

Hydrological and Hydrochemical Studies of the Groundwater Aquifer of Harrat Khaybar Area, North of Saudi Arabia.

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Abstract— Factor analysis (FA) was applied to groundwater chemistry data of northern area of Harrat Khyber northeastern part of Al Madinah region, to assess the usefulness of such method for interpreting commonly collected groundwater. The first two factors represent two major chemical processes were identified and represent 51.3 % of the total variance which may adequate for describing the groundwater chemistry processes that have taken place in the area. Factor 1 represents the degree of the overall mineralization of the groundwater due to weathering of Basaltic rocks and intensive evaporation rates. Factor 2 might display the groundwater pollution by NO₃, which commonly linked to the on-site sewage disposal systems used in the region. The rest of the factors (3 to 7) reflect as a single variable, confirm that these variables are largely independently controlled and describe the unique factors assumed to be uncorrelated with each other and with common factors.

Index Terms —Factor analysis, Groundwater chemistry, Water pollution, Harrat Khyber, Saudi Arabia.

1 INTRODUCTION

HRRAT are Cenozoic lava fields composed mainly of basaltic lava flows erupted from many scoria cones. In the Kingdom of Saudi Arabia, these harrats were created during the tectonic and volcanic activities that also formed the Red Sea, the Gulf of Aden and the East Africa Rift Valley System in the Cenozoic era. This is known as a three-armed rift the forms above a mantle plume.

Most of the harrats in the Kingdom are in its western part and they constitute one of the largest alkali basalt areas in the world (Figure 1). They extend from south to north along the west side of the Arabian Peninsula. Some harrats extend across the northern border of the Kingdom into Jordan. Some small harrats occur along the Red Sea coastal plains, especially on the Tihama Coastal plain between Jeddah and Jizan.

Harrat Khyber differs from all other harrats in Saudi Arabia because of the presence of white felsic rocks present as tuff rings and domes with pyroclastic aprons. On its edges, there are many villages and small towns. In its eastern part, there is Al-Hanaquiyah, Al-Nakheel, Al-Hayit, Al-Huwait and Ash-Shamly. In its western part lie Khaybar and Al-Ashash. Its main volcanic outcrops are Jabal Al-Gadar, Al-Bayda'a, Al-Abyad, and Al-Ekleel. The northern part is called Harrat Thinan, and the western part is called Harrat Alkara. In the eastern part of the Harrat, there are Wadi Al-Rumma branches. In the eastern part, flow the branches of Wadi Al-Hamdh.

2. GEOLOGIC SETTING

According to the Arabian Shield map of Peter Johnson (2006), the following rock units are described (Figs. 2, 3, 4A).

AL AYS GROUP, <745->700 MA

Volcanic and sedimentary rocks of the Al Ays group [1]; [2] (ay) are widespread in the northern part of the Hijaz terrane, extending west as far as the Hudayrah-Jabal Ess fault, east as far as the Hanakiyah fault zone, and north as far as the unconformity with Phanerozoic sandstones that overlie the shield (Fig. 4A). Overall, the rocks include basaltic to rhyolitic flows, breccias, and tuffs, and an abundance of well-bedded volcanoclastic and epiclastic sedimentary rocks. Marble is locally present.

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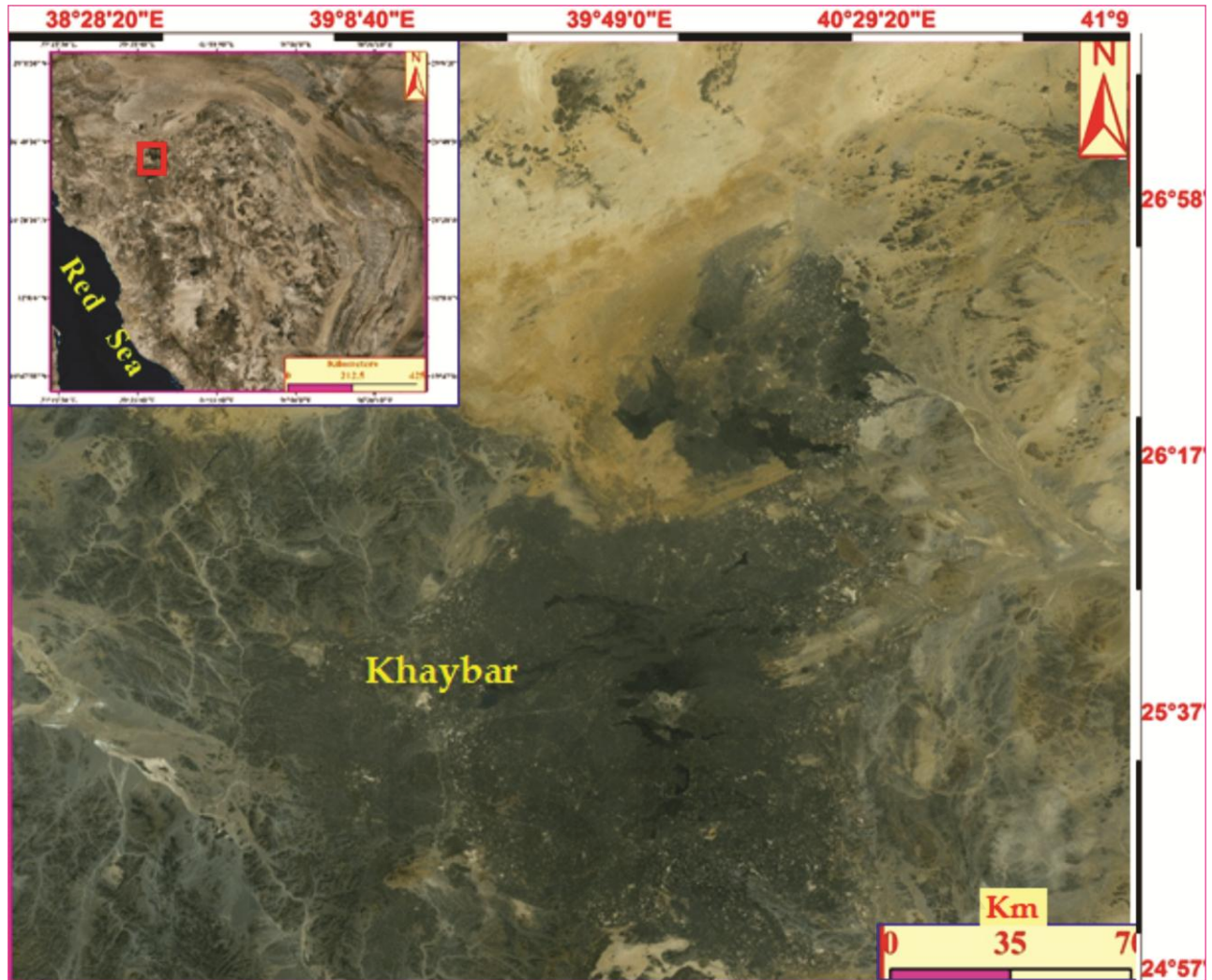


