Evaluation of groundwater quality in district Karak Khyber Pakhtunkhwa, Pakistan

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ABSTRACT
Groundwater is the major source of drinking, domestic, agricultural, and industrial purposes in the arid and semi-arid areas and its quality is important factor determining its suitability. Our objectives were to evaluate the groundwater quality and its suitability for drinking and irrigation, spatial distribution, and homogeneity or heterogeneity levels between the physicochemical parameters. Standards methods were used to analyze the groundwater samples. The result reveals that sodium (Na\textsuperscript{+}) and chloride (Cl\textsuperscript{−}) are the most dominant cation and anions. According to hydro-chemical facies, the majority samples water types are Na-Cl, Na-HCO\textsubscript{3}−. Wilcox diagram was used to evaluate the groundwater quality, and 60% of samples fall in (C3-S2, C4-S2, and C3-S3) water quality class. Highly significant correlation was observed between Cl\textsuperscript{−} and SO\textsubscript{4}2− with Na\textsuperscript{+} and positive correlation between the pH and CO\textsubscript{3}2−. The cluster analyses indicate that Cl\textsuperscript{−} very close similarities with TDS. The 84% of groundwater samples are unsuitable for the potable use as per WHO guidelines. The findings of this study are playing a crucial role in groundwater management.

INTRODUCTION

Freshwater is an essential natural resource for human survival. Globally there are two principal storage sources of freshwaters which are glaciers and groundwater. Groundwater plays a vital role in the socioeconomic, domestic, horticultural and agricultural production (Kanwal et al., 2015). Groundwater suitability for use depends upon its inherent quality, which depends on atmosphere reflection, weathering of soil and rocks, and anthropogenic activities. The development of industrialization, environment ignorance, application of agrochemicals, anthropogenic wastes and untreated sewage discharge results surface and groundwater decline (Krishan et al., 2016).

The importance of groundwater depends on its quality, not only availability (Kanwal et al., 2015). Once the subsurface environment is polluted, it will remain hidden for a long time and spread over large area of the aquifer. The consequences of these spreading will decline groundwater quality for consumption (Akhtar & Zhonghua, 2013). Water chemistry depends on the origin of the water sources, the degree of evaporation, rock, and mineral types (Curtarelli et al., 2015). Since water is a precious natural resource, for sustaining all life on the earth and due to its multiple benefits and the problems created by its excesses, shortage, and quality deterioration, water as a resource requires special attention.

The urban aquifer plays vital role in drinking water supply because it is the only natural resource for drinking water storage, however, this portability decreased by increasing pollution (Jerome & Pius, 2010). Hydrochemistry plays an important role in the assessment of groundwater quality (Daud et al., 2017). Assessment of groundwater quality may give obvious information about the subsurface geologic environment and water contain types of the aquifer (Raju et al., 2011). Numerous, studies were conducted on groundwater quality assessment in many regions of Pakistan (Bangash & Khan, 2001; Daud et al., 2017; Krishan et al., 2016; Ullah et al., 2015; Yousaf et al., 2016). Hydro-geochemical studies of groundwater have been carried out in some parts of district Karak Khyber Pakhtunkhwa, Pakistan (Ullah et al., 2015). However, these studies have some limitations such as spatial distribution hydro-geochemical parameters and homogeneity or heterogeneity level between hydro-geochemical parameters. To achieve these limitations, the following study was designed.

Our main objectives are: (1) assessment of groundwater quality and its suitability for drinking and irrigation (2) spatial distribution of groundwater parameters (3) to assess the homogeneity or
heterogeneity level between the physicochemical parameters.

**Study area**

This study is conducted in the Karak Khyber Pakhtunkhwa district, Pakistan. The Karak district is situated in the south of Khyber Pakhtunkhwa between 70–40° to 71–30° N and 32–48° to 33–23°E (Figure 1). The area has a semi-arid climate with an average rainfall of 450 mm/year, and temperature varies from 45 °C in the summer to 10 °C in the winter season.

