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HYDROCHEMICAL CHARACTERISTICS OF THE ABU SHAYBAH AQUIFER IN MASLATHA AND SURROUNDING AREAS, NORTHWESTERN LIBYA

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Msalatha City, located in the northwestern part of Libya, has grown and urbanized rapidly. The city and surrounding areas depend heavily on the groundwater as a water resource for drinking, domestic and agricultural uses. Understanding the chemistry of groundwater provides insight into the interaction of water with the environment and contributes to better resource management. Descriptive statistics, correlation matrices and factor analysis were used to understand the hydrochemistry of the groundwater in the Abu Shaybah aquifer in Msalatha and surrounding areas. Salinization is the main process influencing the groundwater chemistry, mineral precipitation and dissolution of cations. During recharge periods the water gains salts from the area at the surface and leaches to the subsurface.

INTRODUCTION

The study area is bounded by Mediterranean Sea from the north and Mantaqat Bashar from the south (Figure 1). It lies between latitudes 32° 30' to 32° 45' E and longitudes 13° 45' to 14° 15' N. Maslatha City is located about 120 km southeast of Tarabulus and covers an area about 267.2 km². The population increased greatly from 48,390 in 1995 to 66,756 in 2005. The rapid increase in urbanization and population has modified land use patterns and increased water demands. The groundwater has been used for various purposes such as drinking, agriculture, domestic and industrial uses. The study area is characterized by semiarid to arid climatic conditions.

The chemical composition of groundwater is derived from several sources, such as atmospheric input, interaction of water with rock, and also from human activities.

Groundwater is drawn from Abu Shaybah aquifer, which consists of sandstone and clay with minor calcareous intercalations of Triassic age (Carnian). This paper investigates the hydrochemistry of groundwater and discusses the fundamental processes of water–rock interaction in the area.

GEOLOGIC SETTING

Many authors have studied the geology of the area including Desio et al. (1963), Conant and Goudarzi (1967), Goudarzi (1970), Hammuda (1967), Piccoli (1960), Hecht et al. (1963), El-Hinnawy and Chesthitey (1975) and others. The area contains several outcrops of rock units (Figure 2). A geological cross section is presented in Figure 3. The stratigraphic sequence of the rock formations from older to younger are:

1- The Abu Shaybah Formation is exposed in a small area in Wadi Qirrim and is unconformably overlain by the Sidi As-Sid Formation of Late Cretaceous age. The Abu Shaybah Formation has a thickness that ranges from 75 to 140 m and its age is late Triassic, particularly the Carnian. The formation consists of rusty brown sandstone intercalated with reddish coarse-grained sandstone and fine-grained conglomerate, while the upper part consists of fine grained sediments such as siltstones, claystones and clayey sandstones (El-Hinnawy and Chesthitey, 1975).

2- Desio et al., (1963) divided the Late Cretaceous formations into two formations, the Sidi As-Sid Formation (older) and Nalut Formation (younger). The Nalut Formation is the youngest member of the Late Cretaceous in the eastern part of Jabal Nefusa, which is of Cenomanian–Turonian age. The lower part of this formation consists of yellow and grey dolomitic limestone and abundant spherical and tubular siliceous cherts. The upper part consists of dolomitic limestone, which is intercalated by yellowish grey marly limestone (El-Hinnawy and Chesthitey, 1975). The Sidi As-Sid Formation is exposed in the study area, where the Nalut Formation is eroded. El-Hinnawy and Chesthitey (1975) suggested the term Sidi As-Sid Formation for a succession that consists of two successive rocks units, the Ayn Tobi limestone and Yefren marls.

The Ayn Tobi Member consists mostly of dolomitic sediments, while the Late Yefren Member is characterized by yellowish grey dolomites.

The Sidi As-Sid Formation is conformably overlain by thick bedded dolomite and dolomitic limestone of the Nalut Formation.

3- The Middle Miocene sediments are represented by the Al-Khums Formation, which disconformably overlies Late Cretaceous rock. Al-Khums Formation is of neritic character with numerous brackish phenomena and repeated water level oscillations. According to these

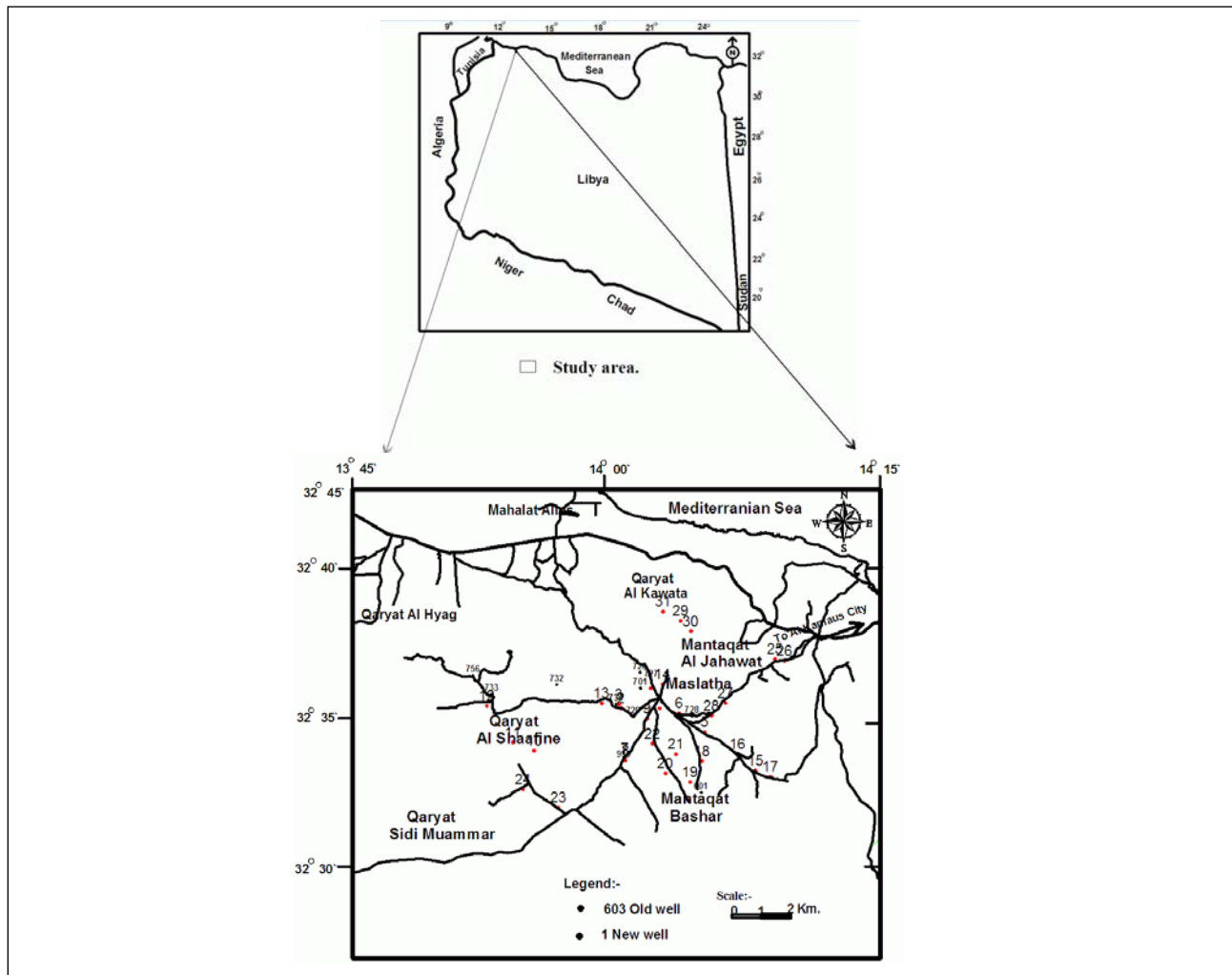


Figure 1. Location map of the study area.

environmental conditions the formation changes from marl at the bottom to brown calcarenite, and a conglomerate consisting of whitish grey limestone calcarenite, yellowish limestone, whitish grey algal limestone and grey to light limestone (Florida ,1939).

4- Many authors studied the Quaternary sediments in northwest Libya especially Hey (1962), Vita-Finzi (1960, 1963 and 1971), Miller (1971), Desio et al. (1963) and Christie (1966). Quaternary sediments always rest disconformably on the earlier formations. In the study area these sediments include the Pleistocene (Jefara Formation and Gargaresh Formation) and the Holocene (Recent Wadi, Eolian, Fluvio-eolian and Sebkha deposits).

The Jefara Formation is made up of continental sediments consisting mostly of silt, sand and occasionally gravel. It is covered by eolian sediments and has thickness about 20 m.

The Gargaresh Formation is built up of marine sediments consisting of whitish calcarenites with shell fragments and minor Quartz grains (Lexique Stratigraphique International, 1960). They are exposed as cliffs on the coastline of the Mediterranean (Figure 2).

Holocene sediments are divided according to lithostratigraphic and genetic classification (El-Hinnawy and Chesthitey 1975) as follows:-

- a- Recent Wadi deposits indicate that all materials were transported by water and deposited on

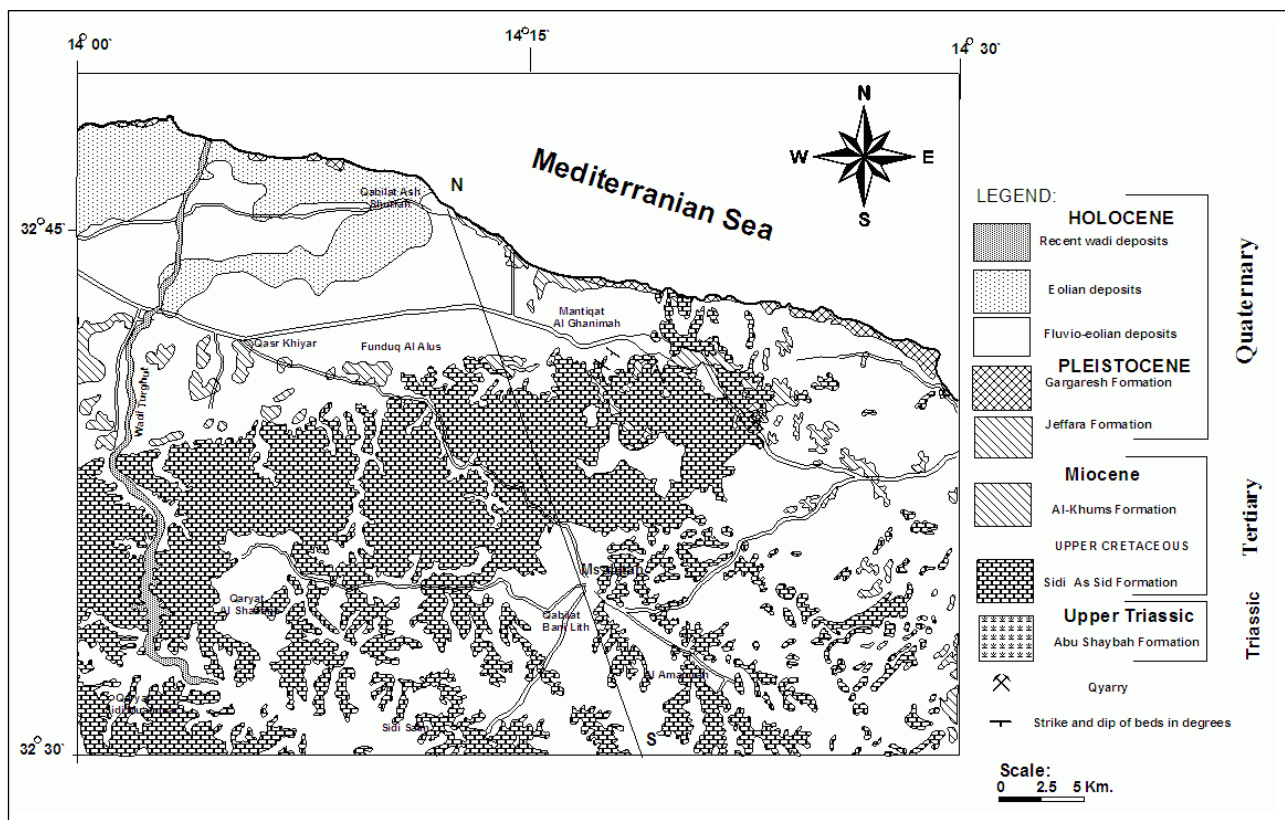


Figure 2. Geological map of the study area (after El-Hinnawy and Chesthitey, 1975).

wadi bottoms and shaped by recent stream activity. These are mainly coarse and fine grained gravel, sand and silt.

b- Eolian deposits are typically developed, particularly in the lowlands in the north of the escarpment foothills and in the lowlands extending along the eastern coast line of the Mediterranean Sea.

c- Fluvio–eolian deposits are mainly sandy, silty and loamy, with irregular lenses of small size and light brown color. Parent rock is mostly carbonate of the Late Cretaceous age, Miocene or a Vulcanite (Hey, 1962). Fluvio-eolian deposits lie disconformably on all formations of the Pre-Quaternary age.

