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Groundwater quality risk assessment using hydro-chemical and geospatial analysis

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Abstract

Groundwater quality risk assessment is vital to protect this precious resource, because increasing anthropogenic and agricultural activities combined with limited precipitation deteriorate the groundwater quality particularly in the arid regions. Therefore, the assessment of groundwater quality using hydro-chemical and spatial analysis can provide the guidelines for efficient management of groundwater resources. In present study, a total of 87 samples were collected from various pumping wells in district Multan, Pakistan. These samples were analysed for groundwater quality parameters like electrical conductivity (EC), total dissolve solids (TDS), pH, Na^+, $Ca^{2+}+Mg^{2+}$, Cl^-, CO_3^{2-}, HCO_3^-, sodium adsorption ratio (SAR), sodium percentage (Na%), total hardness (TH), residual sodium carbonate (RSC) and Kelly's ratio (KR). The Wilcox, United States Salinity Laboratory (USSL) and permeability index (PI) diagrams were drawn to classify the water into excellent, good, marginal and poor-quality groundwater for irrigation obligatory. Using the ArcGIS vs 10, an ordinary kriging method with best fit semivariogram model was applied for preparation of spatial distribution maps. According to Wilcox classification, 40% of groundwater samples fall in 'Excellent to a Good' category. USSL diagram showed that 27% of groundwater samples fall in 'Medium Salinity' and 'Low sodium hazard' (C2S1) class. The PI values were found in the range of 22 to 95 meq/L with an average value of 58.5 meq/L. Similarly, the spatial analysis showed that upper part (northeast and northwest) of the Multan District have good quality of groundwater for irrigation. Furthermore, the finding may help to make the spatial management decision for groundwater in the region.

Keywords Irrigation · Groundwater quality · Salinization/sodification · Permissible limit · Spatial distribution analysis

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1 Introduction

The world's largest supplemental source of irrigation is groundwater, which is naturally built reservoir under the ground surface. In agrarian countries, crop productivity and food demand mainly depend on groundwater quality for human survival (Moharir et al., 2019; Murmu et al., 2019; Singh et al., 2009). Globally, 982 km^3/year of groundwater withdrawal was estimated to fulfil the drinking and irrigation demands (Margat & Gun, 2013). Due to rapid industrialization and urbanization, the stress on groundwater quality is continuously rising, and conservation is one of the foremost challenges for developing countries (Butt et al., 2015; Kumar et al., 2018; Thakur et al., 2013). Like other regions of the world, in Pakistan's, most of the area lies in arid to semi-arid regions where surface water supplies have decreased. Therefore, the groundwater usage has increased to fulfil the human and agriculture needs (Ahmed et al., 2015). A total of 14.88 million hectares of area is irrigated in Punjab, in which 8.37 million hectares is irrigated with tubewells and canal water (Muzammil et al., 2020). During most part of the growing season, the required quantity of surface water is not available to get the maximum potential of crop yield. Therefore, underground water resources have been fully utilized to meet the crop water demand (Ahmad et al., 2015). To meet the water demand of crops, several tubewells have been installed in large areas of Punjab, Pakistan. Annually, 60 billion cubic meters (BCM) of groundwater is being pumped by these tubewells. As a result of huge abstraction, the groundwater quality is deteriorating. Because, the groundwater quality depends on the nature of recharging water (precipitation and surface water) and hydro-geochemical processes in aquifers (Das et al., 2017; Pandey et al., 2016). The quality of groundwater is being affected by the geochemical reactions due to the aquifers recharge or discharge. Therefore, regular assessment of groundwater quality attained utmost importance for sustainable agriculture (Gautam et al., 2018; Jacintha et al., 2017; Rawat et al., 2018). The critical analysis of dissolved elements in the groundwater is useful for adequate supply of safe quality irrigation water to agricultural fields (Singh et al., 2014). The number of mineral elements because of geochemical reaction varies with space and time. These mineral elements have positive or negative impacts on both the soil and plants (Singh et al., 2009). The excessive amount of sodium, potassium, magnesium, calcium, chloride, sulphate, bicarbonate, and nitrate ions in irrigation water results not only in decrement in soil fertility, but also in decrease in the crop yield and net revenue (Rhodes et al., 2006). The combined action of all these ions present in the irrigation water reduces the crop yield. Gautam et al. (2015) reported that SAR, %Na, RSC, KR, TDS, TH and permeability index (PI) are the key water quality parameters which are frequently used to determine quality of groundwater for irrigation. The irrigation and groundwater quality are highly interlinked. Several studies have been conducted to evaluate the hydro-chemical features of aquifer, groundwater pollution and quality for agriculture in various basins and urban regions (Ahamed & Loganathan, 2017; Ahmed et al., 2015; Iqbal et al., 2018; Islam & Shamsad, 2009; Khattak et al., 2012; Patel et al., 2016; Shakoor et al., 2017; Sharma et al., 2017). Therefore, to safeguard the long-term sustainability of groundwater resources, the hydro-chemical analysis of groundwater quality parameters should continuously be carried out. Furthermore, development of spatial distribution map has been proved a more convenient to identify the specific area of suitable groundwater quality for irrigation (Murmu et al., 2019; Nas, 2009; Pandian & Jeyachandran, 2014; Rahman et al., 2017). However, no research study has been conducted so far in the region using the hydro-chemical and spatial analysis to evaluate suitability of groundwater for agriculture application. Therefore, the present study focussed on combined application of hydro-chemical and spatial analysis to evaluate groundwater quality and to identify the area of suitable quality for development of groundwater resources in the region.

2 Material and methods

2.1 Description of study area

The experimental study was conducted in Multan district Punjab, Pakistan. The Multan district is located between 29° 20′ to 30° 18′ N and 71° 9′ to 71° 49′ E (Fig. 1). It covers an area of 133 km^2. It is the seventh most populous city of Punjab, Pakistan. It has fertile land which is more suitable for agricultural production. It is known for its hottest weather and highest recorded temperature is approximately 52 °C. The Multan district has a flat topography. The soil of the Multan district is mostly used for production of citrus, mango, fodder, and cash crops.