The study area northern part oil mining industrial profiles east part uranium mining. Chemical fertilizers used in agriculture and salt mines are often seen in the vicinity. Groundwater is the only source of drinking water, and impacts of the above factors affect the drinking water. During the sampling stage, a lot of complaint about waterborne diseases like diabetes mellitus, stomach problems, and hair fall, etc., was recorded.

**Hydrogeology**

The estimated thickness of the aquifer ranges from 10 to 30 m. Generally, the aquifer is confined and semi-confined. The groundwater quality in the northeast part of the northwest catchment is very poor. This is caused by the presence of rock salt in the northern mountains, which is dissolved by runoff water and contaminates the groundwater by deep percolation. Groundwater flows under a phreatic condition in the weathered layer and fractured zones at deeper levels. The alluvial fill of very heterogeneous and contain much silt and clay. Locally, sand and gravel beds have been encountered in the boreholes. The discharge through open wells is calculated as 0.035 Mm³/yr. The average annual recharge of the alluvial aquifer is probably equal to the average annual discharge and will be in the order of 2.7 Mm³/yr (3.0 cusec) (Kruseman & Naqavi, 1988). The groundwater level ranged from 29.03 to 238.66 m (Figure 2). That indicates a vague groundwater divide that corresponds with the surface water divide.

**Methodology**

**Samples collection and analysis**

For the evaluation of groundwater (N = 60), water samples were collected from different locations of the study area. The samples were collected randomly based on the demand, and complaints of the residents about the waterborne diseases. Samples were collected in plastic bottles. Before the sampling, the bottles were cleaned with 1 N-hydrochloric and rinsed 2–3 times with distilled water. The standard method for the evaluation of water was used for the analysis (APHA, 2012). Portable water quality analyzers were used for pH and Electrical conductivity.

![Figure 1. Map of study area showing sampling locations.](image_url)
(EC) measurements in the field. Total-dissolved solids (TDS) meter was used to measure the TDS. Total hardness (TH) of CaCO$_3$ and calcium (Ca$^{2+}$) were analyzed titrimetrically using standard EDTA. Magnesium was calculated by taking the difference between the total hardness (TH) and calcium (Ca$^{2+}$) concentrations. Chloride (Cl$^{-}$) value is determined titrimetrically by AgNO$_3$ as a standard. The flame photometer was used for the determination of sodium (Na$^+$) and potassium (K$^+$) concentrations. All parameters are measured in milligrams per liter (mg/l), excluding pH (no units), and EC (microsiemens/centimeter (µS/cm)) at 25°C. A geo-statistical (Kriging/ordinary/log transformation/first order) technique (ArcGIS 10.3) was used to develop the spatial distribution maps of parameters.

**Statistical analysis**

To identify the correlation between physicochemical the Pearson correlation coefficient was used:

\[
r = \frac{N \sum xy - (\sum x)(\sum y)}{\sqrt{[N \sum x^2 - (\sum x)^2][N \sum y^2 - (\sum y)^2]}} \quad \ldots \ldots  \ldots \ldots  \ldots  \ldots  \ldots  (1)
\]

Where:

- $N$ = number of pairs of scores
- $\Sigma xy$ = sum of the products of paired scores
- $\Sigma x$ = sum of x scores
- $\Sigma y$ = sum of y scores
- $\Sigma x^2$ = sum of squared x scores
- $\Sigma y^2$ = sum of squared y scores

**Result and discussion**

The physicochemical parameters (EC, TDS, pH, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, and Cl$^-$) of groundwater samples were analyzed, and the descriptive statistics of the analyzed parameters are shown in Table 1. Results were compared with the WHO standard maximum permissible limits.