Figure 3 shows the N-S geological cross section N-S of the study area.

HYDROGEOLOGIC SETTING

SAMPLING AND ANALYTICAL PROCEDURES

A total of 18 boreholes (government wells) were sampled for chemical analyses, each sample was analyzed in September, 2003, for the parameters listed in Table 1. The parameters include electrical conductivity (EC), pH and temperature. The National Organization of Water Laboratories in Tarabulus carried out the major and minor ion analyses from the data set. Thirty wells scattered in the same area and same aquifer were sampled in November 2006 (Table 2). They were compared to 2003 samples to show the difference in groundwater chemistry over this period. The SPSS computer program was used to perform all statistical analysis. The extent of mineral saturation of all sampled water was determined using the Phreeqc software package, through a Wateq subroutine (Plummer et al., 1992).

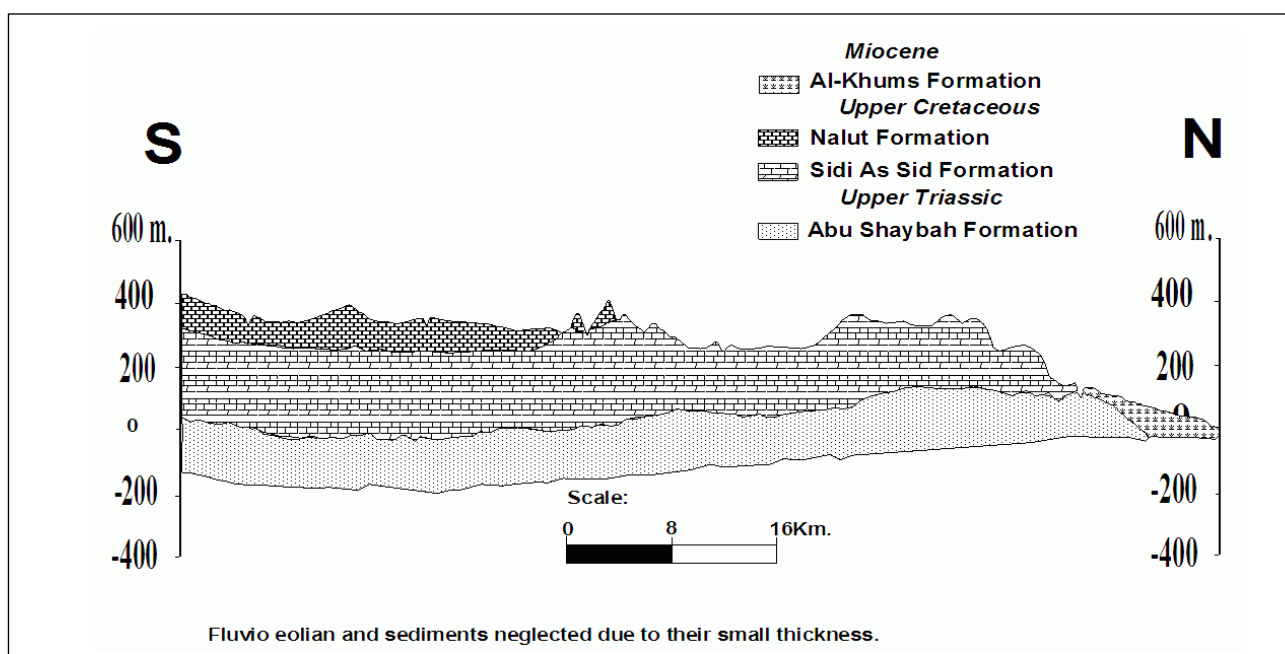


Figure 3. Geological cross section N-S of the study area (after El-Hinnawy and Chesthitey, 1975).

CHEMICAL CHARACTERISTIC OF GROUNDWATER

The groundwater has concentrations of major cations and anions higher than rainwater. The dissolution of salts and other processes during rainwater infiltration into the subsurface, changing the chemical composition of the rain water. The pH of the groundwater ranges between 6.5 and 8.24 (Tables 1 and 2). The chemical composition of the groundwater varies over a wide range and this indicates that the groundwater in the study area differs in both salinity and ionic concentration.

The dissolution, precipitation processes and cation exchange are actively taking place within the groundwater. The saturation of calcite and aragonite in groundwater are summarized in Table 3. The mineral phases of calcite and aragonite are saturated and undersaturated in some groundwater samples (Table 3) (Figures 4 and 5). It is known that mineral phases that are undersaturated will tend to dissolve and mineral phases that are oversaturated will precipitate. The dissolution of minerals and the subsequent exchange between cations leads to the precipitation of minerals.

Statistical Analyses

Statistical study helps to understand the chemistry of water samples and investigating the relationships among the dissolved constituents and environmental parameters such as lithology (Drever, 1997).

The hydrochemical data were analyzed using R-mode factor analysis to determine the main factors or processes responsible for the groundwater chemistry in the study area. In the dendrogram (R-mode) analysis (Figures 6 and 7) two categories of elements can be distinguished as follows:-

1) The 1st set elements are pH, NO₃, CO₃, K, Ca and Mg. The best correlation coefficient was observed between pH and NO₃ ($r = 0.9$), and also with Ca and Mg ($r = 0.9$) (Figure 6). While in Figure 7 the elements Ca, Mg, pH and K is the 1st set and the best correlation coefficient was clear between Ca and Mg ($r = 0.9$). Also the best correlation coefficient was clear between pH and K ($r = 0.9$).

2) The elements Na, SO₄, HCO₃ and Cl define the 2nd set in which, $r[\text{Na and SO}]_4 = 0.9$ and $r[\text{Na}$

Table 1. Descriptive statistics for chemical analysis of groundwater samples (2003).

| Constituents (mgL ⁻¹) | Minimum | Maximum | Mean | Std. Deviation |
|-----------------------------------|---------|---------|----------|----------------|
| Na | 5 | 250 | 135.1944 | 67.08404 |
| K | 2.8 | 34 | 13.29444 | 10.80199 |
| Ca | 40 | 240 | 87.61556 | 44.05784 |
| Cl | 223.3 | 531.75 | 315.9778 | 80.04407 |
| Mg | 41 | 119 | 63.14222 | 20.41625 |
| HCO ₃ | 15 | 305 | 134.2667 | 130.443 |
| CO ₃ | 0 | 42 | 3.055556 | 9.943796 |
| SO ₄ | 102 | 485 | 203.4944 | 87.37889 |
| TDS | 705 | 1939 | 1059.136 | 303.2195 |
| PH | 6.5 | 8.24 | 7.275556 | 0.396132 |
| NO ₃ | 0 | 32.05 | 8.390625 | 9.162245 |

Table 2. Descriptive statistics for chemical analysis of groundwater samples (2006).

| Constituents (mgL ⁻¹) | Minimum | Maximum | Mean | Std. Deviation |
|-----------------------------------|---------|---------|----------|----------------|
| Na | 72.5 | 288 | 206.4929 | 70.87095 |
| K | 6 | 360 | 56.08333 | 110.9695 |
| Ca | 8 | 110 | 76.5996 | 32.53057 |
| Cl | 226.12 | 539 | 379.4054 | 83.40316 |
| Mg | 40.4 | 79.358 | 60.62363 | 12.06703 |
| HCO ₃ | 220 | 400 | 280.9997 | 44.64065 |
| SO ₄ | 110.2 | 390 | 218.0629 | 66.348 |
| TDS | 939.7 | 1510.7 | 1280.583 | 170.1259 |
| pH | 6.74 | 8.11 | 7.491333 | 0.337401 |

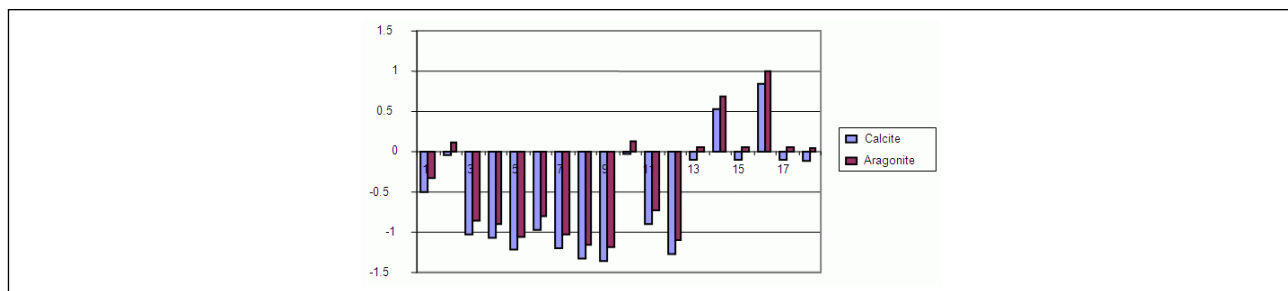


Figure 4. Correlation between saturation indices of aragonite and calcite (2003).

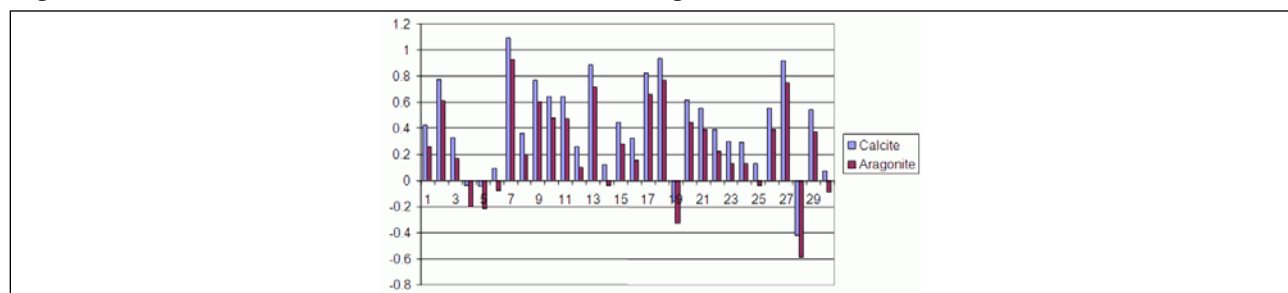


Figure 5. Correlation between saturation indices of aragonite and calcite (2006).

and HCO₃] = 0.9, while r[Na and Cl] = 0.7. The dependence of Na on the Cl was clear in the 2nd set (Figure 6).

