Advances in Environmental Research, *Vol. 10, No. 1 (2021) 43-57*
DOI: https://doi.org/10.12989/aer.2021.10.1.043

Geochemical evaluation of groundwater quality of Peshawar Basin, Pakistan

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(Received August 5, 2020, Revised January 19, 2021, Accepted January 20, 2021)

Abstract. Evaluation of groundwater quality is vital due to its diverse use for several purposes. In the present study, groundwater quality and suitability from the Peshawar basin, Pakistan, were evaluated for drinking and irrigation purposes. The water samples were analysed for major cations (Ca, Mg, Na and K) and anions (chloride, bicarbonate and sulphate) along with other physicochemical parameters (pH, electrical conductivity, total dissolved solids, and total hardness). About 95% of the water samples were found to be within the WHO, US-EPA and Pak-EPA permissible levels for drinking purposes. Seventy percent (70%) of the water samples belonged to the hard water category. Irrigation water quality parameters, such as, chloride, residual sodium bicarbonate, sodium adsorption ratio, percent sodium, magnesium adsorption ratio, Kelly's ration and permeability index were evaluated which demonstrated that the groundwater was highly to moderately suitable for irrigation. A correlation study was conducted to find out the mutual associations among the variables. Piper diagram indicated the overall chemical nature of the study area was calcium-magnesium bicarbonate type. Cluster analysis revealed mutual apportionment of various parameters in the groundwater of the Peshawar basin, Pakistan.

Keywords: groundwater; cations; anions; drinking/irrigation water quality; Pakistan

1. Introduction

Groundwater is a vital and replenishable resource used by one-third of the total population on a global scale. The quality of groundwater depends upon the processes and reactions from the condensation in the atmosphere to the time it is discharged by a well (Sophocleous 2002, Leung and Jiao 2006). Groundwater is the major source fulfilling the demand for freshwater in rural and urban areas of most Asian countries. Numerous anthropogenic and natural factors can deteriorate the quality of water making it unfit for human and industrial use; therefore, regular monitoring of water quality is imperative (Arslan 2017, Hamzaoui *et al*. 2011, Zakir *et al*. 2016). Poor water quality affects health and life expectancy and it is an incessant threat to crops and soil (Sharmin *et al*. 2020, Haque *et al*. 2018, Zakir *et al*. 2018a). Consequently, the evaluation of groundwater quality for its suitability for domestic and agricultural use is very important. Recent studies have

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http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

mostly focused on the evaluation of the quality of water desirable for domestic and irrigation purposes (Asadollahfardi *et al*. 2018, Bhuiyan *et al*. 2016, Khan *et al*. 2016, Kumar *et al*. 2017, Saleem *et al*. 2016, Samo *et al*. 2017, Santos *et al*. 2018, Soldatova *et al*. 2018, Zakir *et al*. 2016, 2018b). These studies suggested significant anthropogenic contamination of the groundwater mostly emanating from the industrial, agricultural and domestic run-offs. The Peshawar basin is well known for the scarcity of freshwater and groundwater is the most important resource in this area. The major factors responsible for the increased reliance on groundwater resources are limited availability of surface water and inadequate storage capacity (Muhammad and Khalid 2017). Unlike surface water, groundwater is resistant to immediate deterioration in its quality as contaminants are either adsorbed/degraded or diluted during water travel through various zones of the soil. However, large and longstanding human settlements and associated uncontrolled anthropogenic activities affect the environmental quality at large (Jan *et al*. 2010, Khan *et al*. 2016, Muhammad and Khalid 2017).

In Pakistan, there is a dire need for monitoring the groundwater quality for human and ecological risks, especially in the wake of recent urbanization and industrial developments (Abbas *et al*. 2018, Awais *et al*. 2017, Naseem and McArthur 2018, Tariq *et al*. 2010). Several small and large industrial units have been installed over the years in and around the Peshawar basin, Pakistan along with a sharp increase in urban population (Jan *et al*. 2010, Khan *et al*. 2016). Major causes for declining water quality (including industrial emissions, agricultural/domestic run-offs, etc.) should be addressed on top priority to improve the environmental conditions. Therefore, the present study was conducted with the following broad objectives; (i) to assess the groundwater quality of the Peshawar basin, (ii) to compare the observed levels of studied parameters with the corresponding international and national guidelines, and (iii) to evaluate the water quality for drinking and irrigation purposes. The physicochemical parameters measured during the present study included the essential metals (Ca, Mg, Na and K), pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), chloride (Cl^-), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), residual sodium bicarbonate (RSBC), percent sodium (PS), sodium adsorption ratio (SAR), magnesium adsorption ratio (MAR), Kelly's ratio (KR) and permeability index (PI). It is anticipated that the study would provide baseline data regarding the groundwater quality. It would be helpful in the management and control of the pollutants in the study area.