The pH of the groundwater samples ranged from 7.61 to 9.43 with an average of 8.74. Generally, pH $>8.5$ could indicate that the water is hard/or alkaline so the average depicted alkalinity. The maximum pH value (9.4) was observed in the sampling station 55, and the minimum pH value (7.61) was observed in sampling station 9. Figure 3 shows the spatial distribution of the pH. The acceptable range of pH for drinking and agricultural purposes is 6.5–8.5 (WHO, 2017; APHA, 2012). Generally, the pH values of all samples were within the permissible limit. However, few samples were higher than the permitted range.

| Parameter | Min | Max | Mean | SD | C.V. |
|-----------|-----|-----|------|----|------|
| EC (µS/cm) | 1210 | 3396 | 1532.42 | 1508.12 | 60.42 |
| TDS (mg/l) | 782.79 | 2167.34 | 1659.50 | 1029.51 | 73.2 |
| pH | 7.6 | 9.4 | 8.7 | 0.40 | 4.57 |
| Na (mg/l) | 81.35 | 600.81 | 348.62 | 178.89 | 51.31 |
| Ca (mg/l) | 4.73 | 59.48 | 32.53 | 10.64 | 32.71 |
| Mg (mg/l) | 16.20 | 31.53 | 21.12 | 6.36 | 30.11 |
| K (mg/l) | 1.50 | 7.51 | 3.51 | 2.25 | 64.13 |
| CO$_3^-$ (mg/l) | 1.36 | 5.53 | 3.76 | 2.49 | 66.19 |
| HCO$_3^-$ (mg/l) | 28.78 | 75.35 | 54.82 | 14.48 | 26.42 |
| Cl (mg/l) | 62.61 | 470.06 | 250.30 | 206.78 | 82.61 |
| SO$_4^-$ (mg/l) | 16.85 | 53.49 | 35.47 | 26.37 | 74.34 |

The acceptable range of pH for drinking and agricultural purposes is 6.5–8.5 (WHO, 2017; APHA, 2012). Generally, the pH values of all samples were within the permissible limit. However, few samples were higher than the permitted range.

**Table 1.** Descriptive statistics and comparison of analytical results with WHO guideline.

**Figure 2.** Ground water levels (GWL) map of study area.

**Figure 3.** Groundwater samples distribution map.
The EC ranged from 1210.32 to 3396.15 µS/cm with an average value of 1659.50 µS/cm, and the maximum value was observed in station 15. The spatial distribution of EC is shown in Figure 3. It can be observed that in EC increased from northeast to northwest which indicating the groundwater flow path. The dissimilarity in EC prevailing in this region is mostly credited to geochemical processes, anthropogenic activities and the salt mine in the vicinity. Generally, the EC increased along with groundwater flow because of the effects of topographic conditions, ion exchange and evaporation (Prasanth et al., 2012). The TDS values range from 782.42 to 2167.32 mg/l and with an average of 1532.42 mg/l. EC and TDS showed similar variation (Figure 4). TDS concentration depends on ions types and characteristics, present in the water. Magnesium and calcium are used to classify the suitability of water for drinking and irrigation.

The hardness of the water was directly related to calcium and magnesium. These ions are most dominated elements in surface and groundwater and existed mainly as HCO$_3^-$ and to a slighter degree in the form of Cl$^-$ and SO$_4^{2-}$ (Shahid et al., 2014). In the study area, magnesium (Mg$^{2+}$) concentration ranged from 16.21 to 31.56 mg/l, and calcium (Ca$^{2+}$) ranged from 4.51 to 59.73 mg/l. Mg$^{2+}$ and Ca$^{2+}$ concentrations were within the permissible limits. The order of profusion of cations sodium (Na$^+$) is the most dominant cations followed by Ca$^{2+}$, Mg$^{2+}$ and K$. In sampling station 10, a higher concentration of Na$^+$ was observed, which may be due to agricultural sources and the salt mine in the vicinity. K$^+$ concentration was almost in the normal range; however,
only a few samples have a concentration higher than the normal range. In the case of anion, Cl$^-$ was the dominant ion followed by HCO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$ (Table 1). The chloride in groundwater may be from various sources such as domestic and municipal effluents, weathering, sedimentary rocks leaching. The chloride ion is the major natural form of the chlorine element and tremendously stable in water (Shahid et al., 2014). Weathering of rock and dissolution of silicates may increase the concentration of HCO$_3^-$. Srinivasamoorthy et al. (2008) observed that high Cl$^-$ concentration was frequently found with a combination with Na$^{2+}$ higher concentration. WHO has prescribed 600 mg/l as the maximum permissible value. However, according to Yousaf et al. (2016) with the presence of sodium in water, the chlorine value may exceed 300 mg/l then the water turns salty. Similar observations were observed in this study area. The spatial distribution of the cations and anions is shown in Figures 5 & 6. The spatial distribution of groundwater visibly shows the direction of the flow which is from northeast to the northwest.