Fig. (1): Regional Satellite Image of Harrat Khaybar area, Saudi Arabia.

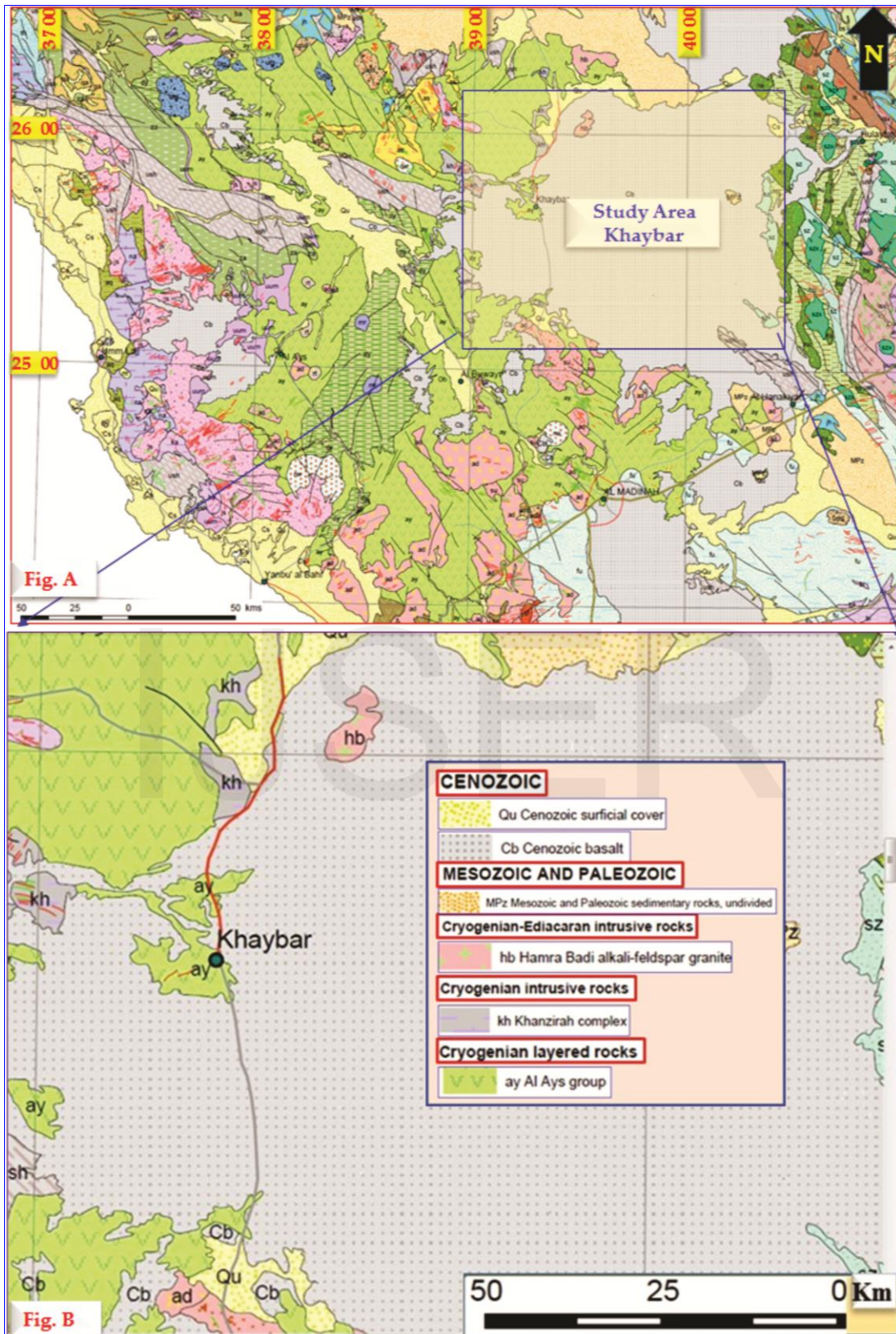


Fig. (2): A=Geologic map for the north central part of Arabian shield, Saudi Arabia; B= Geologic map of the study area (Johnson, 2006).