Q-mode analysis for 2003 (Figures 8 and 9) can be differentiated into three clusters. The 1st cluster includes sample numbers 729, 730, 519, 727, 726, 732, 733, 936 and 731, and is characterized by the lowest salinity (TDS < 1015 ppm). It is attributed to high rainfall and aquifer recharge. The 2nd cluster was in the south eastern part. It is distinguished by the highest salinity (TDS 1330-2000 ppm sample numbers 601 and 488) which is due to high land where there is little

Table 3. Saturation indices of minerals (2003 and 2006).

| Well No. In Figures 2003 | Well No.in the city | Minerals Saturation | | Well No. 2006 | Minerals Saturation | |
|--------------------------------|---------------------------|---------------------|-----------|---------------------|---------------------|-----------|
| | | Calcite | Aragonite | | Calcite | Aragonite |
| 1 | 601 | -0.3297 | -0.494 | 1 | 0.4235 | 0.2592 |
| 2 | 728 | 0.1166 | -0.04775 | 2 | 0.7731 | 0.6088 |
| 3 | 729 | -0.8589 | -1.023 | 3 | 0.3282 | 0.1638 |
| 4 | 730 | -0.9068 | -1.071 | 4 | -0.03772 | -0.202 |
| 5 | 519 | -1.052 | -1.216 | 5 | -0.04824 | -0.2125 |
| 6 | 727 | -0.8008 | -0.9652 | 6 | 0.08968 | -0.07463 |
| 7 | 726 | -1.031 | -1.195 | 7 | 1.089 | 0.9247 |
| 8 | 732 | -1.158 | -1.322 | 8 | 0.3614 | 0.1971 |
| 9 | 733 | -1.187 | -1.351 | 9 | 0.7669 | 0.6026 |
| 10 | 756 | 0.134 | -0.0303 | 10 | 0.6416 | 0.4773 |
| 11 | 936 | -0.7322 | -0.8965 | 11 | 0.6376 | 0.4733 |
| 12 | 731 | -1.107 | -1.271 | 12 | 0.2604 | 0.09608 |
| 13 | 602 | 0.06076 | -0.1035 | 13 | 0.8809 | 0.7166 |
| 14 | 123 | 0.691 | 0.5267 | 14 | 0.1243 | -0.03998 |
| 15 | 603 | 0.06399 | -0.1003 | 15 | 0.443 | 0.2787 |
| 16 | 487 | 1.007 | 0.8423 | 16 | 0.3186 | 0.1543 |
| 17 | 455 | 0.05928 | -0.105 | 17 | 0.823 | 0.6586 |
| 18 | 488 | 0.04505 | -0.1193 | 18 | 0.9293 | 0.765 |
| | | | | 19 | -0.1617 | -0.326 |
| | | | | 20 | 0.6127 | 0.4484 |
| | | | | 21 | 0.5551 | 0.3908 |
| | | | | 22 | 0.3884 | 0.2241 |
| | | | | 23 | 0.2941 | 0.1298 |
| | | | | 24 | 0.2915 | 0.1272 |
| | | | | 25 | 0.1266 | -0.03775 |
| | | | | 27 | 0.5523 | 0.388 |
| | | | | 28 | 0.9116 | 0.7473 |
| | | | | 29 | -0.4227 | -0.587 |
| | | | | 30 | 0.538 | 0.3737 |
| | | | | 31 | 0.07283 | -0.09147 |

chance for infiltration of surface water into the aquifer. The last cluster is characterized by intermediate salinity between 1016 to 1331 ppm (sample numbers 728, 756, 602, 123, 603, 487 and 455).

Q-mode analysis for 2006 (Figures 10 and 11) is differentiated into four clusters. The 1st cluster includes sample numbers 1, 2, 3, 8, 9, 13, 14 and 24; it is characterized by the low salinity (TDS <1030 ppm) which reflects the high recharge from rainfall. The 2nd cluster is characterized by salinity ranges from 1031 to 1332 ppm, which includes well numbers 4, 5, 6, 7, 10, 11 and 25. The 3rd cluster is represented by well numbers 15, 16, 17, 18, 19, 20, 21, 22 and 23 which are characterized by salinity greater than 1332 ppm. The last cluster is an independent case; it is characterized by different characters that all samples contain (samples numbers 27, 28, 29, 30 and 31).

Correlation Matrices

Pearson’s correlation matrices (Swan and Sandilands, 1995) were used to find the relationships between two or more variables (Table 1 and 2). Strong and moderate correlations exist among the major elements, Na, Ca, Mg and Cl, and TDS. (Table 4, analysis of year 2003). These relationships clearly identify the main elements contributing to the groundwater salinity and their tendency to follow a similar trend (e.g. due to concentration by evaporation). Also, correlation between SO₄ with TDS indicates that the ions tend to increase in concentration as the salinity of the water

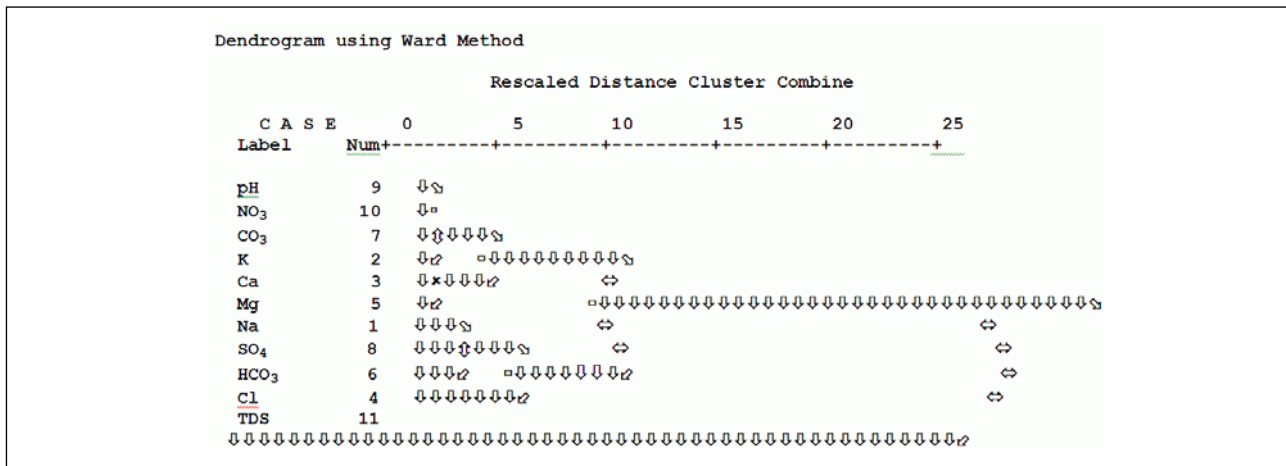


Figure 6. R-mode analysis of 2003 groundwater samples. Dendrogram using average linkage (between groups).

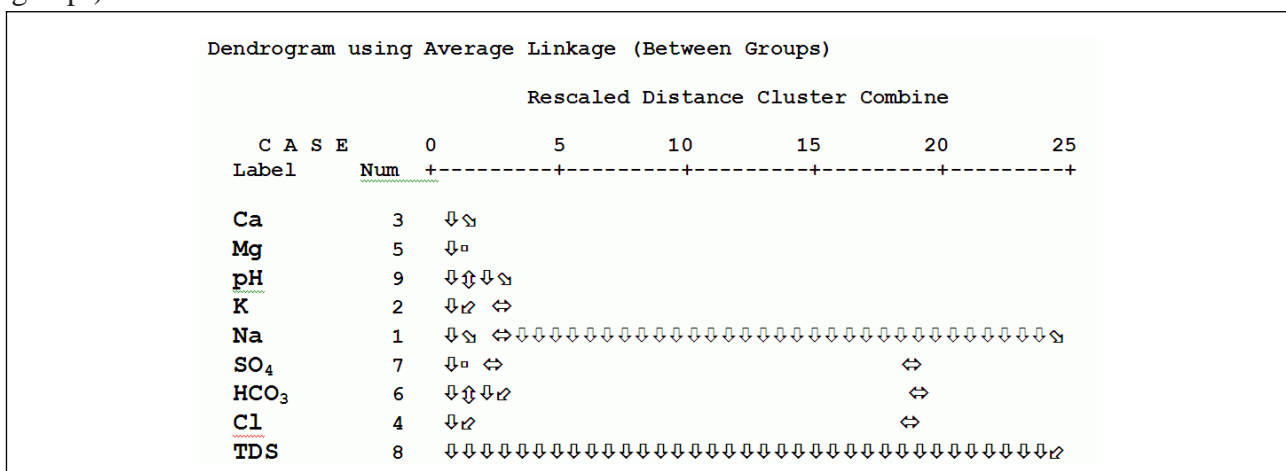


Figure 7. R-mode analysis of 2006 groundwater samples.

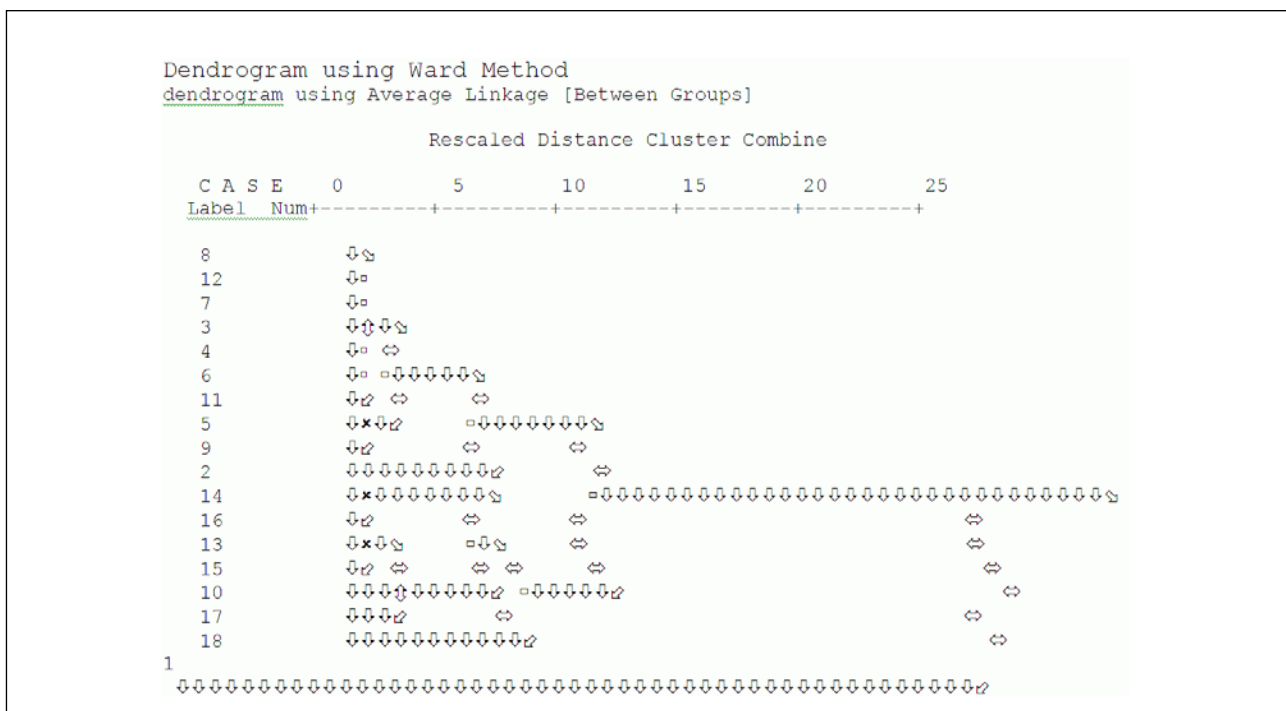


Figure 8. Q-mode analysis of 2003 groundwater samples.

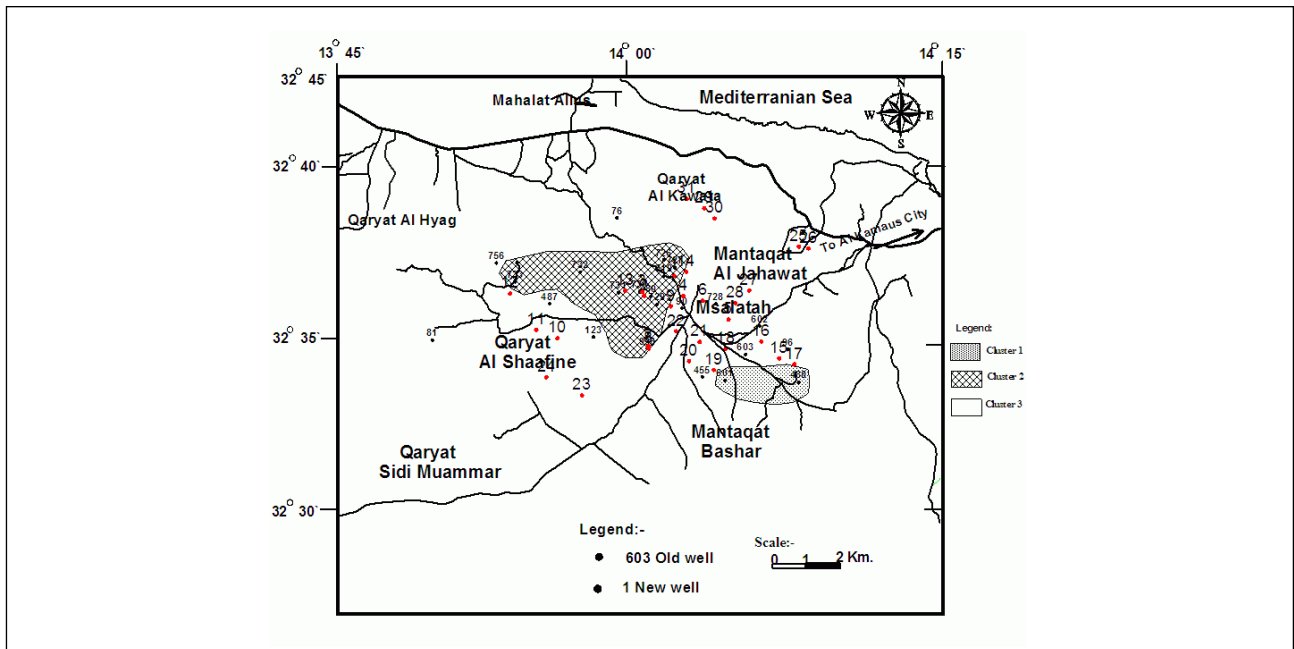


Figure 9. Areal distribution of clusters derived from hierarchical cluster (2003).