2. Materials and methods

2.1 Study area

The present study was conducted in the southern part of Peshawar basin, Pakistan which is intra-plate basin and located at the southern foothills of the North-West Himalaya fold (Fig. 1). The rocks in the area are highly complex structurally deformed and ranging in age from Precambrian to recent. The bedrock is overlain by alluvial cover of Quaternary age having a thickness of several hundred meters. This structural complexity in the area is the result of Indian continental plate and Eurasian plate interaction. The mountain ranges around the study area are mostly composed of sandstone, shale and limestone. Predominantly the area is composed of fluvial sediments and flood plain deposits. The fluvial deposits are in the form of alluvial fans which are derived from hills and flood plain deposits. Gravel, boulder, coarse sand with inter-bedded clay is dominating lithology of the area. The basin is drained by three major rivers Kabul, Swat and Indus

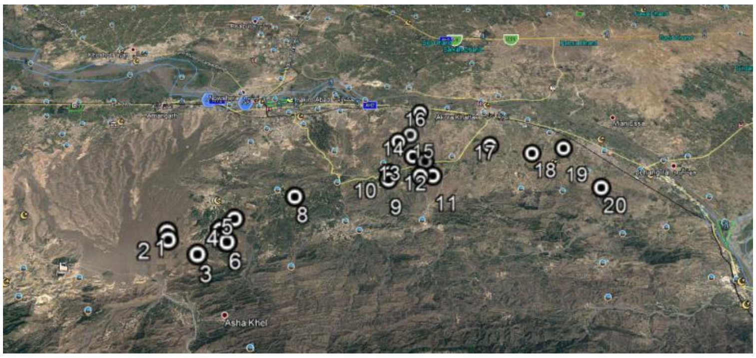

Fig. 1 Location map of the study area and sampling sites

Table 1 Description of the sampling locations included in the present study

Location ID	Location address	Geographical coordinates		Depth (m)	No. of samples
		N	E		
WS-01	Mehrajee	33.91361	71.95806	97	6
WS-02	Mehrajee	33.91778	71.95639	112	5
WS-03	Mehrajee	33.90639	71.97389	110	7
WS-04	Mehrajee	33.91889	71.98222	96	9
WS-05	Ziart Kaka Sahib	33.92472	71.98806	85	10
WS-06	Mehrajee	33.91250	71.98667	80	8
WS-07	Ziart Kaka Sahib	33.95917	72.08500	93	8
WS-08	Ziart Kaka Sahib	33.93722	72.01667	112	7
WS-09	Nowshera	33.94778	72.06500	108	9
WS-10	Walai Nowshera	33.95167	72.06556	115	5
WS-11	Ziart Kaka Sahib	33.95000	72.08861	111	7
WS-12	Ziart Kaka Sahib	33.95000	72.08194	95	8
WS-13	Ziart Kaka Sahib	33.96250	72.07861	83	9
WS-14	Nowshera	33.97250	72.07083	110	8
WS-15	Nowshera	33.97722	72.07778	107	8
WS-16	Akora Khattak	33.99361	72.08417	92	10
WS-17	Akora Khattak	33.97028	72.12194	89	9
WS-18	Shaidu eidgah	33.96500	72.14444	101	10
WS-19	Shaidu eidgah	33.96861	72.16278	125	8
WS-20	Pitaw payan	33.94333	72.17639	120	9

along with several perennial/non-perennial streams which eventually join these rivers. The mean annual rainfall in the study area is 635 mm (Farid *et al*. 2017, Muhammad and Khalid 2017).