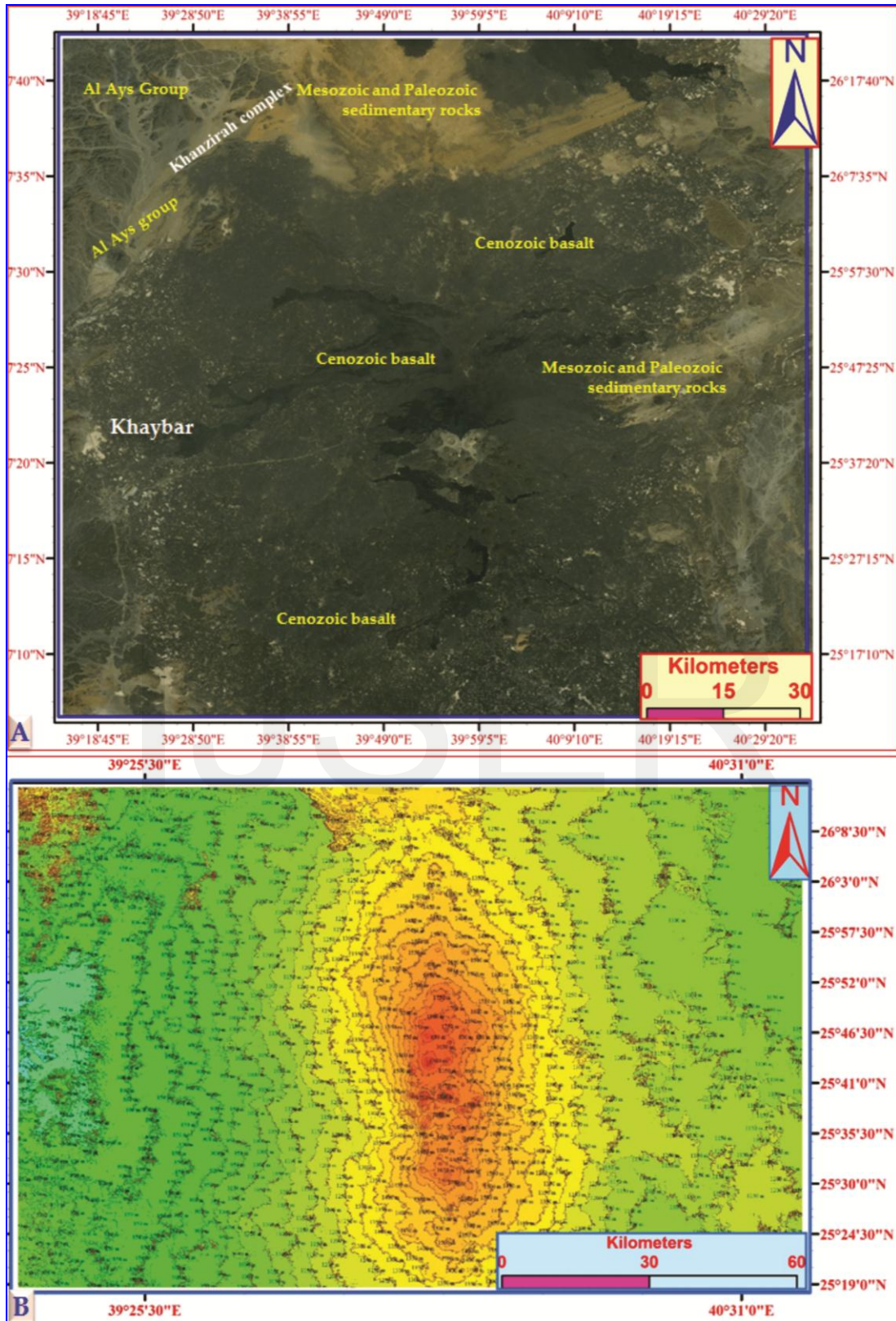


Fig. (3): **A**= The different rock units of harrat Khyabar on the satellite images; **B**= Satellite image showing the topography of the study area