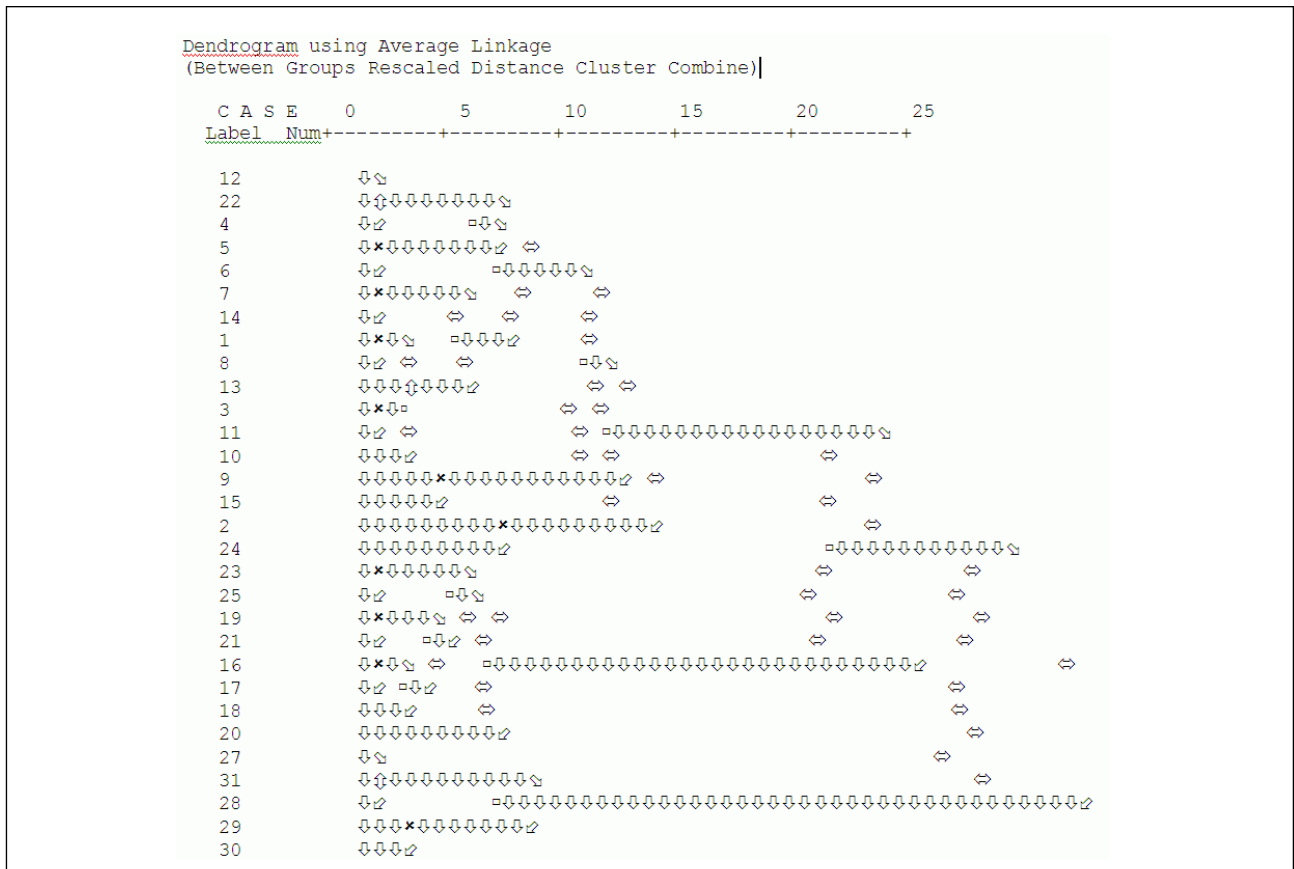


Figure 10. Q-mode analysis of 2006 groundwater samples.

increases. The salinization of the groundwater is a result of the ionic concentrations increasing due to both evaporation of recharge water and to the effects of interactions between the groundwater and the geological formations. The major exchangeable ions Na–Ca and K–Na show positive correlation, while the Na–Mg displays negative correlation, which gives an indication that the two elements are not from the same source.

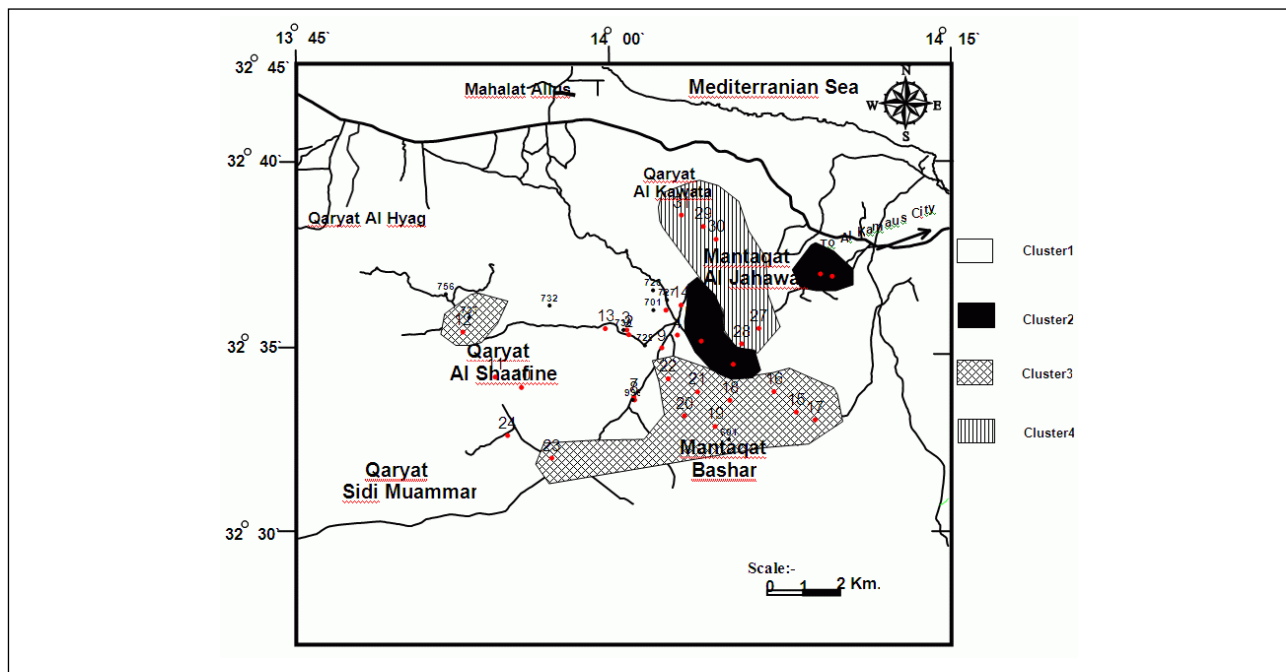


Figure 11. Areal distribution of clusters derived from hierarchical cluster (2006).

Table 4. Pearson`s correlation matrices for the values of anions and cations (2003).

| | Na | K | Ca | Cl | Mg | HCO ₃ | CO ₃ | SO ₄ | TDS | PH | NO ₃ |
|------------------|-------|---------|--------|--------|------|------------------|-----------------|-----------------|-------|-------|-----------------|
| Na | 1 | | | | | | | | | | |
| K | 0.08 | 1 | | | | | | | | | |
| Ca | 0.48 | -0.0041 | 1 | | | | | | | | |
| Cl | 0.38 | 0.3263 | 0.7879 | 1 | | | | | | | |
| Mg | -0.21 | -0.0959 | 0.4635 | 0.59 | 1 | | | | | | |
| HCO ₃ | 0.55 | -0.4523 | 0.5718 | 0.259 | 0.21 | 1 | | | | | |
| CO ₃ | 0.07 | -0.09 | -0.112 | -0.239 | -0.3 | 0.091 | 1 | | | | |
| SO ₄ | 0.64 | 0.2737 | 0.8133 | 0.756 | 0.34 | 0.276 | -0.333 | 1 | | | |
| TDS | 0.56 | -0.0751 | 0.9207 | 0.832 | 0.58 | 0.615 | -0.3 | 0.836 | 1 | | |
| PH | -0.08 | -0.0279 | -0.625 | -0.49 | -0.4 | -0.189 | 0.685 | -0.57 | -0.64 | 1 | |
| NO ₃ | 0.3 | -0.3389 | -0.105 | -0.193 | 0.11 | 0.171 | 0.176 | 0.037 | 0.044 | 0.201 | 1 |

Any possible negative correlations present due to the increase or decrease in the cations is the result of dissolution or precipitation reactions and concentration effects.

The pH is negatively correlated with all of the cations and anions except NO₃ and CO₃, which indicating that higher pH water often has a higher NO₃ and CO₃ concentrations.

Table 5, for the analysis 2006, shows that the correlation of Na with Ca is strong, while Cl, HCO₃ and SO₄ are weak correlations, and Mg and TDS have a negative correlation. Also, correlation between SO₄ and TDS indicates that the ions decrease with increase of the salinity of water. Moreover, the Na-Ca ions are positively correlated, while K-Na and Na-Mg are negative correlations indicating that these elements are not from the same source.

The pH shows negative correlation with the all cations and anions except K and SO₄ which are positively correlated, indicating that the pH increased with increasing of K and SO₄.

Factor Analysis

Factor analysis has proved useful as an aid in the interpretation of geohydrological data (Schot

Table 5. Pearson`s correlation matrices for the values of ions (2006).

| | Na | K | Ca | Cl | Mg | HCO ₃ | SO ₄ | TDS | pH |
|------------------|----------|----------|----------|---------|--------|------------------|-----------------|-------|----|
| Na | 1 | | | | | | | | |
| K | -0.8295 | 1 | | | | | | | |
| Ca | 0.8675 | -0.9322 | 1 | | | | | | |
| Cl | 0.0368 | 0.405629 | -0.17294 | 1 | | | | | |
| Mg | -0.184 | 0.561152 | -0.32599 | 0.735 | 1 | | | | |
| HCO ₃ | 0.3408 | -0.1576 | 0.1038 | -0.119 | -0.097 | 1 | | | |
| SO ₄ | 0.156767 | 0.011504 | 0.134262 | -0.0018 | 0.51 | -0.05129 | 1 | | |
| TDS | -0.38308 | 0.298025 | -0.38908 | -0.1341 | 0.018 | -0.16223 | -0.058 | 1 | |
| pH | -0.09286 | 0.001526 | -0.0446 | -0.253 | -0.19 | -0.1107 | 0.086 | 0.005 | 1 |

and Van der Wal, 1992; Usunoff and Guzman-Guzman, 1989; Ashley and Lloyd, 1978; Dawdy and Feth, 1967).