The subsurface lithology of the region consists of alluvial soil which were brought from the Himalayas mountains by the Indus River systems and its tributaries. The hydrogeological conditions are un-confined throughout the area. The major sources of irrigation water in region are the groundwater and Haveli canal system (Farid et al., 2019; Shahzad et al., 2020). The length of the Haveli main canal is 295 km having discharge of 140.5 m^3/s. The gross command area of this canal is 418,850 hectares, out of which 414,398 hectares are cultivable. It almost covers all the area of district Multan. The average depth of

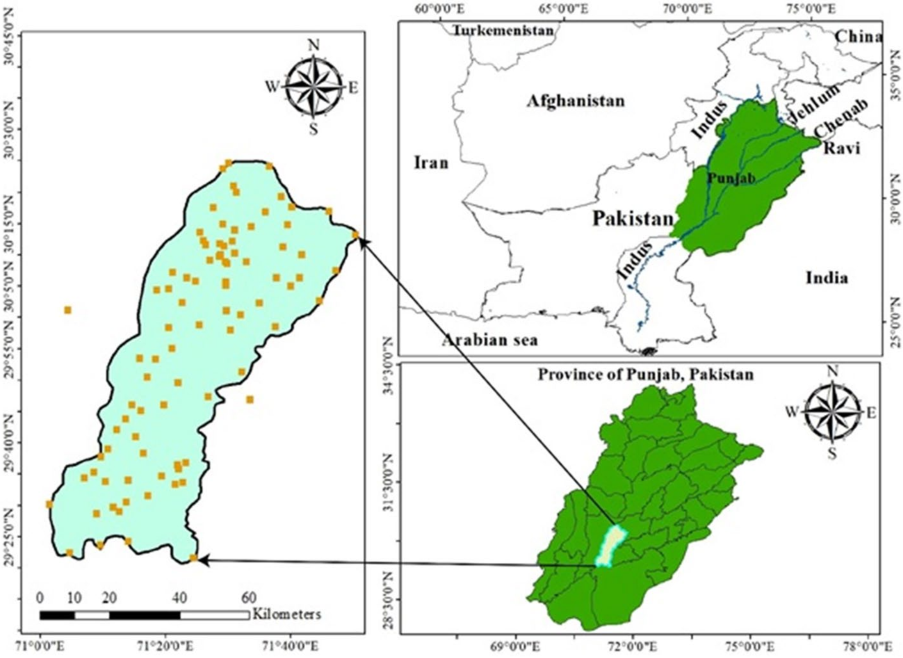

Fig. 1 Location of the Multan district and sample points

groundwater from the ground surface is about 40.24 m. The major sources of the groundwater recharge are mainly river Chenab and rainfall. The average annual precipitation in the region is about 186 mm (Abbas et al., 2014; Shahzad et al., 2020).

2.2 Data collection

For collection of data, the Multan district was divided into four parts. A total of 87 groundwater samples were collected from different pumping wells (Fig. 1). The boring depth of these pumping wells varies from 100 to 120 m. These samples were covered the whole area of district Multan. The groundwater samples were then stored in distilled bottles that were initially washed with nitric acid (Ahmed et al., 2015). The collected samples were analysed for different groundwater quality parameters for its suitability for irrigation. The groundwater quality parameters like pH, EC and TDS were analysed at the time of sampling using the field kit. It has been reported that TDS is important parameter to analyse the quality of irrigation water. Different toxic solids are present in the groundwater, and due to leaching or weathering of aquifer, the concentration of TDS increases in groundwater (Narsimha & Sudarshan, 2017). Similarly, the data regarding the boring depth were recorded by face-to-face discussion with the farmers. Through the chemical analysis, the other parameters like cation and anions, i.e. $Ca^{2+} + Mg^{2+}$, Na^{2+}, CO_3^-, HCO_3^- and Cl^-, etc., were analysed in the Soil and Water Testing Laboratory, Multan Government of Punjab, Pakistan (Fig. 2).

2.3 Calculation and measurements

2.3.1 Charge balance error (CBE)

The charge balance equation was used to calculate the accuracy of the chemical ion data (Eq. 1, Table 1). It has been reported that the positive value of charge balance error (CBE) for groundwater quality parameters indicating the higher concentration of cations than that of anions (Hounslow, 1995).

2.3.2 Total hardness (TH)

Total hardness (TH) was calculated using Eq. 2 (Table 1). Total hardness is an important parameter to determine the fitness of groundwater for domestic, industrial and irrigation purposes (Todd, 1980). The groundwater was classified into three categories. The groundwater was considered as soft if $TH < 75$ mg/L, moderately hard if $TH = 75–150$ mg/L, hard if $TH = 150–300$ mg/L and very hard if $TH > 300$ mg/L as reported by Selvakumar et al. (2017) and Soleimani et al. (2018).

2.3.3 Sodium adsorption ratio (SAR)

The groundwater suitability for irrigation can also be analysed using the sodium adsorption ratio (SAR). An extreme concentrations of Na^{1+}, CO_3^{2-} and HCO_3^- ions have direct effect on groundwater water quality and plant growth. The salinity in groundwater has influence on soil physiochemical properties, soil fertility and productivity (Nemcic-Jurec et al. 2019). The SAR was computed using the relationship of Na^+ concentration to the Ca^{2+} and Mg^{2+}concentrations (Eq. 3, Table 1). If the quantity of Ca^{2+} and Mg^{2+} is higher,