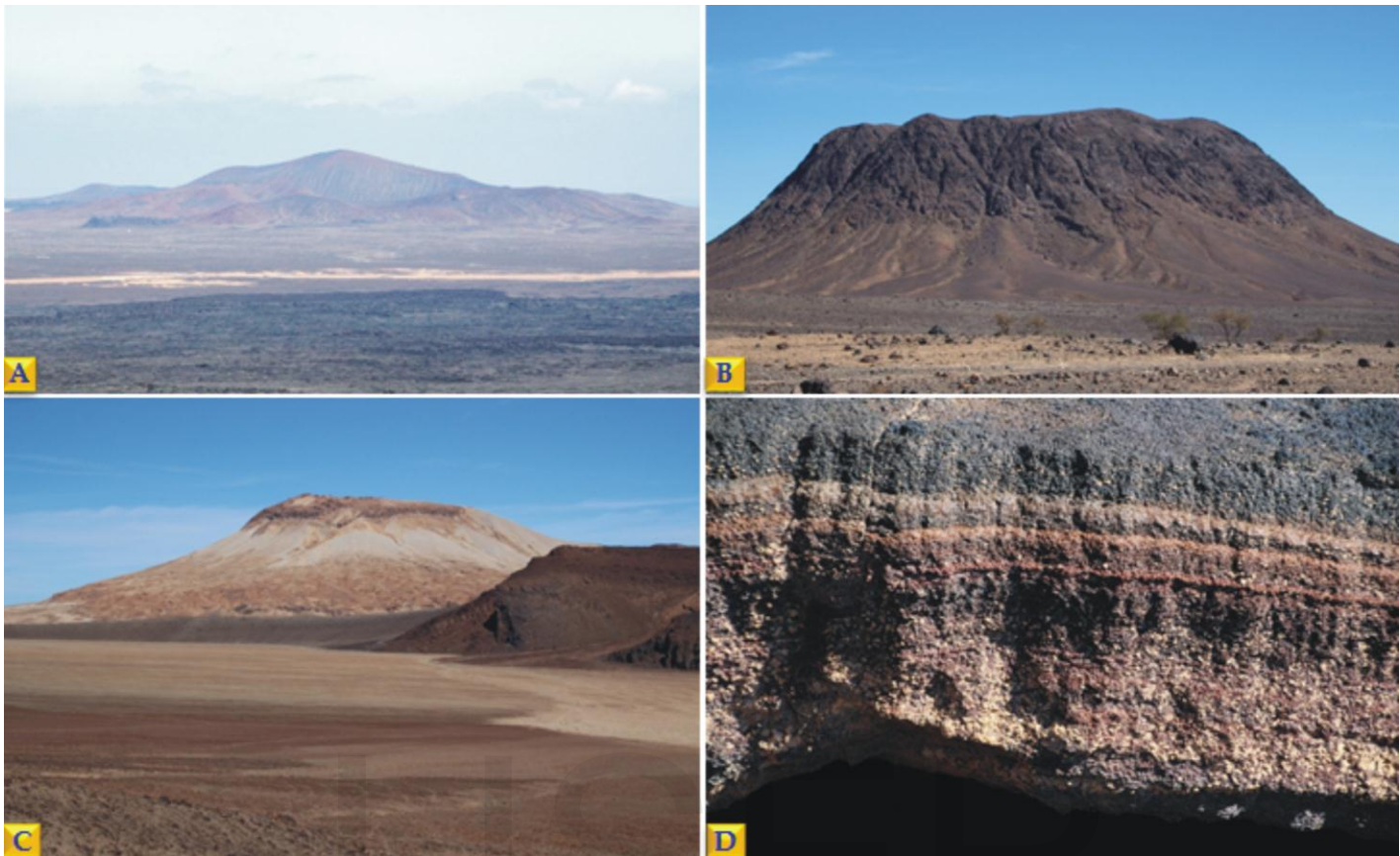


Fig. (4): A= The Arabian Shield rock faulted down against the Tertiary volcanics of Harrat Khayber; B= Basic black volcanic cone hills of harrat Khayber; C= White color cone hills of the Tertiary volcanics; and D= Thin laminations within the scoria deposits of harrat Khayber

KHANZIRAH COMPLEX, AGE UNCERTAIN

The Khanzirah complex (kh) was named by [3] for bodies of biotite-muscovite monzogranite and granophyre exposed in the north-central part of the shield and was extended by [4] to include monzogranite and syenogranite in adjacent parts of the Khaybar and Wadi al 'Ays geologic source maps.

HAMRA BADI ALKALI FELDSPAR GRANITE, AGE UNCERTAIN

This unit (hb) comprises two plutons at the north-central margin of the Arabian shield, partly covered by Lower Paleozoic sandstone and Cenozoic flood basalt. The plutons consist of coarse-grained pink hypidiomorphic granular biotite alkali-feldspar granite. The unit intrudes rocks belonging to the Al 'Ays group and is correlated by [3] with rocks in the Khaybar quadrangle that are here compiled with the Khanzirah complex. The granite is treated here as late Cryogenian to Ediacaran.

PALEOZOIC SEDIMENTARY ROCKS

Saq Sandstone

The northern part of the coalesced harrats overlaps the

Phanerozoic rocks that overlie the Precambrian Arabian shield. Flat-lying, thick-bedded, pink-weathering sandstone form spectacular cliffs and mesas and underlie much of Harrat Ithnayn and are exposed to the west and north. Inliers of the same sandstone crop out through the basalts of northeastern and central-eastern Harrat Khaybar. They have been identified as the Cambrian Siq Sandstone member (Cs) of the Sag Sandstone of Cambrian-Ordovician age [3].

The sandstone overlies the Precambrian is thickly bedded, quartzose, and medium grained to conglomeratic, and is locally cross-bedded. Sparse quartz pebbles are very well rounded and polished. The sandstone is usually well sorted and cemented by quartz and calcite. Outcrops of sandstone immediately south of Harrat Khaybar contain beds of conglomerate.

CENOZOIC

Harrat Khayber: This is represented by the main black rock unit of the study area. It is present either as flat-topped black sheet or separate cone hills of basic basaltic composition (Fig. 4B) or white color cones of acidic affinities (Fig. 4C). In many areas well bedded scoria deposits (volcaniclastics) are present (Fig. 4D).

CENOZOIC SEDIMENTARY ROCKS

Tertiary boulder conglomerate: Boulder conglomerate (Tbc) of Tertiary age crops out on the the northeastern margin of Harrat Khaybar. The main exposure is at Jabal al Usayfir [3] (also known as Jabal al Jadhiban) a prominent gullied ridge oriented north- northwest and measuring 12 by 5 km. The hills of conglomerate protrude as steptoes through the cover of volcanic rocks and have a relief of 100 m above the flat basalt plain of the harrat margin. The conglomerate is composed mainly of well-sorted and well- rounded boulders as much as 1 m in diameter. Almost all of the boulders are coarse-grained pink porphyritic rhyolite with bipyramidal quartz and feldspar phenocrysts, but rare, green chloritized pebbles are also present. The boulder deposits were assigned to the Quaternary by fairer (1986). However the fact that Tertiary lava flows have been diverted around the conglomerate hill indicates their Tertiary Age. The presence of fissile shale intercalations and the lithified matrix of the boulder deposits are also typical of Tertiary rocks. The deposit is interpreted as a fanglomerate composed of locally derived Precambrian basement material.