**Hydro-chemical fancies**

The evaluation of water quality for various purposes using different conservative techniques such as statistical techniques and trilinear plots is extensively conventional methods. The areas which have shallow groundwater tube wells, high pollution, in addition to intensive coastal and industrialization activities will have problems of groundwater quality more acutely (Selvam et al., 2013). Hydro-chemical fancies have been widely used for the evaluation of groundwater quality and flow. However, the Piper diagram is well known for the evaluation of water quality (Piper, 1953), so in this study, Piper diagram we used. In the Piper diagram, the elevation of hydro-chemical parameters of groundwater can be understood by plotting the concentrations of the major cations and anions (Figure 7). The trilinear plots showed that the majority of the samples fall in the field of Na-Cl, Na-HCO3, followed by Ca-Mg and some samples in Cl-SO$_4$ class. It can also be observed from the figure that Na$^+$ and K$^+$ (alkalis) surpass on alkaline earth (Ca$^{2+}$ and Mg$^{2+}$) and Cl$^-$ surpasses on the other anions.

**Wilcox diagram**

Wilcox diagram has been widely used for the evaluation of water quality. Wilcox diagram evaluates the samples in different classes from low to very high salinity and sodium (alkali) hazards (Figure 8). According to the Wilcox diagram, about 22% of the samples fall in low range (C3-S1) water quality class which means medium salinity hazard and low sodium hazard, 38% of the samples fall in (C4-S1) range which is permissible to doubtful means medium salinity hazard, these quality class water are suitable for both drinking and irrigation. 60% of

![Figure 5. Spatial variation of distribution of cations in study area.](image)
the samples fall in (C3-S2, C4-S2, and C3-S3) water quality class with a very much doubtful region. The majority of study area revealed high TDS and high Na$^+$ concentration. As excess salt affects the human health and plants, the groundwater in the majority of the study area is unsuitable for drinking and irrigation purposes.

**Statistical analysis**

To predict the behavior and relationship between the variables, the correlation coefficient is broadly used (Bagyaraj et al., 2013). It can be observed from (Table 2) Cl$^-$ and SO$_4^{2-}$ that highly significant correlation with Na$^+$. Similarly, there is a positive correlation between Ca$^{2+}$, Mg$^{2+}$, and K$^+$ with Cl$^-$. The hydro-chemical

![Figure 6. Spatial variation of distribution of anions in study area.](image)

![Figure 7. Piper diagram.](image)
behaviors of alkalies explain the correlation between Na\(^+\) with Cl\(^-\) ion. A positive correlation was observed between pH and CO\(_2\)\(^3-\); which signify in the water the changes in the hydrogen ion concentration will affect directly correlation of carbonate (Raju et al., 2011). Between the cations, Ca\(^{2+}\) with Mg\(^{2+}\) and anions Cl\(^-\) with SO\(_2\)\(^4-\) showed a significant correlation. A low correlation exists between K\(^+\) with Cl\(^-\), Na\(^+\) with HCO\(_3\)\(^-\). Na\(^+\) and Cl\(^-\) are the dominant ions.