Factor analysis is a tool used to rearrange data to present it in a manner that better explains the structure of the underlying system that produced the data (Dawdy and Feth, 1967). Also, is used to quantify the contribution of natural chemical weathering to the chemical composition of groundwater in the aquifer. A set of factors is created in a simple structure to explain the interrelations of the chemical parameters.

Figure 12 shows the principal component analysis (PCA), weights of components, and associated variance explained in the physio-chemical data. PCA is applied to reduce a large number of observed variables down to a small number of principal components that reflect underlying processes. Factor 1 explains 44.56% of the total variance, while Factor 2 explains 18.59%, and Factor 3 is 13.5%. Factor 1 is interpreted as relating mainly to the salinization of the groundwater due to infiltration of the groundwater through evaporation and dissolution. The main sources of the groundwater salinity are Ca, Cl, SO₄, Na, Mg and HCO₃. The main cation exchange elements Ca, Na and Mg correlate positively indicating the influence of the geological source. The significant positive correlation between Ca and SO₄ suggests that processes of dissolution and precipitation of evaporitic and sulfide minerals are active. While Factor 2 differentiates ions of lithogenic sources such as Na, HCO₃, CO₃ and NO₃. The 3rd factor has a negative loading with NO₃ and negative with HCO₃; suggesting that the two have the same source freshwater resulting from dissolution of fertilizer materials by the rain water. It can be concluded that Factor 1 represents the natural processes by which water gained its chemical characteristics (a mix of rainfall, wastewaters, and evaporated water), where as Factor 3 reflects the effect of pollution.

In Figure 13, Factor 1 explains 36.63% of total variance, while Factor 2 is 21.43 and Factor 3 is 13.55. Here, the salinity is affected by K, Cl, Mg and pH.

The Ca and Na correlate positively indicating the influence of the geologic source rocks, while Factor 2 differentiates ions of lithogenic sources such as K, Mg, Cl and SO₄. The 3rd factor has a negative loading with Na, Cl and HCO₃.

CHEMICAL CLASSIFICATION OF GROUNDWATER

Based on the major cations and anions, three water types are found in the study area. They are represented by NaCl, MgCl₂ and CaCl₂ (Table 6 - analysis of year 2003). The chemical characters of the studied groundwater types were distinguished and grouped by their position on a Piper

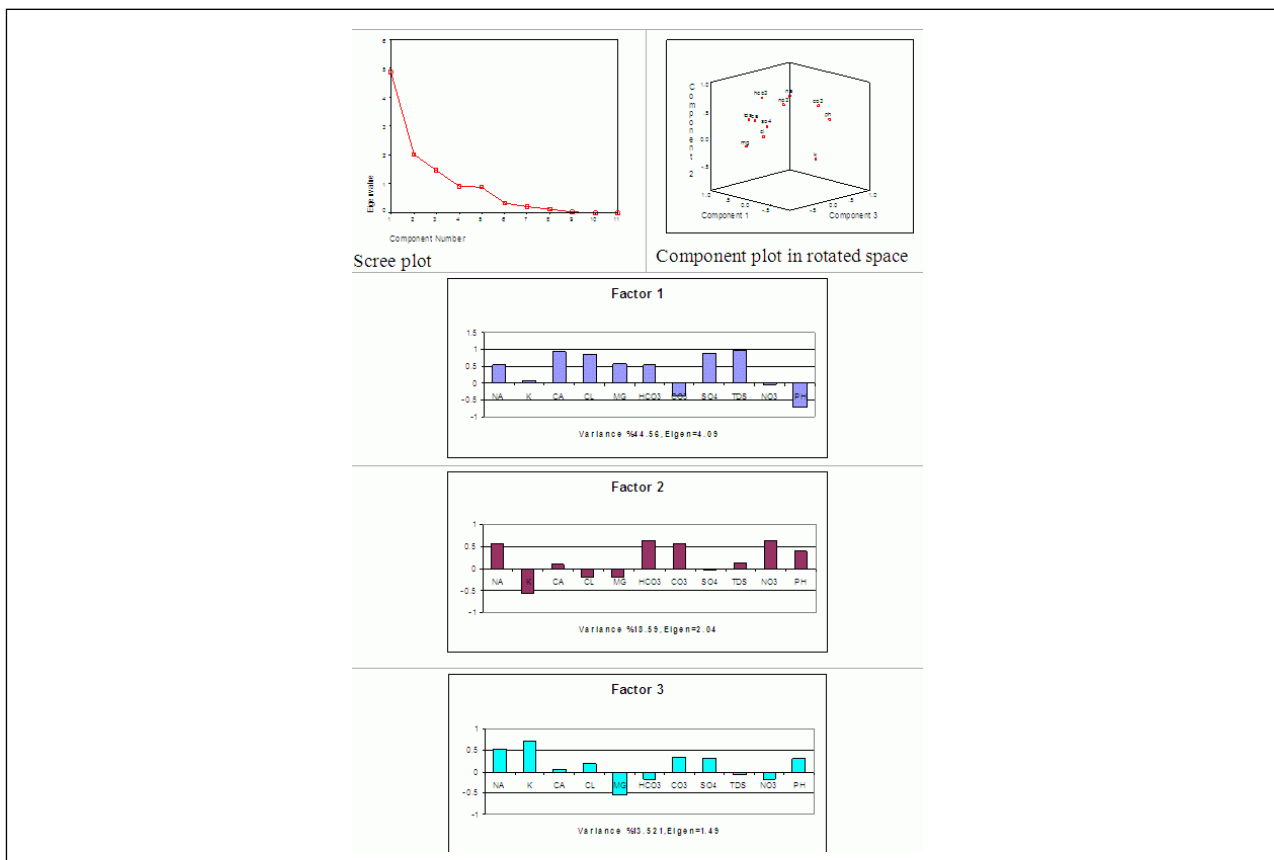


Figure 12. Factor analysis of the groundwater chemistry (2003).

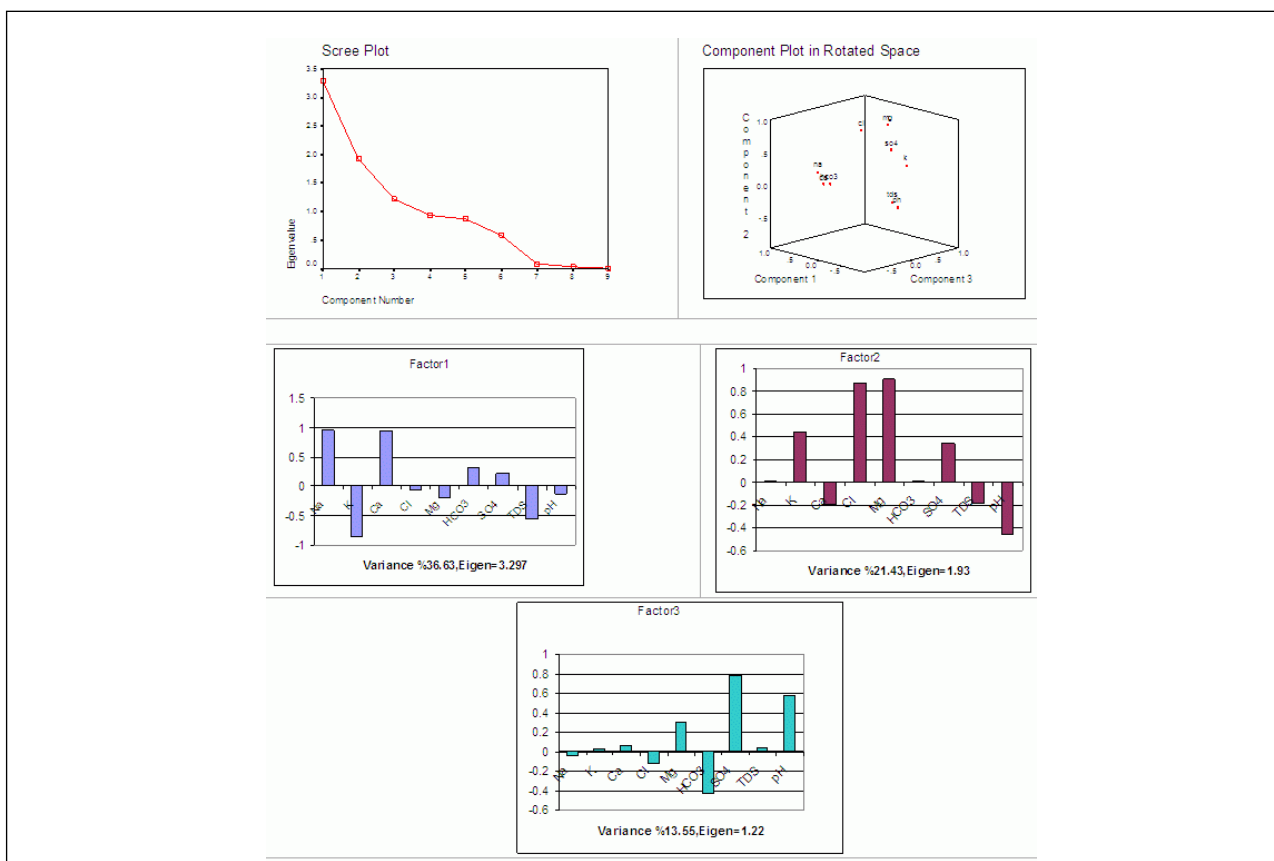


Figure 12. Factor analysis of the groundwater chemistry (2006).

diagram (Piper, 1944; Ophori and Toth, 1988; Kirchner, 1994). The main anion in the groundwater is the chloride with a corresponding increase in TDS. This is generally related to the relative age and the length of the groundwater flowpaths. Table 7 also indicates that the water types which are dominated by chlorides occur in areas where there is no or very little groundwater flow. This may be due to short flowpaths in the study area. On the other hand the new chemical analysis (2006) indicates that all samples belong to NaCl water type.

The replacement of calcium by sodium through cation exchange results in the formation of Na (HCO₃)₂ water type. Removal of calcium, through the precipitation of carbonate minerals, may cause a disturbance in the chemical equilibrium resulting in the dissolution of minerals containing calcium such as gypsum (Freeze and Cherry, 1979). The formation of NaCl and CaCl₂ water types is a result of progressive salinization of waters. At higher salinities, the process of reverse cation exchange may create CaCl₂ waters due to the removal of Na out of solution for bound Ca. Alternatively, the CaCl₂ water type could be also due to the process of mixing between younger, fresher water with more saline older water.

The chemical analyses of the groundwater are plotted on trilinear diagrams (Piper, 1944, Durov, 1948 and Schoeller, 1963) (Figures 14, 15, 16, 17, 18 and 19). Generally, water is characterized by dominance of Ca, Mg, Cl, and SO₄. The graphical representations give the same hydrochemical

Table 6. Groundwater types (2003).

| Water type | Well numbers | Mean TDS (mg/l) |
|-------------------|---|-----------------|
| MgCl ₂ | 488,519,727,731,733 and 936 | 980.9 |
| NaCl | 123,487,455,602,603,726,728,729,730,732 and 756 | 1021.8 |
| CaCl ₂ | 601 | 1939 |

Table 7. Irrigation water chemistry (2003).

| Well No. | Salinity hazard | Sodium Adsorption ratio | Exchangeable Sodium ratio | Magnesium hazard | Total hardness |
|----------|-----------------|-------------------------|---------------------------|------------------|----------------|
| 601 | Very high | 3.55 | 36 | 36 | 936.96 |
| 728 | Very High | 3.02 | 35 | 59.7 | 563.26 |
| 729 | High | 2.79 | 48 | 57.9 | 320.15 |
| 730 | High | 2.44 | 33 | 52.9 | 350.11 |
| 519 | High | 104×10 ⁻³ | 21 | 58.7 | 435.1 |
| 727 | High | 2.15 | 33 | 64.1 | 514.22 |
| 726 | High | 2.37 | 37 | 48.4 | 348.62 |
| 732 | High | 2.95 | 42 | 53 | 318.66 |
| 733 | High | 1.84 | 32 | 58.2 | 346.61 |
| 756 | High | 3.66 | 41 | 43.2 | 457.35 |
| 936 | High | 2.52 | 36 | 63.9 | 463.8 |
| 731 | High | 2.19 | 32 | 59.5 | 401.15 |
| 602 | High | 4.48 | 49 | 39.7 | 497.3 |
| 123 | High | 3.56 | 50 | 67 | 302.49 |
| 603 | High | 4.5 | 50 | 50.1 | 460.33 |
| 487 | High | 3.32 | 49 | 47.8 | 382.6 |
| 455 | High | 3.83 | 44 | 55.1 | 567.7 |
| 488 | High | 285×10 ⁻³ | 44 | 58.4 | 839.62 |

facies and the flow from either fresh groundwater or rainfall to the present conditions. The water samples are characterized by low to moderate alkali sodium hazard and high to very high salinity hazard (Table 8).