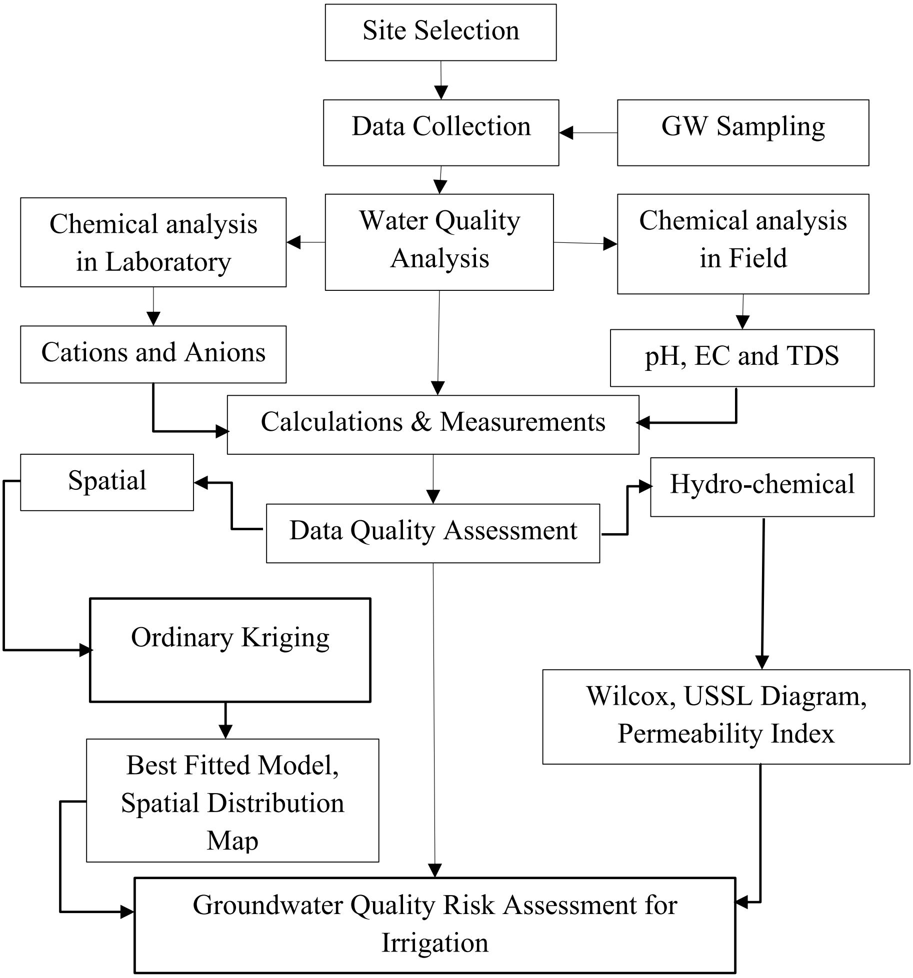

Fig. 2 Methodology of groundwater quality risk assessment

Table 1 Equations used for calculation of groundwater quality parameters

Sr. No	Groundwater quality parameters	Equations
1	Charge balance error (CBE)	$\mathrm{CBE}(\%) = \frac{\sum \mathrm{cations(meq)} - \sum \mathrm{anions\ (meq)}}{\sum \mathrm{cations\ (meq)} + \sum \mathrm{anions\ (meq)}}$
2	Total hardness (TH)	$\mathrm{TH} = \mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} \times 50$
3	Sodium adsorption ratio (SAR)	$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})/2}}$
4	Residual sodium carbonate (RSC)	$\mathrm{RSC} = (\mathrm{CO}_{3^-} + \mathrm{HCO}_{3^-}) - (\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})$
5	Sodium percentage (Na%)	$\mathrm{Na}\% = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+}} \times 100$
6	Kelly's ratio (KR)	$\mathrm{KR} = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}$
7	Permeability index (PI)	$\mathrm{PI} = \frac{\mathrm{Na}^{+} + \sqrt{\mathrm{HCO}_3^-}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+}} \times 100$

it will minimize the effect of sodium in the water and helps to sustain good soil fertility (Fipps, 2003). It has been reported that higher concentrations of HCO_3^- in groundwater have tendency to form a precipitation of Ca^{2+} and Mg^{2+} ions in the water. As a result, the relative proportion of Na^+ ions increased in the form of sodium bicarbonate (Sadashivaiah et al., 2008).

2.3.4 Residual sodium carbonate (RSC)

Groundwater was classified based on the RSC (Eq. 4, Table 1). Groundwater was considered safe for irrigation if values were $RSC < 1.25$ meq/L. The groundwater was termed as marginal quality if RSC values were 1.25 to 2.5 meq/L. The marginal quality groundwater can be used for irrigation by applying some good management techniques and practices. The groundwater was considered unsuitable for irrigation if RSC values were > 2.5 meq/L (Moharir et al., 2019). The groundwater suitability for irrigation is also influenced if the concentrations of CO_3^{2-} and HCO_3^- are excess. The concentration of sodium ions Na^+ increases in the water due to excess number of CO_3^- and HCO_3^-. Because of higher concentration of sodium ions, soil dispersion takes place and efficiency of nutrients uptake decreases by plants. Water infiltration capacity of the soil surface is also reducing and further down to the soil profile. Ultimately the aeration through the plant root zone is reduced and the crop growth process becomes limited (Singh et al., 2013).

2.3.5 Sodium percentage (Na%)

The Na% indicates the concentration of soluble Na content in the groundwater (Eq. 5, Table 1). It was used to evaluate the Na hazard in the groundwater. The Na% is a common parameter to evaluate the suitability of irrigation water because Na reacts with soil and reduces the soil permeability (Kumari & Rai, 2020). The alkalinity of soil increases when Na ions react with inorganic carbon, i.e. like inorganic CO_3^- and HCO_3^-. The salinity of soils increases when sodium ions combine with chloride ions Cl^-. Both alkaline and saline soil are not favourable for plant growth. The effects of alkalinity and salinity in term of Na% were described by Wilcox (1955). All concentrations of Na^+, Ca^{2+} and Mg^{2+} ions are in mg/L. The Na% value of up to 60 in the groundwater is considered as acceptable for irrigation (Sadashivaiah et al., 2008).

2.3.6 Kelly's ratio (KR)

The groundwater suitability for irrigation can also be evaluated using the Kelly's ratio (Kelly, 1963). KR was calculated using Eq. 6 (Table 1). KR depends on the level of Na^+, Ca^{2+} and Mg^{2+} ions in the groundwater. Based on the classification, the groundwater with a KR value > 01 is considered as unfit for irrigation.

2.3.7 Permeability index (PI)

Permeability index (PI) was also used for the analysis of groundwater suitability for irrigation. The groundwater quality was classified into three categories based on PI value (Doneen, 1964). PI was calculated using Eq. 7 (Table 1). In Eq. 7, all concentrations of sodium ions (Na^+), bi-carbonates (HCO_3^-), and calcium ions (Ca^{2+}) or magnesium ions

(Mg^{2+}) are in mg/L. The higher concentrations of Na^+, HCO_3^-, Ca^{2+} and Mg^{2+} ions are more accountable for influencing the permeability of soil (Selvakumar et al., 2017).

2.4 Data analysis

Preliminary, data were analysed by statistical approach using a software named as Statistix 10 version. The preliminary analysis of the data was conducted to visualize normality, homogeneity and to find the outlier in the data as described by (Farid et al., 2019; Shahid & Rahman, 2021; Shahid et al., 2017). The mean, maximum, minimum and standard deviation values for all groundwater parameters were also measured to describe the physical behaviour of the data. These types of information have lot of importance during the communication with the local farming community. Spatial variation for all the parameters was observed with the help of Box-whisker plot. Box-whisker plot for all groundwater parameter was plotted in an excel spreadsheet by using stacked column 2D chart type in column chart tool (Rishi et al., 2017). The top end and bottom end of the box for all parameters represent upper and lower quartile values of data along with the interquartile range. The median value for each parameter is marked by a horizontal line inside the box.

Groundwater suitability for irrigation, Wilcox, United States Salinity Laboratory (USSL) and permeability index (PI) diagrams were prepared to recognize different hydrochemical characters of groundwater. Wilcox diagram (Wilcox, 1955) was plotted between Na% and electrical conductivity (EC) using the water quality software named as AquaChem 2014 version. Using the tab menu, click on "plot" tab, chose new option than search for Wilcox. The United USSL diagram provides a detailed analysis of groundwater suitability with respect to irrigation application (USSL, 1954). USSL diagram was plotted between EC (dS/m) and (SAR) and was prepared using the AquaChem software. USSL diagram was plotted to classify the groundwater into low, medium, high and very high categories. The quality of irrigation water was also influenced by its Permeability index (PI). Similarly, Doneen (1964) classified the groundwater into three categories based on PI and total concentration (TC) of ions. Spatial analysis for all the groundwater quality parameters was also accomplished using the Arc GIS vs10.1. Spatial analyst tool was used for the interpolation of the data, and the ordinary kriging interpolation technique was selected for the analysis of all the parameters (Elumalai et al., 2017; Moharir et al., 2019). A semivariogram model was obtained by calculating values of the semivariogram at different lags to identify the fitness of a theoretical model, i.e., Gaussian, spherical, and exponential models (Nas, 2009). The nugget to sill variance ratio was also examined to identify the spatial dependency of all groundwater quality parameters (Table 2). The variables have strong, moderate and weak spatial dependence if the ratio ranged (<0.25), (0.25–0.75) and (>0.75), respectively (Karami et al., 2018; Mehrjardi et al., 2008).