QUATERNARY DEPOSITS

Unconsolidated Quaternary deposits mainly overlie the Precambrian basement around the harrats. They have been subdivided into four mappable units based on those of the published 1:250,000-scale geologic maps: (1) wadi alluvium (Qal) composed of poorly sorted and unconsolidated sand and gravel;(2) eolian sand (Qe) in the form of small dune fields;(3) Sabkhah deposits (Qsb) formed in seasonal inland lakes; and (4) terraced, slightly consolidated alluvium of older wadi deposits, and undifferentiated gravel fan deposits and talus (Qu).

3. HYDROGEOLOGICAL SETTING

3.1 TEMPORAL AND SPATIAL RAINFALL PATTERN

The Harrat Khyber is considered as an arid region with high temperatures throughout the whole year with less than 13 mm rainfall per year Table 1. This implies high evaporation and relatively less infiltration rates. The annual rainfall amounts varied from year to year and it often occurs as thunderstorms of very high intensity during a local storm followed by dry periods, while the seasonality of the rainfall almost shown strong. They indicate that high percentage of the rain takes place in winter and spring seasons. However, the rainfall distribution over the study area is also variable in time and space. Data from the seven rainfall gauges were used to establish. According to available meteorological data, most often the rainfall occurrences are in Spring and Autumn seasons (Table 1), while Summer season is the lowest.

The climate can be considered as always evolving and living entity. Although weather and climate are used synonymously, weather can be distinguished as the condition of the atmosphere at any particular time and space. Climate is the average of weather conditions temporally, spatially or spatio-temporally. In water resources planning and management rather than weather, i.e., meteorologic events, their long term averages, i.e., climatic variables are considered for design and operation studies.

In arid and semi-arid regions, weather plays the most significant role whereas the climate has its long-term effects that do not show variations in shorter durations such as days, months and few years. Since weather and meteorological events change in an uncertain manner during short intervals of time, their assessment and prediction give rise to essential and final water resources assessment through methods of uncertainty. The climate represents the average behavior based on the accumulation of daily and seasonal weather events over long periods of time. Extremes of weather, such as heat waves

| Order | Seasonal Rainfall (mm) | Season |
|-------|------------------------|--------|
| 1 | 6.55 | Summer |
| 2 | 17.84 | Spring |
| 3 | 12.46 | Winter |
| 4 | 15.35 | Autumn |
| 5 | 12.69 | Annual |

Table (1): Seasonal rainfall variations over the study area.

in summer and cold spells in winter, help in differentiating the climate of one particular region from the other having the similar weather conditions on the average. Traditionally, regional climates are classified on the basis of their two most important elements that are temperature and precipitation. The geographical distribution of the climates shows warm and moist characteristics in the low latitudes, and warm and much drier features in the subtropics where the Kingdom of Saudi Arabia and hence Khyber area are located.

In Khyber area, the major source of any natural water storage is the rainfall, which is occasional and sporadic within the Kingdom of Saudi Arabia. The rainfall amounts are measured by rain gauges and the records are kept for future use. These records provide a very precious document. Otherwise, the water resources planning, project, construction and especially management and operation cannot be achieved in the best possible manner. Rainfall is among the major hydrological elements, but unfortunately its measurement in the Kingdom is not made in a systematic manner. It is possible to find old stations with several years of data that have stopped due to some maintenance or other problems.

4. HYDROGEOLOGICAL SETTING

4.1 INTRODUCTION

The study area is composed mainly of lava flows and underlain by alluvial deposits of various types of sediments (gravel, sand, clay) and both are resting on Precambrian crystalline rocks. Such a configuration provides rather potential groundwater possibilities in the region.

Significant water-bearing formations occur in two different lithological units, namely, the subbasaltic alluvial deposits as well as the basalt flows itself. Information on the hydrogeology of the area was obtained from the well inventory, pumping tests and geophysical survey that carried out in the study area.

4.2 WELL DESCRIPTION

Groundwater in the study area is used for a wide variety of purposes including water supply, domestic activities and irrigation. Wells are drilled in order to satisfy one or more of these purposes and are designed and completed accordingly. They mainly concentrated closed to the edges of the harrat. The locations of the studied water wells are shown in Figure 5. The majority of the wells are drilled wells having between 12" and 16" diameter. The total depths and the levels in the three sectors are shown in the Table (2).