The abundance of carbonate rocks in the area and their rapid weathering and erosion rate suggest that dissolution of carbonate minerals will add significant amounts of Ca and Mg to the reservoir. The most common weathering reaction for calcite is simple dissolution (Drever, 1988) giving a $1/2 \text{ Ca:HCO}_3$. Figure 20(A), (analysis 2003) shows that only the sample number 728 is located on the limestone line. Groundwater samples numbers 487, 488, 519, 726, 727, 729, 730, 731, 732, 733 and 936 are above the line. On the other hand, the majority of samples in 2006 occur above the limestone line, while sample no. 6 falls on the limestone line and sample no. 22 lies under this line. The samples that lie above or on the limestone line indicate the presence of more than one source of Ca, which may be attributed to the weathering and erosion of gypsum and clay.

In mudstone and marl, the dissolution of gypsum is the source of SO_4 and Ca in water. A plot of Ca and SO_4 (analysis 2003) shows that most of the groundwater sample numbers 123, 455, 603, 726, 727, 728, 729, 730, 731, 732 & 936 fall above the line. While other samples numbers 456, 487, 488, 519, 601, 602, 733 & 756 lie below the line of Ca:SO_4 suggesting that Ca may have been incorporated and removed from the system during clay formation. Figure 21 (B) (analysis of year 2006) indicates that all the groundwater samples except sample no. 28 fall above the line, indicating another source of Ca as previously shown.

If Na was only derived from dissolution of evaporite minerals, then Na should balance Cl. Sample numbers 123, 455, 487, 602 & 603 fall above the line Na:Cl (1:1) (Figure 20C analysis 2003), while in Figure 21 (C), (analysis 2006) groundwater sample numbers 1, 2, 6, 7, 8, 9, 10, 14, 15, 17, 18, 24, 25 & 31 lie above the line which shows that the Na is in excess. The source of excess Na is weathering from feldspars which are found in sandstone. Groundwater samples numbers 601, 728, 729, 730, 519, 727, 726, 732, 733, 936, 731 & 488 are found below the line Na:Cl. But groundwater sample numbers 3, 4, 5, 11, 12, 13, 16, 19, 20, 21, 22, 23, 27, 29 & 30 (analysis of year 2006) are falling below the line, while sodium is a potential sink for Na ions during clay formation. The chemistry of the groundwater samples appears to be dominantly controlled by the dissolution and reprecipitation of minerals in the catchment host rocks.

The total hardness is given in Tables 7 and 8, and is a moderate water type. According to Wilcox classification all samples in the study area fall under the zone of good to permissible quality.

According to the U.S. Salinity Laboratory Staff (1955) all samples lie in class one ($\text{SAR} < 10$), which are used for all soils.

Very high salinity water shown in Tables 7 and 8 is suitable only for salt tolerant crops and soils of good permeability with special good drainage.

While high salinity water in Tables 7 and 8 is satisfactory if only used for plants having moderate salt tolerance and soil of moderate permeability. Irrigation by this water requires regular leaching and special management.

SALINITY DISTRIBUTION

Total dissolved salts (TDS) denote that the various types of minerals are dissolved in water. In natural waters, dissolved solids are composed mainly of bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium. Concentration of TDS is an important parameter in

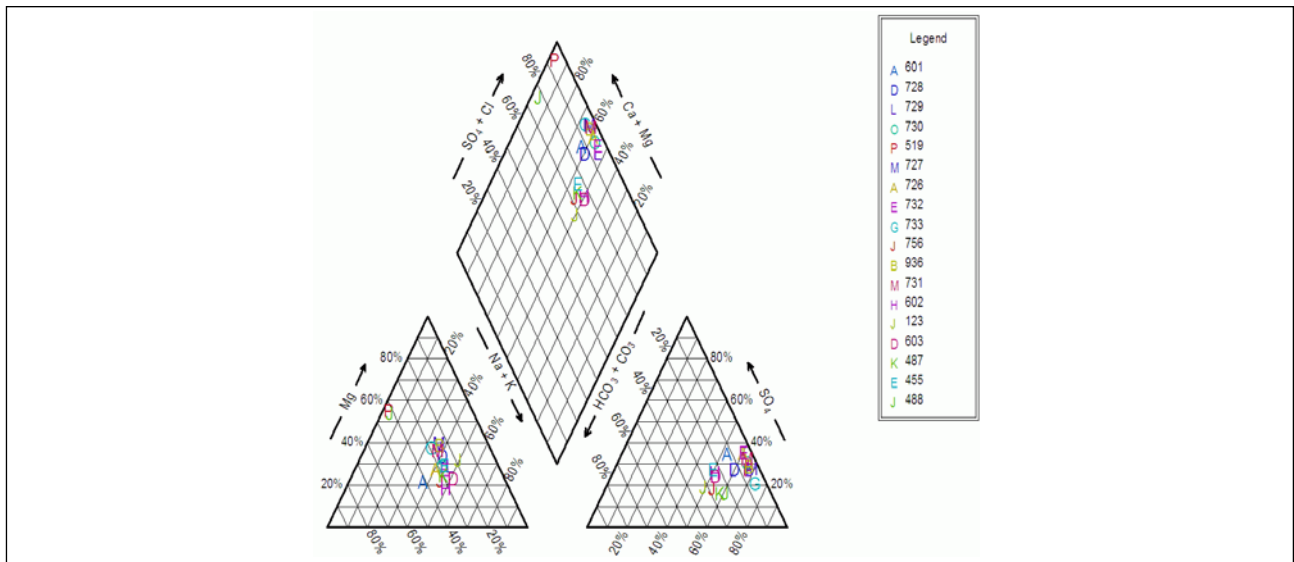


Figure 14. Piper diagram of the groundwater (2003).

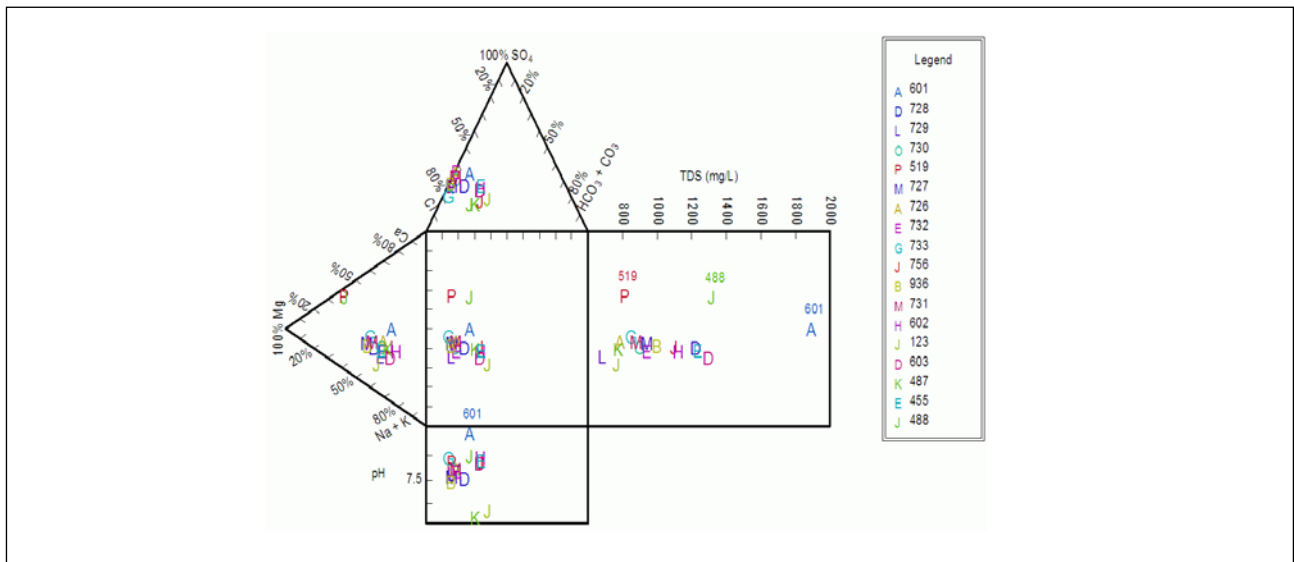


Figure 15. Durov diagram of the groundwater (2003).

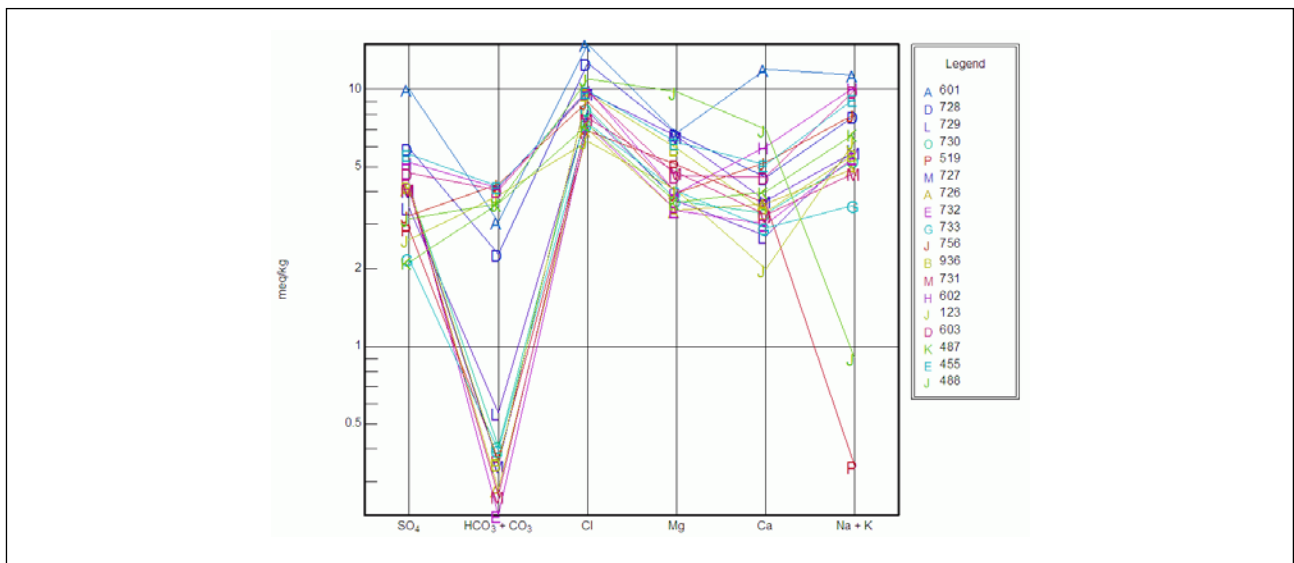


Figure 16. Schoeller diagram showing the difference between major ions (2003).