3 Result and discussions

The range, mean, skewness (S_k), kurtosis (K_t), and coefficient of variation for all the groundwater quality parameters are shown in Table 3. The results showed that the EC values of groundwater were found in the range of 0.293–9.13 dS/m with a mean value of 1.64 dS/m. This indicated that the mean value was higher than that of permissible range for irrigation purpose (Malik et al., 1984). The higher mean of EC values was due to the dissolved salts and the other chemicals breaks down in the water and convert into positively and

Table 2 Best fitted semivariogram model for groundwater quality parameter

Parameters	Model	Range (m)	C_o	$C_o + C_1$	$[C_o]/[C_o + C_1] \times 100$	r^2
EC	Gaussian	1.318	1.240	5.489	0.744	0.646
TDS	Gaussian	1.571	0.560	3.130	0.821	0.652
pH	Spherical	0.049	0.002	0.099	0.984	0.299
$Ca^{2+} + Mg^{2+}$	Gaussian	1.181	72.40	355.70	0.796	0.626
Na^+	Spherical	1.248	17.30	105.60	0.836	0.811
Cl^-	Exponential	0.483	1.999	3.999	0.500	0.613
CO_3^{2-}	Spherical	0.077	0.043	0.341	0.874	0.490
HCO_3^-	Exponential	1.524	1.390	7.789	0.822	0.837
SAR	Spherical	0.276	1.700	11.200	0.848	0.659
TH	Gaussian	1.136	792.000	3694.00	0.786	0.623
PI	Spherical	0.027	25.900	277.400	0.907	0.000
KR	Gaussian	0.073	0.014	0.349	0.960	0.662
RSC	Gaussian	1.327	73.800	358.500	0.794	0.553

C_o = nugget variance, $C_o + C_1$ = sill variance

Table 3 Statistic of groundwater parameters

Sr. no	Parameter	Units	Min	Max	Mean	Sk	Kt	CV
1	EC	dS/m	0.293	9.130	1.643	2.454	7.159	0.950
2	TDS	mg/L	196.310	6117.1	1100.8	2.453	7.150	0.930
3	pH	–	6.980	8.460	7.945	−0.766	−0.060	0.040
4	$Ca^{2+} + Mg^{2+}$	mEq/L	1.140	63.880	10.606	2.759	7.703	1.205
5	Na^+	mg/L	1.450	35.850	7.074	2.132	3.701	1.104
6	Cl^-	mEq/L	0.000	7.450	1.885	1.177	1.104	0.987
7	CO_3^{2-}	mg/L	0.000	2.530	0.742	0.764	0.721	0744
8	HCO_3^-	mg/L	0.240	12.860	2.578	2.070	5.093	0.880
9	SAR	–	0.980	18.380	3.700	2.379	6.108	0.885
10	RSC	–	−.60.020	2.550	−7.285	−.2.990	9.092	1.658
11	TH	mg/L	3.770	211.190	35.06	2.759	7.703	1.205
12	PI	–	23.000	96.000	56.190	0.244	−0.393	0.290
13	KR	–	0.190	3.320	0.880	1.705	3.406	0.666

EC: electrical conductivity, TDS: total dissolved salts, TH: total hardness, PI: permeability index, KR: Kelly's ratio. SAR: Sodium absorption ratio, RSC: residual sodium carbonate, S_k: skewness and K_t: kurtosis

negatively charged ions. It has been reported that dry climatic condition and high evaporation rate may be accountable for the enrichment of groundwater EC (Srinivasamoorthy et al., 2014). The TDS range for groundwater was found between 196 and 4509 mg/L with mean value of 751 mg/L. The groundwater pH was ranged from 6.98 to 8.46 with mean value of 7.94. The groundwater pH variation reflects that groundwater in the Multan District is not highly impacted by microbial or other processes (Keesari et al., 2015). Similarly, the mean values for groundwater quality parameter such as $Ca^{2+} + Mg^{2+}$, Na^+, Cl^-,

CO_3^{2-}, HCO_3^- showed that the whole Multan District reflects the groundwater quality fit to marginal fit as mean values for these parameters were found greater than permissible limit (Ashraf et al., 2011; Bilgehan Nas & Berktay, 2010; Pandian & Jeyachandran, 2014).

The mean values for groundwater quality indices such as SAR, RSC, TH, KR, PI showed that the whole Multan District did not reflect the poor groundwater quality as all the indices were found within the permissible limit (Sadashivaiah et al., 2008; Soleimani et al., 2018). All the groundwater quality parameters such as $Ca^{2+} + Mg^{2+}$, Na^+, Cl^-, CO_3^{2-}, HCO_3^-, EC, TDS, SAR, RSC, TH, KR, PI show high dispersion of data as CV > 15% shows spatial variability effects (Zhou et al., 2012). Similarly, skewness (S_k) and kurtosis (K_t) values did not confirm the conditions of normal distribution for groundwater quality parameters ($Ca^{2+} + Mg^{2+}$, Na^+, Cl^-, CO_3^{2-}, HCO_3^-, EC, TDS, SAR, TH, KR). It has been reported that S_k and K_t must be equal to zero (0) and Three (03), respectively, for the condition of normal distribution (Ahmad et al., 2015; Farid et al., 2019). Similarly, variation in groundwater quality data was also analysed by plotting the Box-whisker plots as shown in Fig. 3. The variation for each parameter was