2.2 Sample collection and processing

The groundwater samples were collected from 20 major locations of the study area (Fig. 1) and about 5 to 10 samples were collected from each location. A total of 160 water samples were collected and analysed during the present study. The samples were collected in pre-cleaned and dried high-density polyethylene bottles (1.5 L) following the standard procedure (APHA 2001). The samples were collected from the permeable zone with average depth ranges 80-125 meters, as shown in Table 1. Each water sample was divided into two parts: the first part was filtered to remove any suspension and after that it was used for the measurement of various physicochemical parameters without the addition of any chemical reagent, while the second part was preserved by acidifying with concentrated nitric acid (AR grade) to pH < 2 for the metal analysis (US-EPA 2003, Yesmeen *et al*. 2018). The physicochemical parameters (pH, EC and TDS) were determined immediately after the sample collection (APHA 2001, Mohanty and Nayak 2017, Radojevic and Bashkin 1999). During the present study, pH was measured using a digital pH meter (Model: Martini Mi 180, Romania); EC and TDS were measured by a digital conductivity meter (Model: Jenway 470, EU). Total hardness, chlorides, bicarbonates and sulphates and were determined following the standard methodology (APHA 2001, Radojevic and Bashkin 1999). The hardness estimation was done by EDTA titrimetric method employing EBT indicator, while chloride contents were determined by the standard Argentometric method using potassium chromate indicator (APHA 2001, Yesmeen *et al*. 2018). The bicarbonates were determined by titrating with a standard solution of mineral acid (HCl) to the successive bicarbonate and carbonate equivalence points using phenolphthalein and methyl orange indicators (APHA 2001). Finally, the sulphate was estimated indirectly by precipitating sulphate as lead sulphate, which upon separation on the micro-pore filter was digested in 65% HNO_3 and analysed by AAS method (APHA 2001, Radojevic and Bashkin 1999). Major essential metals (Ca, Mg, Na and K) in water samples were analysed using flame atomic absorption spectrophotometry (Shimadzu AA-670, Japan) under optimum analytical conditions, employing the calibration line method. A reagent blank (containing distilled water and few drops of HNO_3) was processed in the same manner along with each batch of the samples. Standard reference material (SRM 1643d) was also used to ensure the reliability of the metal data; it showed excellent recoveries ranging from 97.5% to 102%. Inter-laboratory comparison of the data was also exercised at an independent laboratory and a maximum of ± 2% deviation was observed in the results of the two laboratories (Lab-I: PCSIR Labs & Lab-II: Department of Chemistry, Quaid-i-Azam University). All the measurements were made in triplicate. Analytical grade chemicals were used throughout the study. Working metal standards were prepared from a stock solution of 1000 mg/L by succeeding dilutions.

2.3 Statistical analysis

Statistical methods were applied to treat the analytical data in terms of their distribution and interrelationships among the studied parameters using STATISTICA software. Basic statistical parameters such as, range, mean, median, standard error (SE) and skewness were computed. Spearman correlation coefficients were also calculated to envisage the mutual relationships among the variables (Shah *et al*. 2012).

2.4 Irrigation water quality evaluation

Other physicochemical parameters including residual sodium bicarbonate (RSBC), percent sodium (PS), sodium adsorption ratio (SAR), magnesium adsorption ratio (MAR), Kelly's ratio (KR) and permeability index (PI) were calculated from ionic concentrations (meq/L) of Ca, Mg,

Table 2 Statistical summary of the water quality parameters measured in the groundwater samples and their guideline values

	Range	Mean	Median	SE	Skew.	WHO	US-EPA	Pak-EPA
pH	7.50-7.80	7.73	7.75	0.02	−2.73	6.5-8.5	6.5-8.5	6.5-8.5
EC (µS/cm)	332-720	478	458	21.8	1.15	1500	-	-
TDS (mg/L)	202-439	293	279	13.7	1.12	1000	500	1000
TH (mg $CaCO_3$/L)	95.8-251	177	188	9.19	−0.25	500	-	-
Ca (mg/L)	14.0-72.1	46.5	45.1	3.39	−0.27	100	-	200
Mg (mg/L)	4.86-23.1	14.7	14.6	1.02	−0.42	50	-	-
Na (mg/L)	13.6-61.2	29.6	24.0	3.19	1.05	200	-	-
K (mg/L)	0.78-4.30	2.01	1.56	0.24	0.77	12	-	-
Cl^- (mg/L)	10.6-42.5	17.4	14.2	1.60	2.48	250	250	250
HCO_3^{1-} (mg/L)	177-366	244	244	9.62	1.19	-	-	-
SO_4^{2-} (mg/L)	4.80-52.8	21.9	21.6	3.07	0.73	200	-	-
RSBC (meq/L)	0.59-4.52	1.67	1.55	0.20	1.82	-	-	-
PS	15.4-58.5	27.5	21.6	2.73	1.07	-	-	-
SAR	0.45-2.72	1.02	0.74	0.13	1.47	-	-	-
MAR	13.6-63.4	35.6	32.2	2.77	0.41	-	-	-
KR	0.16-1.39	0.41	0.26	0.07	1.98	-	-	-
PI	52.0-108	68.4	62.3	3.12	1.30	-	-	-
Reference	Present study					(WHO 2008)	(US-EPA 2009)	(Pak-EPA 2008)

Na, K and HCO_3^- using the following relationships (Abbas *et al*. 2018, Awais *et al*. 2017, Doneen 1964, Kelly 1963, Saleem *et al*. 2016, Yesmeen *et al*. 2018).