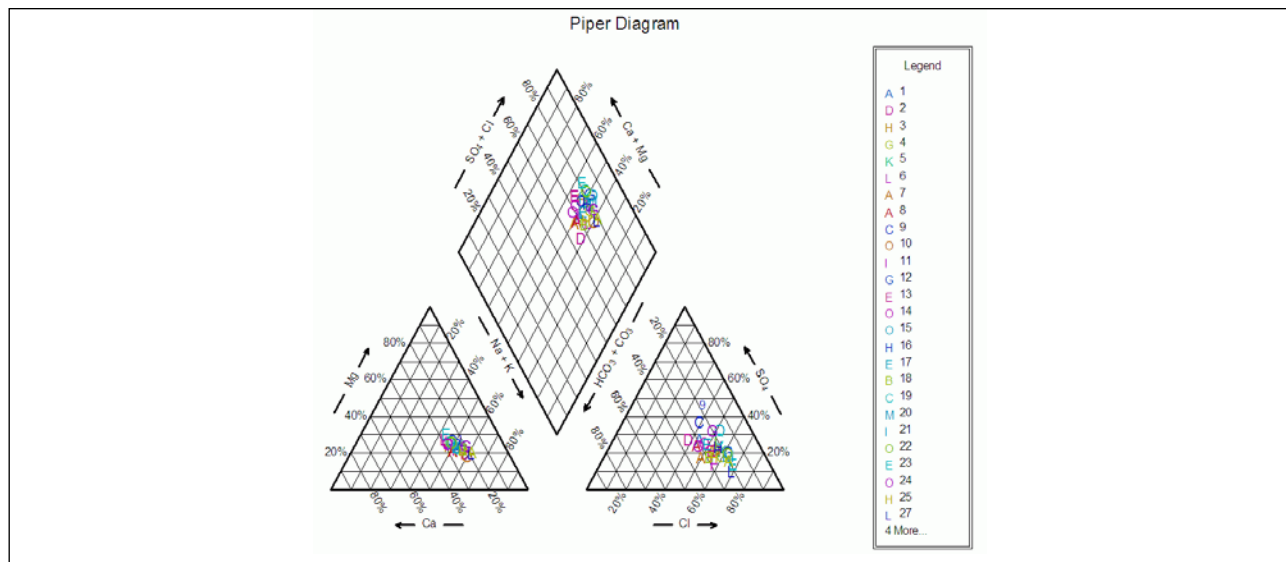


Figure 17. Piper diagram of the groundwater (2006).

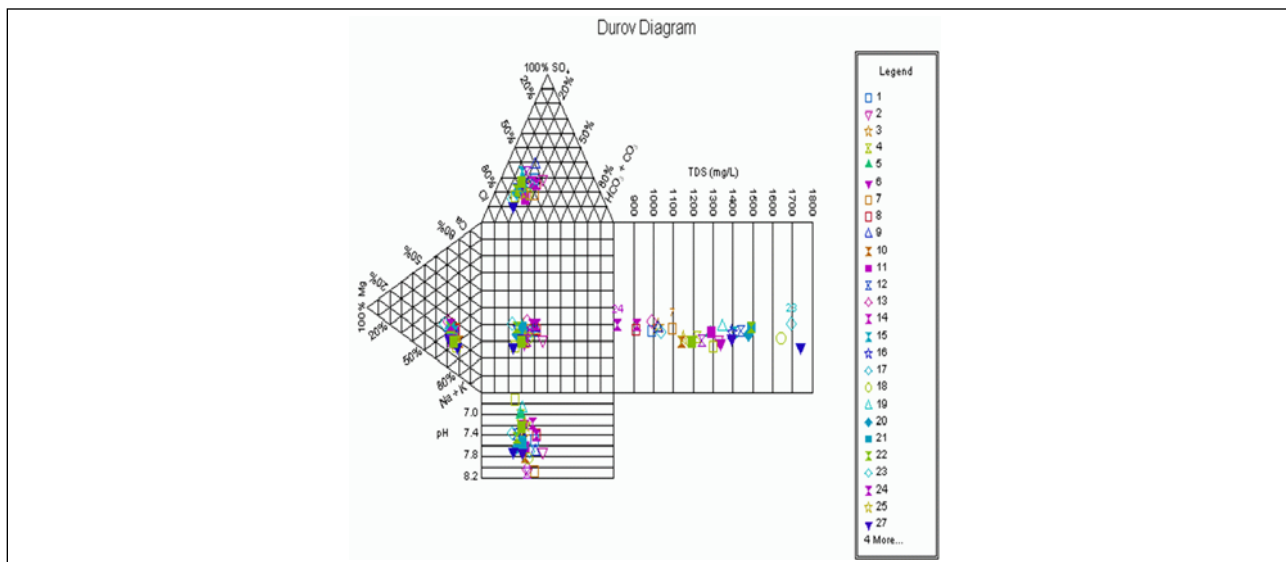


Figure 18. Durov diagram of the groundwater (2006).

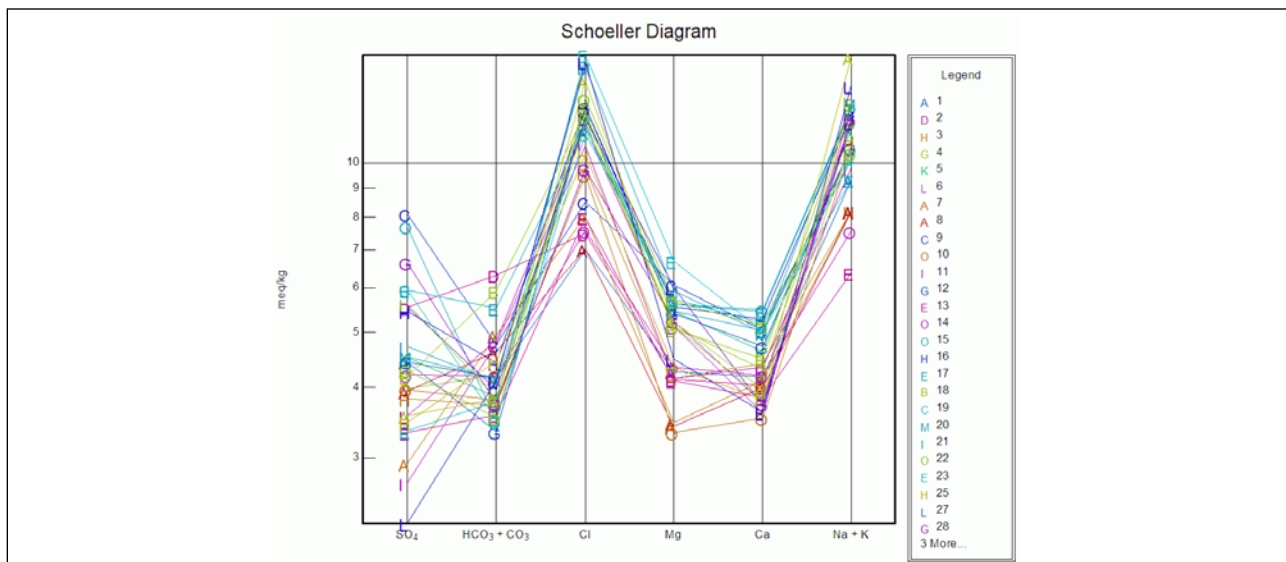


Figure 19. Schoeller diagram showing the difference between major ions (2008).

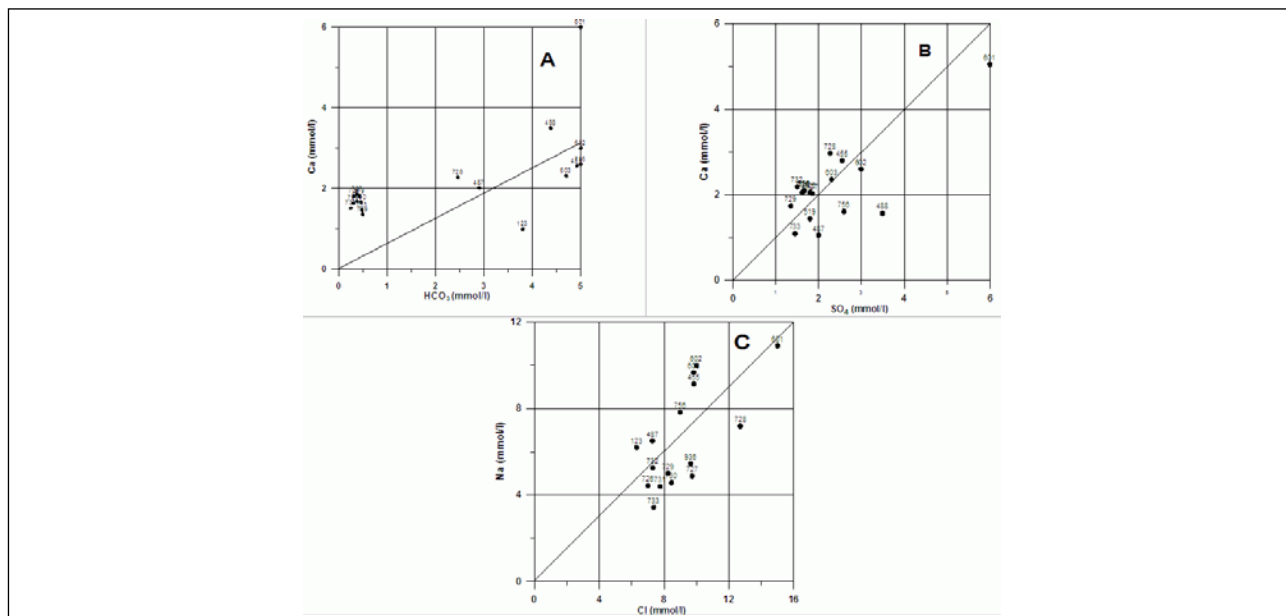


Figure 20. Chemical relationships for the groundwater samples (A) Ca vs HCO₃ (B) Ca vs SO₄ (C) Na vs Cl (2003).

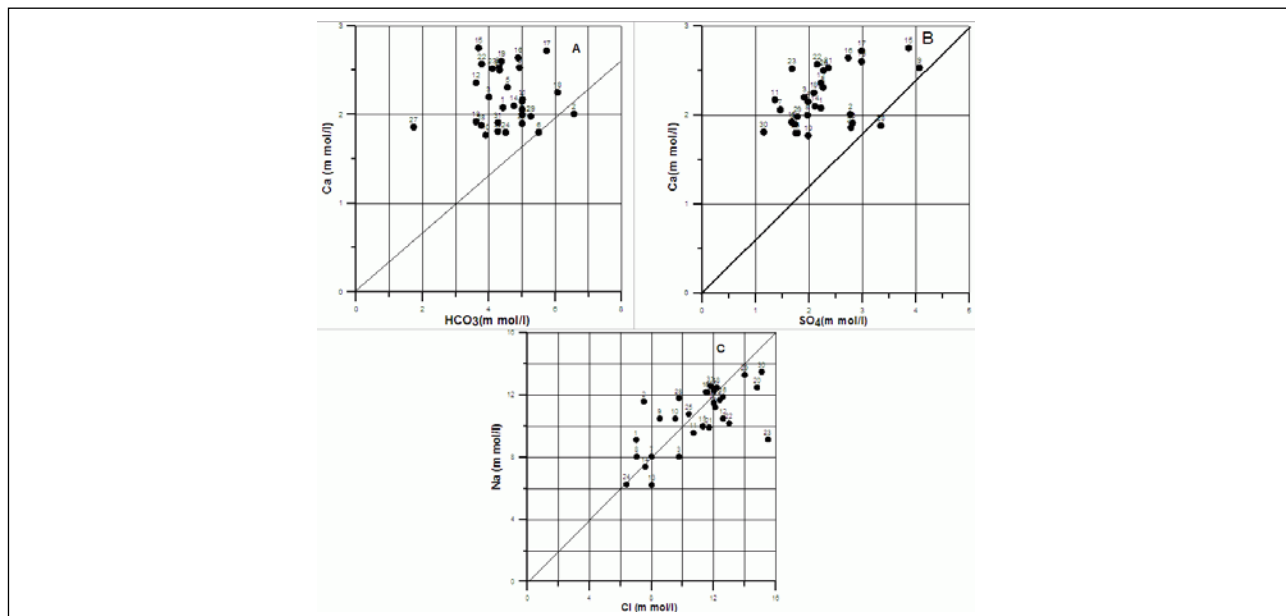


Figure 21. Chemical relationships for the groundwater samples (A) Ca vs HCO₃ (B) Ca vs SO₄ (C) Na vs Cl (2006).

drinking water and other water quality standards. Carroll (1962) proposed four classes of water based on TDS values. The TDS in the study area falls into two classes: fresh water and brackish water. Hence the study area was delineated into two classes: (a) desirable (sample numbers 123, 487, 519, 726, 727, 729, 730, 731, 732 and 733), (b) undesirable (sample numbers 455, 488, 601, 602, 603, 728, 756 and 936) for the old samples (Figure 22). On the other hand the new samples which were collected in November 2006 by the author and analyzed in the industrial research center, Tripoli, Libya, also fall into two classes: (a) fresh water (sample numbers 1, 2, 3, 8, 13, 14 and 24), (b) brackish water (sample numbers 4, 5, 6, 7, 9, 10, 11, 12, 15, 16, 17, 18, 19, 20, 21, 22, 23, 25, 27, 28, 29, 30 and 31) (Figure 23).