4.2 AQUIFER DESCRIPTION

The study was conducted in north eastern part of Harrat Khyber (Basaltic Plateau). It is nearly located in north eastern part of Saudi Arabia (Fig.1). The climate is typically arid and the rain is irregular and of torrential nature when it occurs. In

the area, the agricultural activities are wide spread. Groundwater occurs in basaltic aquifer. In the top of harrat Khyber, there are surficial deposits consisted of pebbles alternating with coarse and fine sand with gravel that serve as a permeable conduit for the percolation of surface water into the aquifers. The depth to the water level varied between 8 to 30 meters. The existing aquifer is mainly recharged through runoff and rainfall events. The present day geologic investigations revealed the presence of the following four main geologic units from the oldest to the younger:

The most important aquifer system of the Harrat Khyber area is formed by the basalt flows and the underlying siltstones, sandstones and conglomerates. These two separate hydrogeological units can be considered as being

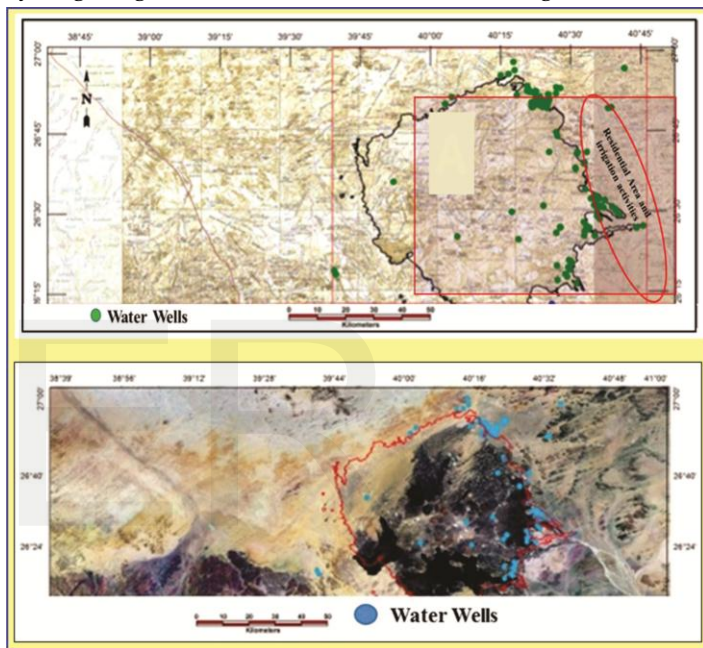


Fig. (5): Location of the studied water wells of the study area.

| Parameter | Study Area | |
|-----------|--------------------|-----------------|
| | Depth to water (m) | Total Depth (m) |
| MAX | 207 | 280 |
| MIN | 3.9 | 7.71 |
| MEAN | 31.96 | 62.2 |

Table (2): Water table and total depths for wells in the study area.

inseparable, giving rise to an aquifer complex in unconfined to semi-confined and confined condition. The extent of these hydrogeological units is more or less the same as that of the basaltic plateau and the saturated thickness of the aquifer is very variable. The basalt lava flows differ in their ability receive recharge as well as to hold water in storage and to transmit it in the form of groundwater than the underlying clastic rocks as a result of the variation in their inherent physical characteristics, such as their porosity and permeability. The unit underlying the basalt of harrat is composed from clastic rocks generally angular to sub-angular and poorly sorted gravel and sand with silty sands.

4.3 GROUNDWATER MOVEMENT

The rate of groundwater movement within an aquifer is a function of the hydraulic conductivity of the water bearing formation, and the hydraulic gradient. However, regional groundwater movement is dependent entirely on the availability of direct and indirect recharge. Generally, the regional pattern, i.e. geometric dimensions of groundwater flow can be defined from a map of piezometric surface. Nevertheless, locally and in the presence of the complex condition which occurs with the lava flows and the subbasaltic alluvium it may be difficult to establish accurately the flow direction. Where the groundwater occurs in a fractured medium in which the predominant fractures have different preferred directions that are independent from the hydraulic gradient the water can make its way only through the fracture system. In other words, the route of travel of the groundwater is likely to be indirect and may deviate substantially at many places from the general direction of hydraulic gradient due to the erratic distribution of fractures as well as their extent, inter-connection and width.

On the basis of water level measurements made during the field survey, it has been possible to prepare the piezometric surface map for the study area. This map helps to determine the general direction of flow as well as the piezometric surface gradient along any desired line. Water level elevations were measured with reference to sea level. The piezometric surface contours map was constructed. It shown that the regional groundwater movement is to the north and northwest

4.4. GROUNDWATER DISCHARGE

The groundwater in the study area is discharged either naturally by direct evaporation from the shallow water table areas (see Table 4.1) and subsurface outflow or artificially by withdrawals from wells which depend upon the duration and rated of pumping. These factors have caused a great decline of the groundwater level because they exceeded the total recharge. Among theses aspects, evaporation is the least important quantitatively, because the depth to the saturated zone is generally large enough to minimize the evaporation processes, with the exception the shallow water table therein. On the other hand, the amount of natural discharge by the subsurface outflow will depend chiefly on the regional hydraulic gradient, the hydraulic conductivity of the aquifer

system, and the cross -sectional areas that join the basalt aquifer and the shrouding alluvial deposits.

Artificial abstruction by pumping the wells in the cultivated areas accounts for the largest discharge component. To make a reasonable estimate of the total annual volume of water extracted for irrigation, information about pumping hours and days, discharge rates, and total number of pumping wells in the area are needed.

4.5 AQUIFER PARAMETERS

Aquifer parameters are key decision variables in the evaluation of groundwater storage availability and ability to pump water through the wells. Storativity and transmissivity, as two basic hydraulic parameters, are required in any groundwater resources evaluation for aquifer potentiality assessments. Their estimations should be based on field data obtained from aquifer tests that show the drop (drawdown) of groundwater (piezometric) level with time starting from the beginning of pumping. It is possible to match the field data sheet with the most suitable type curves that are prepared by considering a set of assumptions through mathematical models. Unfortunately, these models provide average parameter estimations, and do not take into consideration local spatial variations.