$$RSCB = HCO_3^- - (Ca + Mg) \tag{1}$$

$$PS = \left(\frac{Na + K}{Ca + Mg + Na + K}\right) \times 100 \tag{2}$$

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \tag{3}$$

$$MAR = \frac{Mg \times 100}{Ca + Mg} \tag{4}$$

$$KR = \frac{Na}{Ca + Mg} \tag{5}$$

$$PI = \frac{\left(Na + \sqrt{HCO_3^-}\right)}{(Ca + Mg + Na)} \times 100 \tag{6}$$

Table 3 Correlation coefficient matrix for the water quality parameters (n = 160)

	pH	EC	TDS	Ca	Mg	Na	K	Cl^-	HCO_3^-	SO_4^{2-}	TH	RSBC	PS	SAR	MAR	KR	PI
pH	1.00																
EC	0.14	1.00															
TDS	0.15	1.00	1.00														
Ca	−0.08	0.20	0.22	1.00													
Mg	−0.20	0.22	0.22	−0.08	1.00												
Na	0.34	**0.53**	**0.53**	−0.40	−0.21	1.00											
K	−0.12	0.08	0.09	0.26	−0.15	−0.04	1.00										
Cl^-	0.14	**0.83**	**0.82**	−0.16	0.16	**0.50**	0.06	1.00									
HCO_3^-	0.09	**0.92**	**0.92**	0.27	0.23	**0.53**	0.10	**0.68**	1.00								
SO_4^{2-}	0.16	0.36	0.36	0.12	−0.05	0.23	0.02	0.24	0.08	1.00							
TH	−0.17	0.29	0.31	**0.89**	0.39	−0.47	0.17	−0.08	0.35	0.09	1.00						
RSBC	0.15	**0.56**	**0.54**	**−0.64**	0.25	**0.77**	−0.15	**0.68**	**0.57**	−0.04	−0.48	1.00					
PS	0.32	0.29	0.28	**−0.65**	−0.33	**0.93**	−0.08	0.42	0.23	0.22	**−0.75**	**0.74**	1.00				
SAR	0.31	0.45	0.44	**−0.58**	−0.24	**0.96**	−0.09	**0.53**	0.39	0.25	**−0.65**	**0.81**	**0.98**	1.00			
MAR	−0.01	0.18	0.17	**−0.76**	**0.65**	0.27	−0.27	0.42	0.08	0.01	−0.39	**0.72**	0.36	0.39	1.00		
KR	0.28	0.39	0.38	**−0.67**	−0.24	**0.90**	−0.12	**0.56**	0.30	0.27	**−0.73**	**0.81**	**0.97**	**0.98**	0.46	1.00	
PI	0.28	0.17	0.15	**−0.78**	−0.34	**0.82**	−0.12	0.40	0.10	0.10	**−0.88**	**0.75**	**0.96**	**0.93**	0.43	**0.96**	1.00

* Significant coefficient values are shown in bold ($p < 0.001$)

3. Results and discussion

The major quality criteria parameters for drinking and irrigation purpose are pH, EC, TDS, TH, Cl^-, HCO_3^-, SO_4^{2-}, Ca, Mg, Na and K, etc. The statistical summary related to the distribution of various water quality parameters in the groundwater samples is given in Table 2. The inter-relationships among these variables in terms of correlation coefficients are shown in Table 3 while various parameters related to the irrigation water quality are given in Table 4. Classification of the water samples based on the permeability index is shown in Fig. 2 in the form of Doneen's chart. Multivariate apportionment of the measured variables was carried out by cluster analysis as shown in Fig. 3. At the same time, the predominant chemical composition of the groundwater samples was assessed by piper diagram which is shown in Fig. 4. The suitability of the groundwater for drinking and irrigation along with statistical analyses are discussed in the following sections.

3.1 Physicochemical parameters

Generally, the water quality can be gauged by determining its pH which should be in the range of 6.50 to 8.50 for desirable characteristics (WHO 2008). In the presents study, pH values ranged from 7.50 to 7.80 with a mean value of 7.73 which was almost comparable to the median value (7.75) as shown in Table 2. Therefore, the groundwater samples from the Peshawar basin were classified as desirable water category. The measured pH values were also within the permissible limits for drinking water as recommended by WHO (2008), US-EPA (2009) and Pak-EPA (2008)

Table 4 Classification of groundwater based on irrigation water quality parameters*

Hazard	Parameter	Range	Rating	Suitability	Number of samples (%)
Salinity hazard	EC (µS/cm)	< 700	3	High	100
		700-3000	2	Medium	Nil
		> 3000	1	Low	Nil
Specific ion toxicity	SAR	< 3	3	High	100
		3-9	2	Medium	Nil
		> 9	1	Low	Nil
	Cl^- (mg/L)	< 140	3	High	100
		140-350	2	Medium	Nil
		> 350	1	Low	Nil
Miscellaneous effects on sensitive crops	HCO_3^- (mg/L)	< 90	3	High	Nil
		90-500	2	Medium	100
		> 500	1	Low	Nil
	pH	7-8	3	High	100
		6.5-7 & 8-8.5	2	Medium	Nil
		< 6.5 or > 8.5	1	Low	Nil

(Table 2). The water samples from most of the locations exhibited almost comparable pH values. However, it showed almost independent variations and insignificant relationships with other parameters as mentioned in Table 3. These groundwater samples were also found to be highly suitable for irrigation purpose with respect to pH (Ayers and Westcot 1985, Simsek and Gunduz 2007) as shown in Table 4.