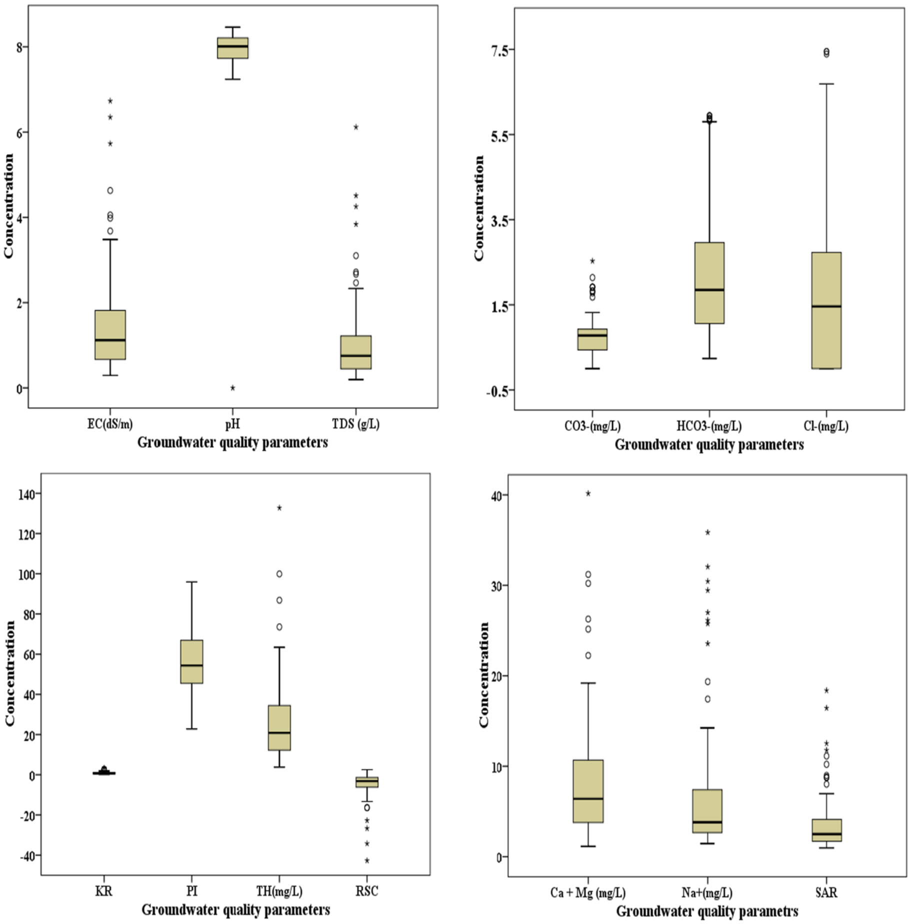

Fig. 3 Box-whisker plot for groundwater quality parameters of district, Multan

analysed through their median, first and third quartile values. During the analysis, the variations in the data were also observed for each groundwater quality parameter. The relative length of whisker on both sides and box position of the median bar showed the variability of each parameter (Salifu et al., 2017). It was also observed that most of the groundwater quality parameters showed lower concentration which may be indicative of natural processes and anthropogenic activities. It has been reported that water–rock interaction has changed the groundwater chemistry. Furthermore, poor sanitary conditions and higher use of fertilizer for higher yield may also affect the groundwater quality in the region (Farid et al., 2019; Rahman et al., 2017; Salifu et al., 2017).

The analytical results of groundwater suitability have been examined for irrigation purpose as shown in Table 4. It was observed that the 41.6% groundwater samples have EC values under suitable category for irrigation purpose and 40.4% groundwater samples have unsuitable category (Malik et al., 1984). Similarly, 37.1, 47.2, 43.8, 48.3 and 36% of the total groundwater samples have TDS, $Ca^{2+} + Mg^{2+}$, CO_3^{2-}, HCO_3^-, Na^+ and Cl^- values in suitable categories for irrigation purpose, respectively. The groundwater suitability analysis based on SAR, % Na, RSC, TH and KR showed that 93.3. 5.6, 96.6, 96.6 and 71.9% of the total groundwater samples, respectively, were found in suitable categories as classified by different researchers (Lloyd, 1985; Sadashivaiah et al., 2008). Overall analysis also indicated that the groundwater quality parameters fall from fit to unfit categories (Table 4).

The concentrations of dissolved constituents in the groundwater were examined to assess the suitability of groundwater for irrigation. The various types of dissolved solids in groundwater have impacts on soil health when it is being used for irrigation. In irrigation water, the excessive dissolved salts such as sodium, magnesium, chlorides, and bicarbonate may change the osmotic pressure in the crop root zone. EC is another important parameter which has influence on groundwater quality. Analysis of the salinity hazard gives a guideline to about the quality of groundwater because the production of crop is mainly depending on EC of both the soil and water (Nas, 2009). The groundwater suitability for irrigation depends upon many factors: water, soil texture, salt tolerance characteristic of the plants, climate change and drainage parameters (Kumar et al., 2018). Groundwater with EC value < 1000 µS/cm is classified as fit water for irrigation (Moharir et al., 2019). The EC value between 1001 and 1250 µS/cm is termed as marginal fit water for irrigation, and above 1250 µS/cm of EC value indicates that water is not fit for irrigation (Malik et al., 1984).

Table 5 shows the correlation coefficients between the groundwater quality parameters and indices. The correlation coefficients analysis provides an indication of quick water monitoring method (Khan et al., 2019; Rehman et al., 2018). The results indicated that most of the correlation coefficients found significant ($\alpha = 0.05$) for various groundwater quality parameter and indices. A highly significant positive correlations were observed for groundwater EC with $Ca^{2+} + Mg^{2+}$, HCO_3^-, Na^+, SAR, TDS, TH and RSC and significant negative correlations of groundwater EC were found with pH. The SAR has significant positive connection TDS, $Ca^{2+} + Mg^{2+}$, HCO_3^-, Na^+ and RSC. The pH has significant negative connection with TDS, HCO_3^-, $Ca^{2+} + Mg^{2+}$, Na^+ and RSC. The strong relationship between the HCO_3^- and Na^+ was found with correlation coefficient value of 0.478. The strong correlation between the HCO_3^- and Na^+ indicated that groundwater has salts of sodium carbonates. Significant weak negative relationship was observed between the Na^+ and Cl^- with correlation coefficient value of −0.232. This indicated that groundwater has minimum amount of sodium chloride salts (Rehman et al., 2018). This also showed that paired parameters have strong to moderate influence with each other (Rahman et al., 2017).

Table 4 Suitability of groundwater quality for irrigation in Multan district

Parameters	Range	No. of samples	% of samples	Water status	Reference
EC (dS/m)	<1.5	37	41.6	Fit	Malik et al. (1984)
	1.50–2.50	16	18.0	Marginal fit	
	>2.50	36	40.4	Unfit	
TDS (mg/L)	<500	24	37.1	Fit	Davies and DeWiest (1966)
	500–1000	33	27.0	Slight to moderate	
	1000–2000	22	24.7	Moderate to Unfit	
	>2000	10	11.2	Unfit	
$Ca^{2+} + Mg^{2+}$(mEq/L)	<4.5	28	47.2	Fit	Pandian and Jeyachandran (2014)
	4.5 – 13.5	42	31.5	Marginal fit	
	>13.5	19	21.3	Unfit	
CO_3^{2-} (mg/L)	<0.5	38	42.7	Fit	Ashraf et al. (2011)
	0.5–1.00	33	37.1	Marginal fit	
	>1.00	18	20.2	Unfit	
HCO_3^- (mg/L)	1.64	39	43.8	Fit	Pandian and Jeyachandran (2014)
	1.64–4.09	34	38.2	Marginal fit	
	>4.09	16	18.0	Unfit	
Cl^- (mEq/L)	<1.43	43	48.3	Fit	Bilgehan Nas and Berktay (2010)
	1.43 – 2.86	24	27.0	Marginal fit	
	>2.86	22	24.7	Unfit	
Na^+ (mg/L)	<3.0	32	36.0	Fit	Ashraf et al. (2011)
	3.0 – 9.0	36	40.4	Marginal fit	
	>9.0	21	23.6	Unfit	

Table 4 (continued)