Cluster analysis

Cluster analysis determines the homogeneity or heterogeneity level between variables. (Roper et al., 1992) primarily classify the multivariate group techniques into clusters. For the cluster analysis, all the samples sites were grouped, minimize to their number to classify the cluster and then link sample site to an arrangement of a tree with branches (Dendrogram). These provided the summary of the cluster, group picture, and their immediacy. The variables branches that have closer linkage were observed to have a stronger relationship. In this study (Ward, 1963), linkage method and Pearson correlation distance type were used for the grouping of parameters. Cluster 1, comprised of Cl\(^-\) and TDS showing close similarities and Cluster 2, Ca\(^{2+}\) and pH showing close similarities which can be interpreted as natural mineralization and is controlled by cation exchange (Figure 9). The cluster also indicated cations and anions fancies, which resulted from the reverse cations and anions exchange. The cations and anions influence TDS which increases the water’s

![Figure 8. Wilcox diagram.](image)

Table 2. Pearson correlation coefficient for groundwater quality parameters.

|      | EC  | TDS | pH  | Na  | Ca  | Mg  | K   | CO\(_3\) | HCO\(_3\) | Cl  | SO\(_4\) |
|------|-----|-----|-----|-----|-----|-----|-----|---------|----------|-----|---------|
| EC   | 1.00|     |     |     |     |     |     |         |          |     |         |
| TDS  | 0.99| 1.00|     |     |     |     |     |         |          |     |         |
| pH   | -0.09| -0.12| 1.00|     |     |     |     |         |          |     |         |
| Na   | 0.82*| 0.78*| -0.01| 1.00|     |     |     |         |          |     |         |
| Ca   | 0.21| 0.16| -0.01| 0.05| 1.00|     |     |         |          |     |         |
| Mg   | 0.09| 0.04| -0.12| -0.01| 0.82*| 1.00|     |         |          |     |         |
| K    | 0.09| 0.08| -0.17| 0.07| -0.06| -0.09| 1.00|         |          |     |         |
| CO\(_3\) | 0.01| 0.01| 0.13| -0.02| -0.05| -0.05| -0.10| 1.00|         |     |         |
| HCO\(_3\) | 0.89*| 0.05| 0.17| 0.21| 0.03| 0.13| -0.11| 0.02| 1.00|     |         |
| Cl   | 0.65| 0.88*| -0.20| 0.79*| 0.22| 0.17| 0.13| -0.12| -0.13| 1.00|         |
| SO\(_4\) | 0.64| 0.61*| -0.14| 0.77*| 0.25| 0.22| 0.16| -0.07| -0.19| 0.83*| 1.00 |

*Correlation significant at 0.5 level
EC and water becomes saline at high TDS concentration (Hashmi et al., 2009).

**Conclusion**

The groundwater chemistry shows that in the majority of the study area, an extreme amount of Na\(^+\) is present except in few samples. The sequence of Na\(^+\) abundance is the most dominant cation followed by Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\). The anions of the groundwater showed too much of Cl\(^-\) presence except in few locations. The progression of Cl\(^-\) abundance was dominant ion followed by HCO\(_3\)^\(\cdot\), SO\(_4\)^\(2-\), and CO\(_3\)^\(2-\). The results of the hydro-chemical fancies divulge the nature of water as sodium chloride mixed with calcium chloride and magnesium chloride. It can be observed from the statistical analysis that sodium has a highly significant correlation with chloride and sulfate. Salt mines, agriculture, domestic, oil industrial effluence, and rock dissolution is liable for the sodium and chloride increase within the study area. Wilcox plot exemplifies that 45.6% samples water quality are very much doubtful region and 20.58% samples have very high salinity which is considered not suitable for drinking and irrigation purposes. 84% of the samples are not potable as compared with the WHO permissible limits. The major source of all the hydro-geochemical process in the study area is due to salt mines in vicinity and lithology, which make the water unsuitable for drinking and irrigation purposes. This conclusion will be most obliging for the water resource managers to solve environmental trouble in the society. This study provides the potential idea for groundwater monitoring and also provides key information for further studies such as saltwater intrusion and fresh groundwater development potential.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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