In this report, classical matching procedures are used, but prior to their direct applications, individual interpretation of each aquifer test data (drawdown change by time) are explained based on possible geologic structural reflections. In the following, these data are evaluated qualitatively and quantitatively. For this purpose, field time-drawdown data are plotted on semi or double logarithmic papers, and for qualitative interpretations, assumptions based on theoretical type curves are considered.

The qualitative aquifer test interpretations are possible with combined field and theoretical model results. A method has been developed by which the slope between any two successive data points on a time-drawdown plot can be used for determining aquifer parameters in non-leaky and leaky aquifers. The method yields values of transmissivity and storage coefficient which are in good agreement with the results of the classically known techniques. The method of slope analysis offers several advantages in its use. These advantages include the following: Changes in values for the aquifer parameters that might occur during a pumping test can be identified. Confidence limits can be calculated for average values of aquifer parameters. The method yields meaningful aquifer parameter estimates even for short duration pumping tests.

PROCEDURES

79 groundwater samples were taken from the studied area. All the groundwater samples were taken from privately owned wells (Fig. 5). A few drilled wells seem to be abandoned for use either due to their providing insufficient water to remain irrigation through the dry season and/or their water has rather high salinity. During the field survey and

samples collection, groundwater temperature, electrical conductivity (EC) and pH were measured in situ. Most of the groundwater samples were taken from intensively pumped wells in order to avoid any local contamination or change in chemistry caused by evaporation or gas exchange in the well itself.

The 79 groundwater samples described herein were taken from private wells. These water samples were analyzed for the major ions. Electrical conductivity (EC) in $\mu\text{S}/\text{cm}$, Total dissolved solids (TDS) and pH were measured in situ after it had been pumped for at least 3-5 minutes. Variables used are Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , pH, EC, F and SiO_2 . All the chemical constituents were in (mg/l) except where noted (Table 3).

5. HYDROCHEMICAL RESULTS

Due to the complexity of the chemical evolution of groundwater's and the substantially large amount of basic information available, investigators are often unable to obtain a clear picture of the system under study. In general, the measurements, chemicals and non chemicals carried out both in the field and laboratories, might reflect a number of variables which together make up the groundwater chemistry. Such obtained variables could cause rather complexity and confusion for investigation to have a clear picture of the existing system [5].

Several methods of data analysis have been devised to simplify interpretation and presentation such as Trilinear, Semilogarithmic, Duorv diagrams....etc. The existing methods may provide some information. Nevertheless, these conventional techniques are generally limited to major constituents ions. They ignore many parameters which are otherwise important for hydrochemical studies. The limitation that coupled for using the traditional graphical methods were discussed by several authors (Lloyd and Heathcote, 1985). In view of the limitation of the existing methods and increasing number of chemical and physical variables measured in groundwater investigations, multivariate analysis comes into play as a rather essential tool for explaining groundwater chemistry conditions. Factor analysis (FA) is considered the most widely used in groundwater chemistry [6]. The aim of using factor analysis is to simplify the quantitative description of a system by determining the minimum number of new variables necessary to reproduce various attributes of the data. These procedures reduce the original data matrix from one having n variables necessary to describe the N samples to a matrix with m factors ($m < n$) for each of the N samples [7]; [8].

This study attempts to employ the factor analysis (FA) to describe the hydrochemical processes that controls the groundwater chemistry in north eastern part of Harrat Khyber from commonly collected groundwater chemistry data.

6. RESULTS AND DISCUSSION

The out put results for the chemical data are given in Table 3. Two factors had high Eigen values (4.78 and 1.89), while the other almost around 1.0. However, the "sky-slope" diagram suggests that the first 2 factors should be retained (Fig. 6). These two factors account for 51.3 % of the total variance while the other factors represent the residual of the total variance. Therefore, the first two factors are assumed to represent, adequately, the overall variance of the data set. On the other hand, the factor loading in Table 4 indicates that the two factors (1 and 2) are hydrochemically meaningful, which seem to describe the existing conditions of groundwater chemistry, where the other five factors are individually. These factors will be discussed below:

Factor 1 accounts for 36.8 % of the total variance. It has high loading for Ca, Mg, Na, Cl, SO_4 , EC and TDS while the Cl has moderate loading in this factor. The high loading of these constituents most likely result from groundwater mineralization. All are positively correlated with factor 1 weighting. Factor 1, therefore, is interpreted as relating mainly

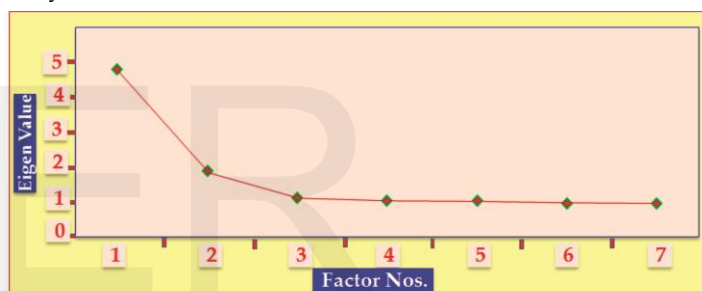
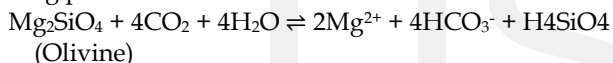


Fig. (6): Number of factors plotted against the proportion of variance it extracted (Eigenvalue).