Parameters	Range	No. of samples	% of samples	Water status	Reference
SAR	< 10	83	93.3	Excellent	Sadashivaiah et al. (2008)
	10–18	5	5.6	Good	
	18–26	1	1.1	Doubtful	
	> 26	0	0.0	Unsuitable	
% of sodium	< 20	5	5.6	Excellent	Kumari and Rai (2020)
	20–40	35	39.3	Good	
	40–60	38	42.7	Permissible	
	60–80	11	12.4	Doubtful	
	> 80	0	0.0	Unsuitable	
RSC	< 1.25	86	96.6	Safe	(Lloyd, 1985)
	1.25–2.5	2	2.2	Marginal Safe	
	> 2.5	1	1.2	Unsuitable	
TH (mg/L)	< 75	86	96.6	Soft	Soleimani et al. (2018)
	75–150	3	3.4	Moderator high	
	150–300	–	0.0	Hard	
	> 300	–	0.0	Very hard	
KR	< 1	64	71.9	Fit	Kelly (1963)
	> 1	25	28.1	Unfit	

Table 5 Pearson correlation analysis for all groundwater quality parameters

	EC	TDS	pH	$Ca^{2+}+Mg^{2+}$	Na^{1+}	CO_3^{2-}	HCO_3^{1-}	Cl^{1-}	SAR	TH	PI	KR	RSC
EC	1												
TDS	1.000^{**}	1											
pH	-0.450^{**}	-0.450^{**}	1										
$Ca^{2+}+Mg^{2+}$	0.767^{**}	0.767^{**}	-0.518^{**}	1									
Na^{1+}	0.821^{**}	0.821^{**}	-0.495^{**}	0.871^{**}	1								
CO_3^{2-}	− 0.164	−0.164	0.288^{**}	−0.187	− 0.193	1							
HCO_3^{1-}	0.540^{**}	0.540^{**}	-0.437^{**}	0.410^{**}	0.478^{**}	−0.157	1						
Cl^{1-}	− 0.153	−0.153	0.296^{**}	-0.243^{*}	-0.232^{*}	0.218^{*}	−0.210	1					
SAR	0.618^{**}	0.618^{**}	-0.220^{*}	0.429^{**}	0.598^{**}	−0.115	0.318^{**}	0.093	1				
TH	0.767^{**}	0.767^{**}	-0.518^{**}	1.000^{**}	0.871^{**}	−0.187	0.410^{**}	-0.243^{*}	0.429^{**}	1			
PI	-0.249^{*}	-0.249^{*}	0.186	-0.355^{**}	− 0.053	− 0.057	− 0.042	− 0.050	0.202	-0.355^{**}	1		
KR	− 0.006	− 0.006	− 0.144	0.022	0.061	− 0.105	0.080	− 0.110	− 0.050	0.022	0.029	1	
RSC	0.497^{**}	0.497^{**}	-0.361^{**}	0.358^{**}	0.425^{**}	0.109	0.965^{**}	−0.152	0.287^{**}	0.358^{**}	− 0.055	0.053	1

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

c. Listwise $N=86+$

According to Wilcox classification, it was observed that 40% of groundwater samples fall in Excellent to a Good category (Fig. 4). Only 2.2% of groundwater samples were found completely unsuitable. With a similar way, the groundwater suitability for irrigation was also analysed using the USSL diagram (Fig. 5). The analysis of groundwater suitability for irrigation has also been explained using the USSL diagram (USSL, 1954). As per classification, low salinity groundwater having value less than 250 µS/cm can be used for all the types of soil. According to the USSL classification, the groundwater can also be categorized into four groups: C1 (low salinity) and S1 (low sodium hazard), C2 (medium salinity) and S2 (medium sodium hazard), C3 (high salinity) and S3 (high sodium hazard), C4 (very high salinity) and S4 (very high sodium hazard).

The sodium is a main responsible component to produce harmful salt and responsible for poor physical conditions in the soil (Selvakumar et al., 2017). In irrigation water, high amount of salts is responsible to modify the osmotic pressure in the plant root zone, which will cause the limiting amount of water taken by plants and consequently hindering the plant growth (Pandian & Jeyachandran, 2014). In this analysis, it was found that 27% samples of groundwater fall in 'Medium Salinity' and 'Low sodium hazard' (C2S1) class. This indicated that groundwater fall in the C2S1 class can be used for irrigation on all the type of soil with little danger and without development of harmful exchangeable sodium. Almost 50% samples of groundwater fall in 'High Salinity' to 'Low sodium hazard' (C3S1) class. The groundwater sample that falls in C3S1 class can only be used to irrigate certain salts tolerant crops (Jafar Ahamed et al., 2013; Salifu et al., 2017).

Groundwater has also been classified by plotting the (Doneen, 1964) diagram using the total concentration of salts and permeability index (PI) into three main classes (Fig. 6). Based on the classification, groundwater samples were analysed to check the suitability for irrigation (Raju, 2007; Singh et al., 2008). The value of PI was found in the range of 22 to