The electrical conductivity is considered as a measure of soluble ions, excess of which reduces the osmotic activity of plants and interferes with the absorption of water and nutrients from the soil. In the present study, EC values ranged from 332 to 720 µS/cm with the mean value of 478 µS/cm (Table 2). Considerable variations in the EC values were observed in the water samples from various locations; such variations can be attributed to the diverse and random anthropogenic activities in the study area. It exhibited significant positive correlations with bicarbonates, chlorides, Na and RSBC (Table 3). The measured EC values were within the permissible limit for drinking as per national and international guidelines (Pak-EPA 2008, US-EPA 2009, WHO 2008), demonstrating the suitability of groundwater for the drinking purpose. The water samples from the study area showed medium suitability (Class II: 250-750 µS/cm) for irrigation with respect to the electrical conductivity (Wilcox 1955).

Total dissolved solids may affect the suitability of water for drinking/irrigation purpose. In the present study, TDS levels ranged from 202-439 mg/L with the mean value of 293 mg/L and the median value of 279 mg/L (Table 2). The water samples contained a considerably lower amount of TDS than the permissible limits as per national/international guidelines (Pak-EPA 2008, US-EPA 2009, WHO 2008), indicating small contents of soluble salts in the water which can be used for drinking without any risk. However, significant differences in TDS levels from various sampling locations were noted thus manifesting anthropogenic intrusions in the study area as the lithology of the area is more or less same. Like the previous case, TDS in the water samples exhibited significantly strong correlations with bicarbonates, chlorides, RSBA and Na apart from a direct relationship with EC, as mentioned in Table 3.

The suitability of groundwater was also assessed based on TH which ranged from 95.8-251 mg $CaCO_3$/L with an average value of 177 mg $CaCO_3$/L. The measured TH values were found to be within the permissible limit for drinking water as per WHO (2008) guidelines. Some noteworthy differences in the TH values were observed for various locations which indicated diverse and random anthropogenic activities in the study area. Generally, water is considered soft, moderately hard, hard and very hard with TH values < 75, 75–150, 150–300 and > 300 mg/L, respectively (Radojevic and Bashkin 1999). Consequently, the water samples from the study area were classified as moderately hard and hard water, although the majority of the samples (70%) belonged to the hard water class. The correlation study revealed significantly positive association of TH with Ca while PS, SAR, KR and PI showed the significant inverse relationships with TH (Table 3).

3.2 Major cations

Statistical evaluation of the major cations revealed relatively higher contributions of Ca (14.0-72.1 mg/L), followed by Na (13.6-61.2 mg/L) and Mg (4.86-23.1 mg/L), whereas lowest for K (0.78-4.30 mg/L). Based on the average levels, the major cations followed the decreasing order in groundwater: Ca (46.5 mg/L) > Na (29.6 mg/L) > Mg (14.7 mg/L) > K (2.01 mg/L). In most of the cases, metal levels exhibited random variations as manifested by individual variations at various sampling points as well as higher dispersion and asymmetry in terms of SE and skewness, respectively (Table 2). Measured concentrations of the metals were found to be within the recommended national and international water quality guidelines (Pak-EPA 2008, US-EPA 2009, WHO 2008), as shown in Table 2. It demonstrated that the groundwater in the study area was of good quality for drinking purpose. The correlation study (Table 3) showed the significant inverse relationship of Ca with RSBC, PS, SAR, MAR, KR and PI; however, Mg exhibited a positive association with MAR. Nonetheless, Na showed significantly strong correlations with PS, SAR, KR, PI, RSBC, bicarbonates and chlorides, while K showed almost independent variations and insignificant relations with other variables. The correlation study indicated opposing variations of Ca and Na in most of the water samples which may affect other geochemical characteristics of the water.

