could be the same. Group 3 comprised TH, Cl^{-}, Eh, EC, and TDS.

5. CONCLUSIONS

Hydrochemical variable concentrations dominantly determine the overall quality and characteristics of groundwater. Chemical parameters in groundwater are derived from both natural and anthropogenic sources. Complex processes govern the distribution of chemical elements in groundwater. Sophisticated data analysis techniques are required to effectively interpret chemical data. Probabilistic data analysis techniques provide an enhanced data analysis capability for complicated chemical parameter distributions in groundwater. The results of this work suggest that chemical parameter data are approximately log-normally distributed, as both their skewness and kurtosis values are close to 0. The study shows that most of the metal pairs exhibit positive relationships (except for Eh, EC, Mg^{2+}, and NO_3^{-}). The parameters showing significantly higher positive correlations are: TDS with EC; TH and EC, TDS; Ca^{2+} and EC, TDS, TH; Cl^{-} and EC, TDS, TH, Ca^{2+}; Mg^{2+} and EC; Na^{+} and EC, TDS, TH, Ca^{2+}, Cl^{-}; NO_3^{-} and Mg^{2+}; SO_4^{2-} and EC, TDS, TH, Ca^{2+}, Cl^{-}, Na^{+}. The Cluster tree shows that they could be generally classified into three main groups. Group 1 comprised Na^{+} and SO_4^{2-}. The relationship within this group is strong. Group 2 consists of Mg^{2+}, NO_3^{-}, pH, HCO_3^{-}, and Ca^{2+}. The fact that this group has a close relationship with group 1 demonstrates that the increase in the concentration to some elements could be the same. Group 3 comprised TH, Cl^-, Eh, EC, and TDS. Some recommendation may considered here as follows:

– A groundwater chemical analysis study should be conducted periodically and a solute transport model is recommended to monitor future deterioration of the water quality.

– Well drilling is one of the major problems in the study area, and there should be control on this factor.

Recommend the growth of crops that have a low demand for water to the agriculture industry.

– Irrigation systems must be changed to modern irrigation ones.

Should some of these problematic factors have been mentioned above in the body of the report, saying why they are an issue rather than just dropping them in here at the end? No conclusion or recommendations should really contain new information that hasn't been mentioned before e.g. what high demand crops are grown and what are the problematic irrigation systems – how and why is well drilling an issue? I am assuming you mean small wells mentioned at the beginning for irrigation? It is much more informative for the reader if you discuss these issues before you make recommendations against them.

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REFERENCES

AL-FAIFI, H.J.A. (2005): Evaluation of groundwater resources in Wajid Aquifer in WadiDawasir area southern Saudi Arabia, using computer simulation.– M.Sc. Thesis, King Saud University, Riyadh.

AMERICAN PUBLIC HEALTH ASSOCIATION (APHA) (1995): Standard methods for the examination of water and wastewater, 19th edn. APHA, Washington DC, USASS.

BATAYNEH, A. & ZUMLOT, T. (2012): Multivariate statistical approach to geochemical methods in water quality factor identification; application to the shallow aquifer system of the Yarmouk Basin of north Jordan.– Res. J. Environ. Earth. Sci., 4/7, 756–768.

CLOUTIER, V., LEFEBVRE, R., THERRIEN, R. & SAVARD, M. (2008): Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system.– J. Hydrol., 353, 294–313.

DABBAGH, M.E. (1981)(ed.):Environmental interpretation and tectonic significance of theWajid Sandstone, Saudi Arabia.– M.Sc. of Science, University of North Carolina, U.S.A., 84 p.

DABBAGH, M.E. & ROGERS, J.J.W. (1983): Depositional environments and tectonic significance of the Wajid Sandstone of southern Saudi Arabia.– Journal of African Earth Sciences, 1/1, 47–57.

GULF COUNTRIES COMMITTEE STANDARDIZATION ORGANIZATION., (GSO) GSO5/ (2008): Unbottled drinking water.

HAKAN, ARSLAN (2013): Application of multivariate statistical techniques in the assessment of groundwater quality in seawater intrusion area in Bafra Plain, Turkey.– Environ monitoring and assessment, 185, 2439–2452.

HELSEL, D.R. (1990): Less than obvious: statistical treatment of data below the detection limit.– Env. Sci and Tech., 24, 1766–1774.

HELSEL, D.R. & HIRSCH, R.M. (1992): Studies in Environmental Science 49. Statistical Methods in Water Resources, Elsevier, New York.

ITALCONSULT (1969): Water and Agricultural Development studies for Area IV, Eastern Province, Saudi Arabian".– Unpublished Report to the Ministry of Agriculture and Water, Riyadh, Kingdom of Saudi Arabia.

KELLOGG, K.S., JANJOU, D., MINOUX, L. & FOURNIGUET, J. (1986): Explanatory notes to the Geologic Map of the Wadi Tathlith Quadrangle, sheet 20 G, Kingdom of Saudi Arabia. Ministry of Petroleum and Mineral Resources, Deputy Ministry for Mineral Resources, 27 p.

MANKU, G.S., RAJAGOPALAN, S. & LINDSAY, B.G. (1999): Random sampling techniques for space efficient online computation of order statistics of large datasets.– In: Proceedings of the ACM SIGMOD International Conference on Management of Data, 251–262.

MOSHRIF, M.A. (1989): Fluvial environment of the southern part of Wajid Sandstone (Cambrian – Ordovician) deduced by textural analysis".– Iraqi Journal of Science, 30/1, 47–71.

MOSHRIF, M.A. & EL-HITI, A. (1989): Lithofacies and petrography of Wajid sandstone (Cambrian-Ordovician) Saudi Arabia.– Journal of African Earth Sciences, 9/3–4, 401–412.

NEWCOMB, W.D. & RIMSTIDT, J.D. (2002): Trace element distribution in US groundwaters: a probabilistic assessment using public domain data.– Appl. Geochem., 17, 49–57.

REGHUNATH, R., MURTHY, S.T.R. & RAGHAVAN, B.R. (2002): The utility of multivariate statistical techniques in hydrogeo-chemical studies: an example from Karnataka, India.– Water Research, 36, 2437–2442.

SALL, J. & LEHMAN, A.(1996): A Guide to Statistic and Data Analysis Using JMP and JMP IN Software SAS Institute Inc. Duxbury Press.

SINCLAIR, A.J. (1974): Selection of threshold values in geochemical data using probability graphs.– J. Geochem. Explor., 3/2, 129–149.

STUMP, T.E. & VAN DER EEM, J.G. (1994): The stratigraphy, depositional environments and periods of deformation of the Wajid outcrop belt, southwestern Saudi Arabia".– Journal of African Earth Sciences, 21/3, 421–441.

U.S. ENVIRONMENTAL PROTECTION AGENCY. (2002): STORET, U.S. Environmental Protection Agency. Office of Water. Available from: <http://www.epa.gov/storet/> (last accessed 08.12.04).

ZHANG, C.S., DEIRDRE, F., DAVID, M., EAMONN, G. & OWEN, T.C. (2008): Statistical analysis of geochemical variables in soils of Ireland.– Geoderma, 146, 378–390.

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