| ELEMENTS | MAX | MIN | MEAN |
|--------------------------------|--------|------|--------|
| Ca | 937.5 | 9.70 | 132.8 |
| Mg | 568.8 | 1.10 | 55.01 |
| Na | 2352.0 | 54.8 | 404.8 |
| K | 66.3 | 0.20 | 9.28 |
| Cl | 1770.0 | 4.11 | 364.1 |
| HCO_3 | 854.0 | 78.0 | 333.2 |
| SO_4 | 3071.0 | 15.0 | 515.3 |
| NO_3 | 440 | 9.0 | 97.8 |
| F | 5.35 | 0.30 | 1.89 |
| SiO_2 | 62.8 | 13.2 | 27.8 |
| TDS | 4750 | 301 | 1423.3 |
| EC ($\mu\text{S}/\text{cm}$) | 7300 | 463 | 2191 |
| pH | 9.35 | 5.95 | 7.45 |

Table 3. The chemical analyses results in (mg/l).

to the groundwater mineralization processes due to intensive evaporation processes on irrigated surface water in irrigated areas and to weathering of silicate minerals existed through dissolution processes. The main cations exchange elements Ca, Mg, and Na correlate positively indicating the influence of the geological matrix. Significant positive correlations between Ca and SO₄ suggest that processes of dissolution and/or precipitation of evaporitic mainly sulphide minerals such as gypsum mineral. Sources of SO₄ could also result from redox reactions, land use practices and oxidation of pyrite (FeS₂) which is more probable primary source of SO₄ and widespread accessory mineral in igneous and metamorphic rocks. The importance of the evaporation process of the water might be deduced from previous detailed hydrochemical studies (e.g [9]; [10] and [11] carried out in most of the western basins. However, they introduced different evaporitic salts (gypsum and pyrite were existed in the irrigated fields and sediments, using the XRD analysis method. Their previous results shown that calcite (CaCO₃), gypsum (CaSO₄.2H₂O) and dolomite [CaMg(CO₃)₂] salts are also common minerals in the surficial deposits and irrigated areas, which probably resulted form intensive evaporation processes. In addition, the basaltic plateau (Harrat Khyber) mainly consists of alkali olivine basalts. An example of weathering processes exited:



Therefore, these processes could be considered as a supply sources of salinity which reach the groundwater when washed down by an excessive application of irrigation waters and recharge waters (rain- flood waters).

Factor 2 accounts for 14.5% of the total variance and has a high loading of NO₃ and Cl. This factor might be indicated that groundwater body probably affected by pollution source(s) provided NO₃ as well as Cl to the groundwater.

6. CONCLUSION

The results of factor analysis have rather clarified two major aspects of groundwater condition from the hydrochemical point of view, and have led to the following conclusions that just the first two factors (1 and 2) can describe the predominate major processes that are taking place in the hydrochemistry system and the groundwater contamination taken place by on-site sewage water and/or chemical fertilizer. While the other factors (3 to 7) almost represent as a single factor of weathering of silicate minerals and intensive evaporation processes taken place in the area.

Since both NO₃- and Cl are the most significant contaminants associated with domestic wastewater (EPA, 2004 and Geary and Whitehead, 2001). Fig 7 show the relationship between Cl and NO₃. Both are show high positive relationship (R² = 0.81) between the tow elements reflecting both are mainly derived from same source.

The other Factors (3 to 7) may represent single variables, HCO₃, F, pH, K and SiO₂. they both indicted they are derived from weathering of silicate minerals processes taken place in the area.

| VARIABLES | FACTOR 1 | FACTOR 2 | FACTOR 3 | FACTOR 4 | FACTOR 5 | FACTOR 6 | FACTOR 7 |
|------------------|----------|----------|----------|----------|----------|----------|----------|
| Ca | 0.78 | | | | | | |
| Mg | 0.52 | | | | | | |
| Na | 0.93 | | | | | | |
| K | | | | | | | -0.885 |
| Cl | 0.51 | -0.81 | | | | | |
| HCO ₃ | | | | 0.974 | | | |
| NO ₃ | | -0.88 | | | | | |
| SO ₄ | 0.94 | | | | | | |
| F | | | | | 0.974 | | |
| SiO ₂ | | | | | | -0.981 | |
| TDS | 0.91 | | | | | | |
| EC | 0.91 | | | | | | |
| pH | | | 0.954 | | | | |
| Eigenvalues | 4.78 | 1.89 | 1.11 | 1.08 | 1.06 | 1.05 | 0.96 |
| Variance (%) | 0.368 | 0.145 | 0.086 | 0.083 | 0.082 | 0.081 | 0.074 |

Table 4: Variables and Factors Loading After Varimax Rotation.

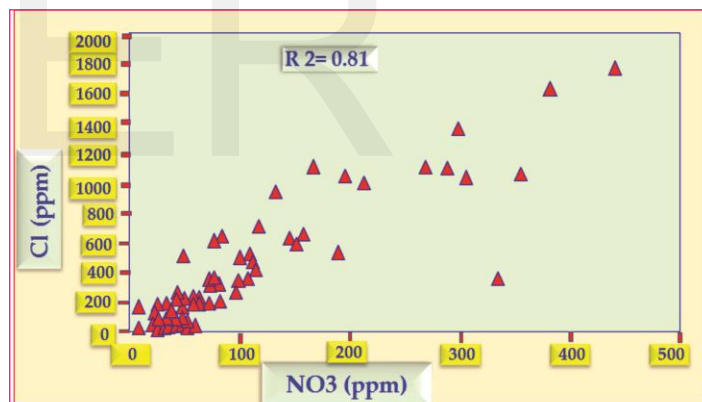


Fig. (7): The relationship between Cl and NO₃

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