3.3 Major anions

Among the major anions, chloride toxicity is most common in the irrigation water. It is not adsorbed or held back by the soil, therefore, it moves readily and taken up by the crop, passes through the transpiration stream and accumulates in the leaves. If the chloride concentration in the leaves exceeds the tolerance limit of the crop, injury symptoms develop such as, leaf burn or drying of leaf tissue. Normally, plant injury occurs first at the leaf tips and progresses from the tip back along the edges. Excessive necrosis is often accompanied by early leaf drop or defoliation (Ayers and Westcot 1985). Generally, Cl^- < 142 mg/L indicated no problem; Cl^- in range of 142-355 mg/L showed moderate problem; and Cl^- > 355 mg/L exhibited severe problem. In the present study, chloride levels in groundwater ranged from 10.6-42.5 mg/L with a mean value of 17.4 mg/L. As a result, the water samples were categorized as 'no problem' water class for irrigation purpose with respect to chloride contents. Moreover, the chloride contents exhibited relatively lower variations and were also within the permissible limit of international and national standards (Pak-EPA 2008, US-EPA 2009, WHO 2008) indicating that the groundwater was suitable for the drinking purpose (Table 2). Chloride contents of the water samples were significantly correlated with RSBC, bicarbonates, KR and SAR (Table 3).

The irrigation water having excessive bicarbonates tends to precipitate insoluble Ca and Mg in the soil as their precipitates which ultimately leave higher Na proportion and increase its adsorption value (Michael 1978). It was also reported that although usual bicarbonate ion is not toxic, it may cause Zn deficiency in crops (Ayers and Westcot 1985). In the present study, bicarbonate contents ranged from 177-366 mg/L with an average value of 244 mg/L. Majority of the sampling locations showed almost comparable bicarbonate contents. Therefore, the water samples from the study area showed medium suitability for irrigation purpose (Ayers and Westcot 1985, Simsek and Gunduz 2007) with respect to bicarbonate contents (Table 4). The positive RSBC values indicated that dissolved Ca/Mg ions were less than those of carbonate/bicarbonate contents. The RSBC values in water samples varied from 0.59-4.52 with an average value of 1.67 meq/L. Accordingly, the water samples were graded as unsuitable for irrigation purpose in relevance to RSBC (Ayers and Westcot 1985). The correlation study revealed significant positive relationships of RSBC with PS, SAR, MAR, KR and PI (Table 3).

Sulphate is one of the major dissolved components of the groundwater. High concentrations of sulphate in the drinking water can have a laxative effect when combined with elevated levels of Ca and Mg. In the present study, sulphate ions ranged from 4.80-52.8 mg/L with a mean value of 21.9 mg/L, which were within the permissible limits of WHO (2008). However, in comparison with the proposed limit of < 20 mg/L in irrigation water by Ayers and Westcot (1985), about half of the water samples (48%) were exceeding the limit. Significant fluctuations in the sulphate ion concentrations were noted in the water samples from various locations. They showed almost independent variations in the water samples supported by insignificant correlations with the rest of the variables as shown in Table 3.

3.4 Percent sodium (PS) & sodium adsorption ratio (SAR)

Sodium concentration is important in classifying the irrigation water because it may reduce the soil permeability. Higher Na concentration in the irrigation water tends to be absorbed by clay particles, displacing Ca and Mg, thus reducing the permeability. Higher concentrations of Na in the soil may affect its physical condition and the soil structure resulting in the formation of crusts, waterlogging, reduced soil aeration, reduced infiltration rate, and reduced soil permeability (Wilcox 1955, Saleem *et al*. 2016). In the present study, PS values ranged as 15.4-58.5% with the mean value of 27.5%. Based on the PS, water is classified as; PS = 0 – 20% indicates excellent water; PS = 20 – 40% indicates good water; PS = 40 – 60% shows permissible water; PS = 60 – 80% shows doubtful water and PS > 80% demonstrates unsuitable water (Wilcox 1955). Accordingly, the groundwater samples in the present study were classified as excellent (48%), good (35%) and permissible (17%) water for agricultural use. About half of the sampling location belonged to excellent water category.

Water suitability for irrigation use was also evaluated based on SAR. It is an important parameter and a measure of alkali/sodium hazard to the crops. Sodium replacing adsorbed Ca and Mg is a hazard as it causes damage to the soil structure which becomes compact and impervious. In the present study, SAR values ranged from 0.45-2.72 with an average value of 1.02. Generally, SAR < 3 indicates high suitability as irrigation water (Richards 1954) and therefore, the water samples in the present study belong to this category which implies that no alkali hazard was anticipated to the crops (Table 4). Both PS and SAR showed significantly strong associations with