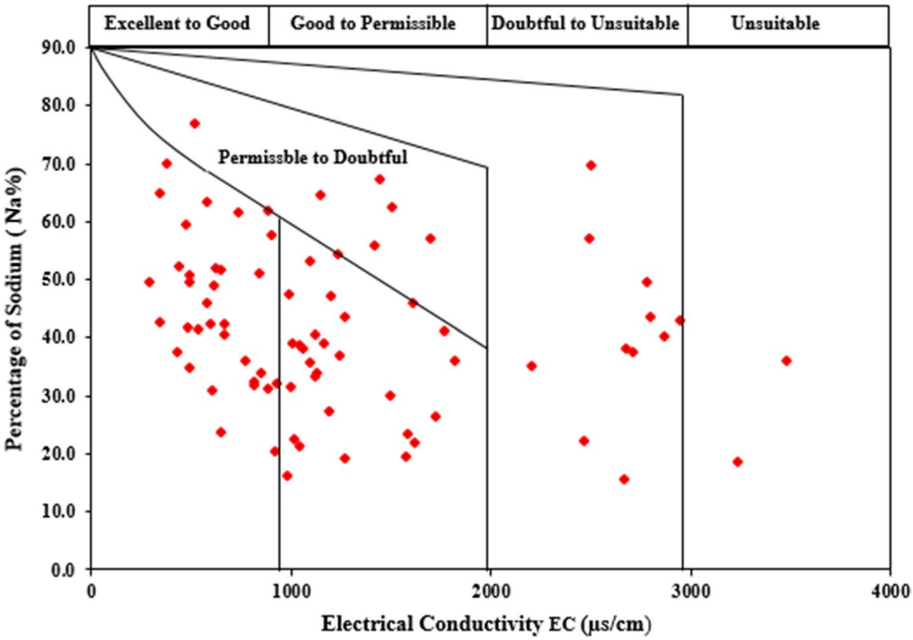

Fig. 4 Wilcox diagram of groundwater samples for Multan district

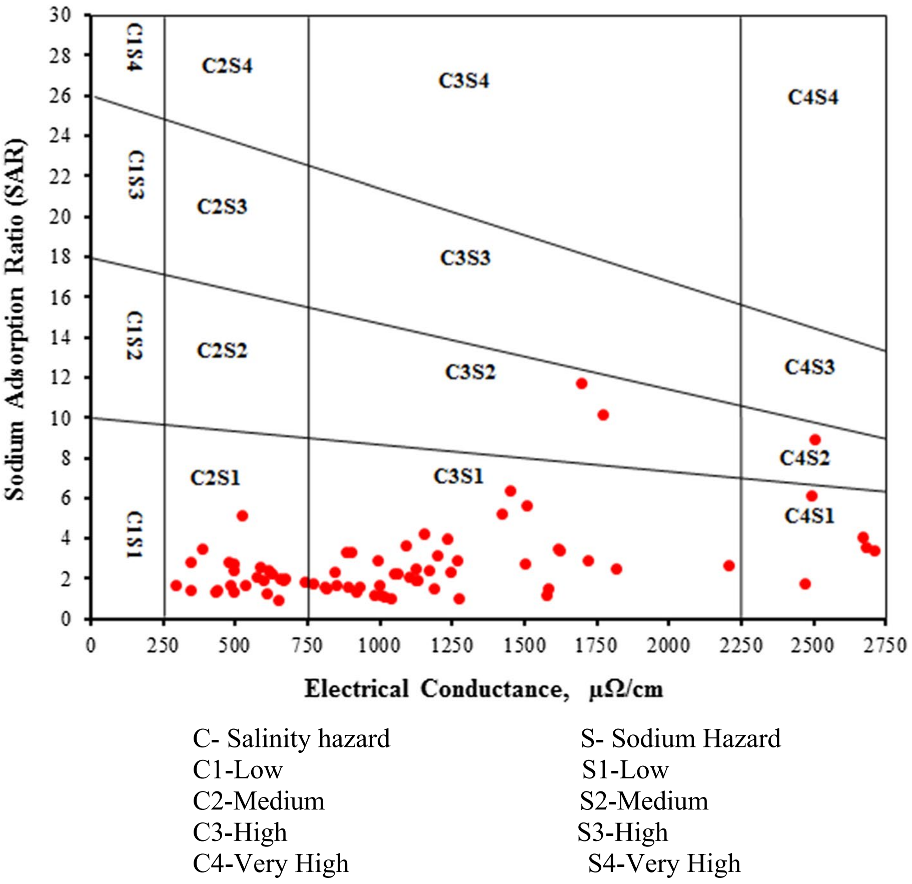

Fig. 5 USSL diagram of groundwater samples for Multan district

95 meq/L during the analysis with an average value of about 58.5 meq/L. Only 4 samples were found in class-1, and majority of groundwater samples were found in class-II which indicated 75% permeability of water, and it is marginally fit for irrigation. Groundwater falling in Class-I showed 100% maximum permeable and it can be used for irrigation. Groundwater falling in Class-II showed 75% maximum permeability and it is marginally suitable for irrigation. Groundwater of Class-III is associated with 25% maximum permeability and is unsuitable for irrigation (Doneen, 1964; Raju, 2007).

3.1 Spatial distribution of groundwater quality

In the present study, spatial distribution pattern for all groundwater quality parameters was analysed as shown in Fig. 7a–j. The spatial distribution map of EC and TDS showed that northeast and northwest part of the Multan District has suitable quality of groundwater for irrigation as EC and TDS values were found less than 1.5 dS/m and 500 mg/L, respectively (Malik et al., 1984). On the other hand, southeast part has unfit quality of groundwater for irrigation as EC and TDS values were found greater than 2.5 dS/m and 2000 mg/L, respectively (Fig. 7a-b). Similarly, good quality groundwater with pH values

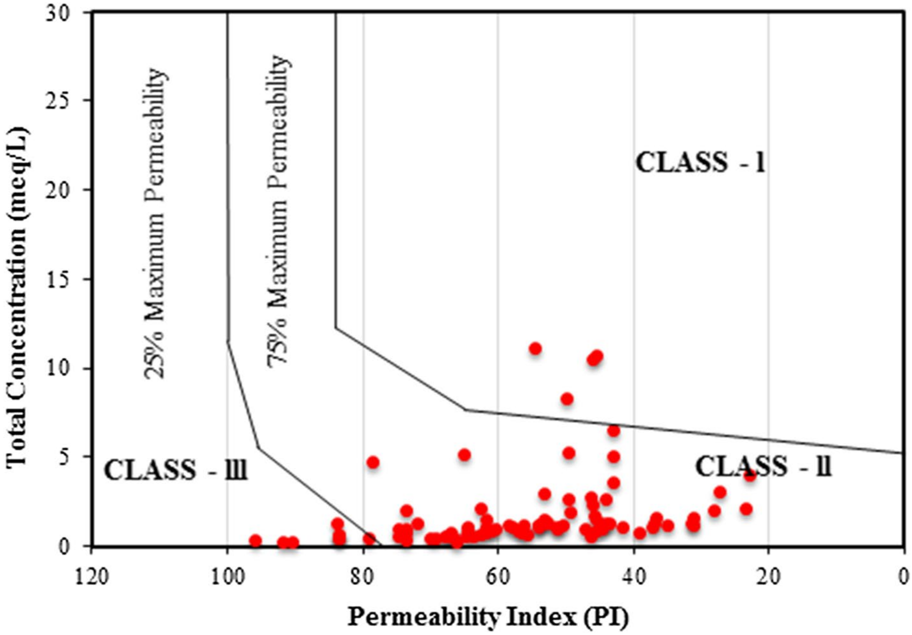

Fig. 6 Permeability index of the groundwater samples for Multan

of 7–8 was observed in northeast east direction (Fig. 7c). The pH values greater that 8 were observed in western part which indicated that the groundwater in the western part has pH greater than permissible limit for irrigation. The concentration of $Ca^{2+}+Mg^{2+}$ ions (0–4.5 mEq/L) showed that upper northeast and northwest part of the Multan district also has suitable groundwater quality for irrigation (Fig. 7d). The groundwater is marginally suitable for irrigation in central southeast and lower southwest part as concentration of $Ca^{2+}+Mg^{2+}$ ions was observed in the range of 4.35–13.5 mEq/L. The lower southeast part has $Ca^{2+}+Mg^{2+}$ ions concentration greater than 13.5 mEq/L, which makes groundwater quality unfit for irrigation. The spatial analysis of sodium Na^+ ions (Fig. 7e) showed that northeast, northwest and western sides have less concentration (0–9 mg/L). The lower southeast part has Na^+ ions concentration greater than 9 mg/L, which makes groundwater quality unfit for irrigation (Ashraf et al., 2011). The concentration of Cl^- showed that the groundwater quality in southern part is fit for irrigation (Fig. 7f) as Cl^- concentration lies between 0 and 1.43 mEq/L (Bilgehan Nas & Berktay, 2010). The CO_3^- concentration (>1.0 mg/L) showed that the groundwater quality in central part is not suitable for irrigation (Fig. 7g). The spatial analysis of HCO_3^- concentration (Fig. 7h) showed that the groundwater quality in upper part of the study area is suitable for irrigation as HCO_3^- concentration lies between 0 and 4 mg/L (Prabahar et al., 2019). The spatial analysis of SAR and TH (Fig. 7i–j) also showed that groundwater quality is not suitable for irrigation in southeast part of the Multan district as SAR lies between 0 to 10 and TH lies between 0 to 75 mg/L (Sadashivaiah et al., 2008; Soleimani et al., 2018). The overall analysis showed that the groundwater quality is suitable in northeast and northwest part of the Multan district because values of all the groundwater quality parameters except CO_3^- lies within the permissible limits. The fresh groundwater quality in northeast and northwest part is due to the recharge