The grid of Figure 23 is subtracted from the grid of Figure 22 to evaluate the change which

Table 8. Irrigation water chemistry (2006).

| Sample NO. | Salinity Hazard | Sodium Adsorption Ratio | Exchangeable Sodium Ratio | Magnesium Hazard | Total Hardness mg/L |
|------------|-----------------|-------------------------|---------------------------|------------------|---------------------|
| 1 | High | 4.44 | 1.084 | 50.6 | 420.88 |
| 2 | High | 5.72 | 1.418 | 50.6 | 407.46 |
| 3 | High | 3.89 | 0.941 | 48.5 | 426.78 |
| 4 | High | 5.36 | 1.236 | 54.4 | 471.17 |
| 5 | High | 4.99 | 1.113 | 54.1 | 503.46 |
| 6 | High | 5.82 | 1.394 | 58.8 | 436.24 |
| 7 | High | 4.13 | 1.062 | 45.7 | 378.31 |
| 8 | High | 4.18 | 1.086 | 46 | 369.8 |
| 9 | High | 4.42 | 0.94 | 54.6 | 554.72 |
| 10 | High | 5.63 | 1.524 | 48.5 | 342.13 |
| 11 | High | 4.64 | 1.129 | 48.8 | 423.26 |
| 12 | High | 4.63 | 1.03 | 53.4 | 506.23 |
| 13 | High | 3.12 | 0.784 | 51.7 | 396.38 |
| 14 | High | 3.57 | 0.865 | 50.8 | 426.63 |
| 15 | High | 5.2 | 1.105 | 50.6 | 554.46 |
| 16 | High | 5.12 | 1.101 | 51.3 | 540.89 |
| 17 | High | 5.18 | 1.103 | 50.7 | 551.38 |
| 18 | Very High | 5.72 | 1.309 | 53.1 | 477.98 |
| 19 | High | 4.28 | 0.916 | 52.4 | 545.76 |
| 20 | High | 5.36 | 1.147 | 54.2 | 545.68 |
| 21 | High | 4.32 | 0.944 | 52 | 524.5 |
| 22 | High | 4.37 | 0.941 | 52.5 | 540.34 |
| 23 | Very High | 3.77 | 0.779 | 57.1 | 585.5 |
| 24 | High | 3.31 | 0.876 | 49.7 | 356.84 |
| 25 | High | 5.34 | 1.324 | 53.3 | 406.72 |
| 26 | | | | | |
| 27 | High | 5.2 | 1.181 | 61.9 | 485.62 |
| 28 | High | 5.53 | 1.306 | 58.3 | 448.97 |
| 29 | High | 6.2 | 1.448 | 56.9 | 459.15 |
| 30 | Very High | 6.69 | 1.662 | 55.4 | 405.21 |
| 31 | High | 5.96 | 1.411 | 57.3 | 446.47 |

occurred in the groundwater for the study area from 2003 to 2006. The results are shown in Figure 24.

The contour lines having positive values indicate that the area did not receive much rain water or the amount of discharge was more than the recharge, hence the TDS in 2006 is more than 2003. The area of contour zero shows that the amount of recharge equals the amount of discharge and there is no change in salinity. The negative contour lines indicate that the amount of recharge was more than the amount of discharge. The salinity decreased by the value of contour from the old analyses indicates improved quality of the water in this area.

CONCLUSION

The research has shown the difference between the chemistry of groundwater between 2003 and 2006. The applied statistical analysis of hydrochemical data provide insight into the regional factors and processes controlling groundwater recharge.

Precipitation of calcite causes an equilibrium disturbance in Ca concentration and leads to the dissolution of gypsum where available. In the higher salinity areas, reserved cation exchange which may have occurred with the formation of CaCl₂ type from NaCl. Salinization resulting from long residence times causes the formation of NaCl and CaCl₂ water types. The precipitation of the calcite and aragonite decreased the pore spaces in the aquifer. The areas which contain positive

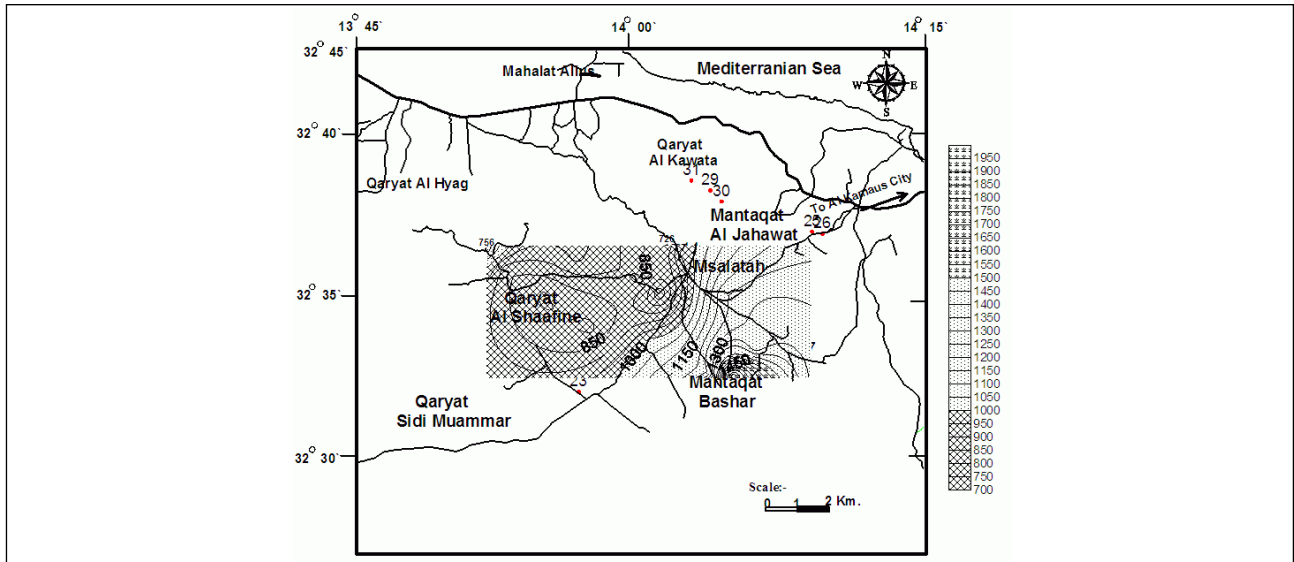


Figure 22. Distribution of groundwater salinity (2003).

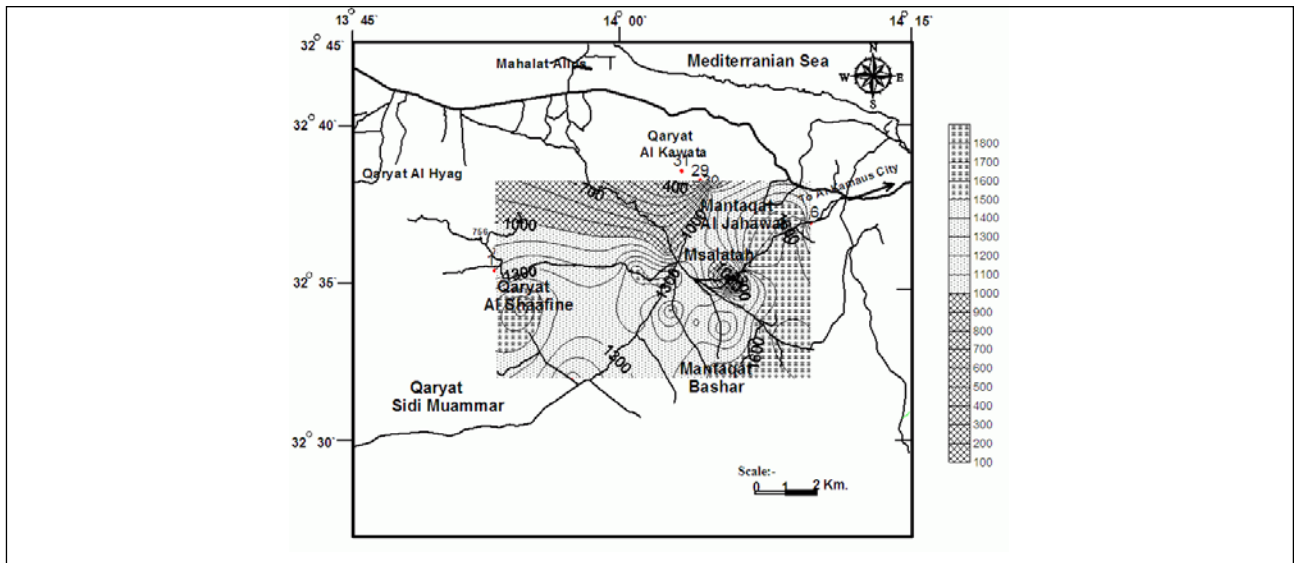


Figure 23. Distribution of groundwater salinity (2006).

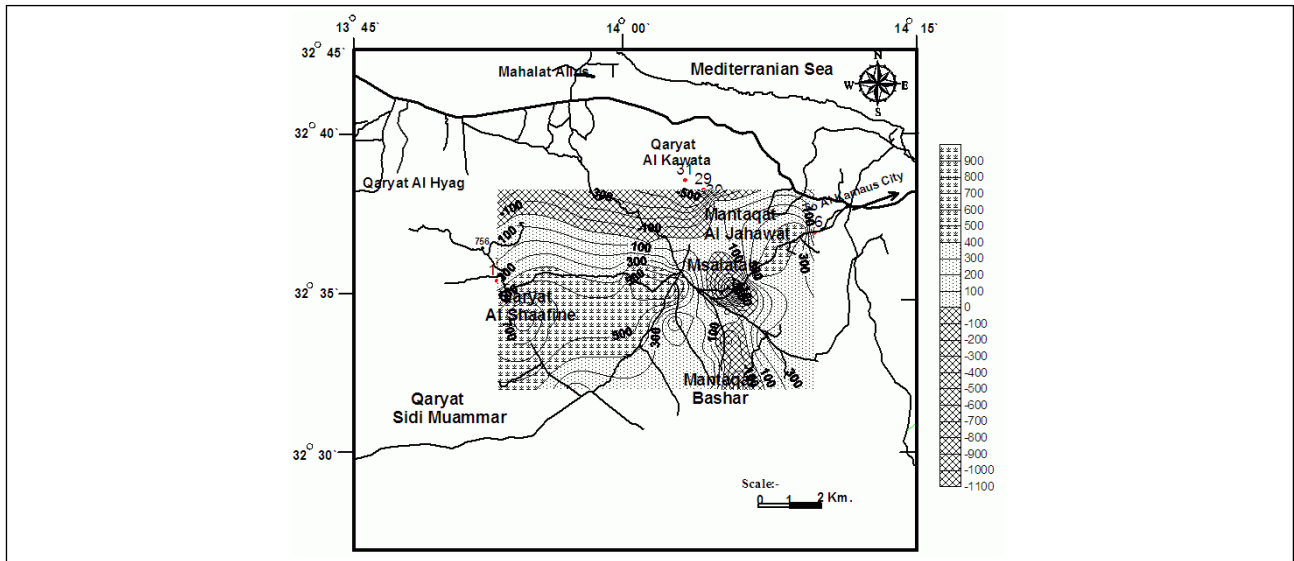


Figure 24. Distribution of results of subtracting grid Figure 23 from grid Figure 22.

saturation values of calcite and aragonite are characterized by high salinity, while the areas of negative saturation are characterized by low salinity. We advise drilling new wells in the area of negative contour values in the map developed from extracting the TDS map of 2006 from the TDS map of 2003 because the areas are characterized by high recharge.

Quantitative analysis of the hydrochemical data using statistical techniques are helpful to show the hydrogeological features of the study area. From the PCA, it can be concluded that Factor 1 represents the natural processes by which water gained its chemical characteristics (a mix of rainfall, wastewaters, and evaporated water), while Factor 2 differentiates ions of lithogenic sources. Factor 3 reflects the effect of pollution.

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