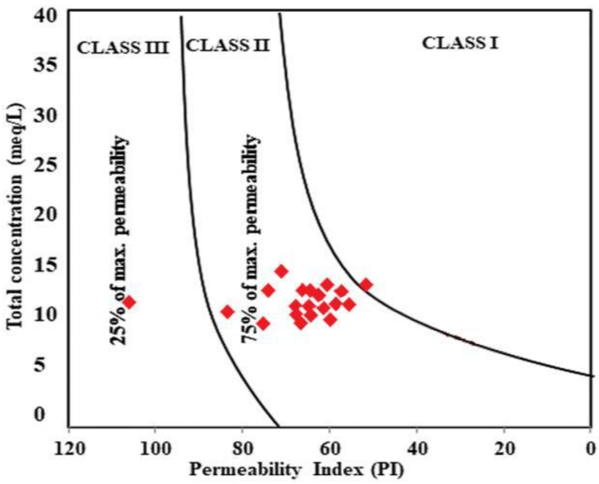

Fig. 2 Doneen's chart for the classification of the groundwater in the study area

KR and PI in the groundwater samples as mentioned in Table 3.

3.5 Magnesium adsorption ratio (MAR) and Kelly's ratio (KR)

Magnesium adsorption ratio was introduced by Paliwal (1972) to assess the water for irrigation purpose. The ratios of more than 50% would adversely affect the crop yield as the soils become too alkaline. The groundwater samples in the present study showed MAR ranging from 13.6 to 63.4% with an average value of 35.6%, indicating moderate suitability of the water for irrigation use. However, a few samples exceeded 50% and thus were unsuitable for irrigation purpose.

Sodium measured against Ca and Mg was considered by Kelly (1963) to calculate this parameter. A ratio of more than one indicates an excessive level of Na in water, while, a ratio of less than one is suitable for irrigation purpose. In the present study, KR ranged from 0.16-1.39 with an average value of 0.41 (Table 2) and most of the sampling locations (95%) showed KR < 1.0; as a result, the groundwater was classified as suitable water for irrigation use. It also showed a strong significant relationship with PI in the groundwater samples (Table 3).

3.6 Permeability index (PI)

The permeability problem occurs when normal infiltration rate of the soil is appreciably reduced and hinders the moisture supply to crops which is responsible for two most water quality factors as the salinity of water and its Na content relative to Ca and Mg. The soil permeability is affected by long-term use of irrigation water and is influenced by Na, Ca, Mg and bicarbonate contents of the soil. Doneen (1964) evolved a criterion for assessing the suitability of water for irrigation based on PI. According to the PI values, the water samples can be classified as Class I, II and III. In the first two classes water samples are categorized as good for irrigation with 50-75% or more of the maximum permeability. Class III water samples are unsuitable with 25% of the maximum permeability. In the present study, the permeability index of water samples varied from 52.0-108% with a mean value of 68.4%. Accordingly, all the water samples (except one) belonged to Class I and II categories of the Doneen's chart which are suitable for irrigation purpose as

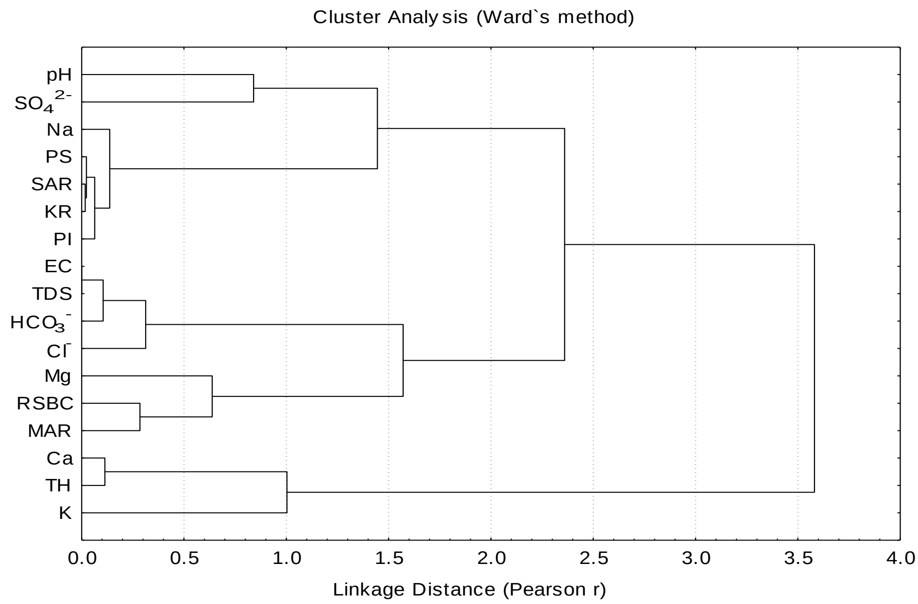

Fig. 3 Cluster analysis of the water quality parameters in the groundwater

shown in Fig. 2. Majority of the sampling locations (70%) in the study area exhibited almost comparable permeability. The correlation study showed that PI was negatively correlated with TH and Ca while positively correlated with Na, RSBC, PS, SAR and KR as shown in Table 3.