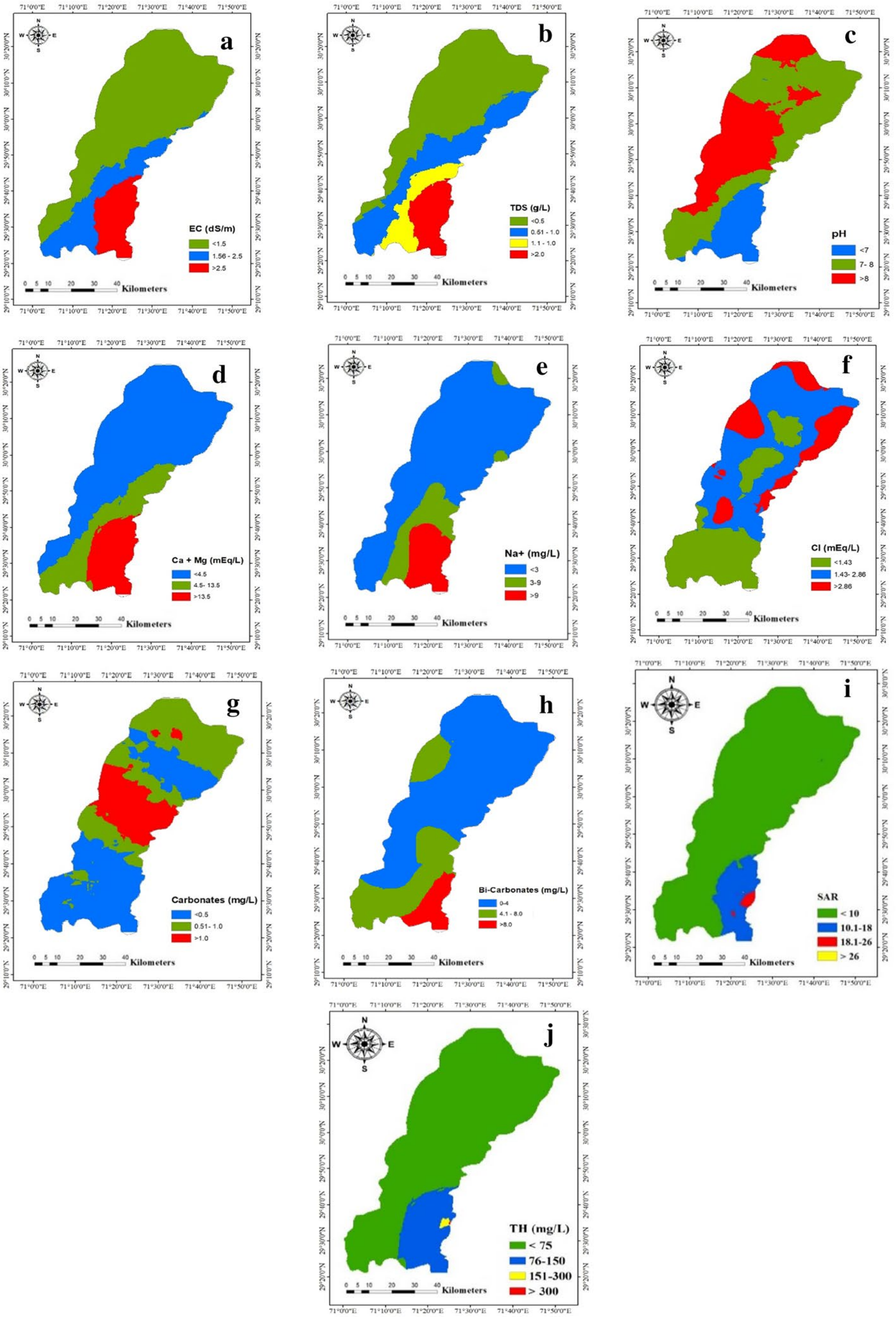

Fig. 7 Spatial distribution maps for groundwater quality parameters

receives from the river Chenab. It has been reported that recharge from the main rivers into the groundwater has resulted in the development of freshwater groundwater belts (Farid et al., 2019; Khan et al., 2018). Similarly, unfit groundwater quality (saline and sodic water) was found in the southeast part of the Multan district for all the parameters. This indicated that the direct use of saline and sodic groundwater for irrigation in south eastern part produces salinization and sodification problems in the soil. The progressive development of salinization and sodification in the soil has been reported as result of high level of salts in the irrigation water (Cucci & Lacolla, 2013). Furthermore, the use of saline/sodic water for a long-term without any amendment resulted in accumulation of toxic ions in the rhizosphere. These toxic ions initially induce osmotic stress and reduces the capacity of water absorption by the plants. The regular accumulation of toxic ions in the plant cells damages the cell membrane, chlorophyll, protein, nucleic acid and photosynthesis efficiency which results in significant yield reduction (Ashraf et al., 2017; Qadir & Oster, 2004). Therefore, farmers of Multan district in the southeast part are suggested to avoid direct use of groundwater without amendment.

4 Conclusion

In this study, a spatial and geochemical analyses were performed for groundwater quality parameters such as EC, pH, TDS, $Ca^{2+} + Mg^{2+}$, CO_3^{2-}, HCO_3^-, Cl^-, Na^+, SAR, RSC, TH and KR to determine the suitability of groundwater for irrigation. Wilcox, USSL and PI classification standards were used to classify the groundwater quality data. According to Wilcox classifications, 40% of groundwater samples fall into the 'Excellent to a Good' category. Based on USSL classification, 27% of groundwater samples were classified in 'Medium Salinity' and 'Low sodium hazard' (C2S1) class. The groundwater fall in the C2S1 class may be used for irrigation on all the type of soil with little danger. Similarly, based on PI classification, only 4 samples were found in class-1, while the majority of groundwater samples were found in class-II, indicating 75% permeability of water and marginal suitability for irrigation. The spatial analysis revealed that the groundwater quality is suitable in the northeast and northwest part of the Multan district because the values of all groundwater quality parameters except CO_3^- lies within the allowable limits. Similarly, unfit groundwater quality (saline and sodic water) was observed in southeast part of the Multan district for all the parameters. This indicated that the direct use of saline and sodic groundwater for irrigation in south eastern part of the region causes salinization and sodification issues in the soil. It was concluded that combined use of hydro-chemical and spatial analysis for groundwater quality assessment may help for sustainable development of groundwater resources.

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Data availability Data will be made available from corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare that there is no conflict of interests regarding the publication of this paper.

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