3.7 Cluster analysis

Various mathematical models have been used for the assessment of water quality (Alves *et al*. 2018, Asadollahfardi *et al*. 2018, Awais *et al*. 2017, Bhuiyan *et al*. 2016, Mohanty and Nayak 2017, Saleem *et al*. 2019, Tariq *et al*. 2010). In the present study, cluster analysis was carried out to explore the multivariate apportionment among the water quality parameters as shown in Fig. 3. The strongest cluster was observed among KR, SAR, PS, PI and Na, thus indicating the dependency of the first four parameters on Na concentration in the groundwater. Similarly, EC and TDS exhibited very strong associations with bicarbonate and chloride thereby showing the major contributions among the anions. Another joint cluster was noted for MAR, RSBC and Mg while TH, Ca and K revealed a common cluster. These two clusters showed the critical effects of Mg and Ca on other water quality parameters. Another mutual cluster was noted for pH and sulphate which demonstrated the effects of pH on the availability of sulphate in the groundwater. Overall, the cluster analysis exhibited communal associations among various parameters in the groundwater; their combined effects can severely affect the water quality.

3.8 Piper diagram

Piper diagram is a geochemical method used to determine the predominant chemical characteristics of the groundwater (Arslan 2017, Piper 1944). Major cations and anions with TDS are plotted in the Piper trilinear diagram as shown in Fig. 4. The lower left triangle showed

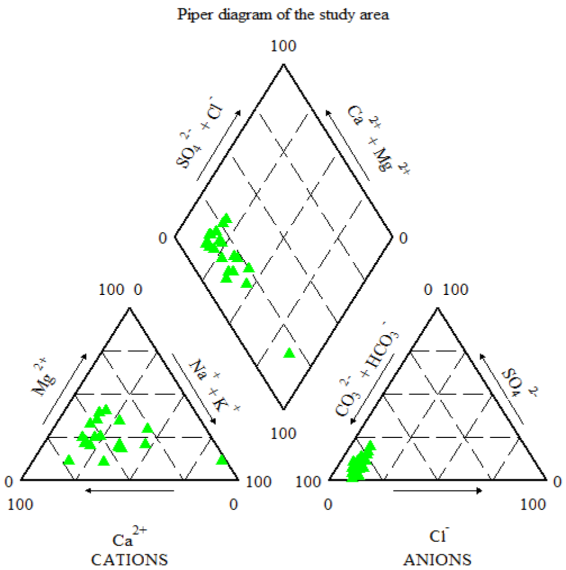

Fig. 4 Piper diagram showing the major composition of groundwater in the study area

relatively higher Ca contents and Na and K levels were comparatively lower. The right triangle indicated predominantly higher carbonate/bicarbonate along with sulphate contents while chloride contents were relatively less. Overall, on the basis of this analysis it was concluded that the groundwater in the study area was generally calcium-magnesium bicarbonate type because exposed rocks in the study area mainly consisted of limestone, argillite and phyllite type (Farid *et al*. 2017, Muhammad and Khalid 2017), although other cations and anions such as, sodium, chloride and sulphate were also present, but their relative contributions were small.

4. Conclusions

The present study revealed that the majority of the groundwater samples (95%) were within the permissible limits of WHO, US-EPA and Pak-EPA for drinking purpose. Most of the measured variables exhibited random distribution in the groundwater samples and the correlation study showed mutual associations among various parameters. About 70% groundwater sample belonged to the hard water category. Among the major cations, the highest contribution was shown by Ca, followed by, Na, Mg and K. The chloride contents were within the permissible limits for drinking and irrigation purposes. In contrast, bicarbonates showed medium suitability for the irrigation. However, RSBC indicated unsuitability for the irrigation purpose. Although no salinity hazard was observed, some of the water samples were not suitable for the irrigation with respect to MAR. Similarly, KR and PI also showed the suitability of the groundwater for irrigation purpose. The Piper diagram indicated that the groundwater in the area was generally calcium-magnesium bicarbonate type. Most of the studied parameters demonstrated that the study area had a slightly good aquifer system for the domestic and irrigation supply. Cluster analysis revealed multiple associations among various parameters in the groundwater. Overall, the water quality evaluation in the study area revealed that the aquifer is under significant anthropogenic stress. However, the extent of pollution/contamination is not very severe, the environmental conditions may deteriorate if it remained unnoticed. Therefore, it is recommended to safeguard the aquifer by implementing the appropriate environmental management strategies thereby limiting the intrusion of the anthropogenic pollutants and reducing the point and non-point emission sources in the study area.

Acknowledgments

The financial assistance provided by Quaid-i-Azam University, Islamabad, Pakistan to carry out this project is thankfully acknowledged.

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