Hydrogeochemical evolution processes and evaluation of groundwater suitability for domestic and agricultural utility in Southern Punjab, Pakistan

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Research Article

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2   **agricultural utility in Southern Punjab, Pakistan**

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Abstract

Groundwater is a vital resource for human life and economic growth. In the Khanewal district of Punjab, Pakistan, environmental changes, and anthropogenic activities have made groundwater extremely vulnerable in the past forty years. Sixty-eight groundwater samples were collected from the study area, major ions and trace elements were analyzed. The Principal Component Analysis and Cluster Analysis were used to identify the major factors influencing groundwater quality, as well as to assess its suitability for drinking and irrigation in southern Punjab. The aquifers are slightly acidic to alkaline, according to the pH (6.9-9.2) of groundwater. Significant cations are distributed as follows: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, while anions are distributed as $HCO_3^- > SO_4^{2-} > Cl^-$. The main hydrochemical facies are mixed $Na \cdot Ca\text{-}HCO_3$ and $Na \cdot Ca\ (Mg)\text{-}HCO_3 \cdot SO_4$. Rock weathering processes, such as the dissolution of calcite, dolomite, and gypsum minerals, governed groundwater hydrochemistry. The water quality index (WQI) indicates that 17.64% of the water samples are unsuitable to drink. However, according to the Wilcox diagram, the USSL diagram, and some other agricultural indices, approximately 68% of the groundwater samples are suitable for irrigation.

Keywords Groundwater; Hydrogeochemical processes; Water Quality Index; Correlation analysis; Khanewal district

1. Introduction

Freshwater makes up about 2.5% of the Earth's water supply, with groundwater accounting for 30% of the total (Colombani et al., 2016). Groundwater is a vital source for irrigation, industrial use, and it is relied on by an estimated 2.5 billion people worldwide (Moe and Rheingans, 2006). In arid and semi-arid areas, groundwater is the most important source of drinking water (Rashid et al., 2020b). As a consequence, groundwater is considered an elixir of life, but that on the other hand, groundwater resources have been experiencing increased problems in recent years, including quality issues (Sakram and Adimalla, 2018). Water quality is just as important as quantity when it comes to meeting basic human needs since a shortage of water and sanitation creates a slew of public health issues (Gleick, 1998). Contamination and overexploitation are responsible for the poor quality of groundwater. Groundwater quality varies over time because of depth, seasonal changes, and the types of rock found in a given area (Vasanthavigar et al., 2010). Understanding the major factors influencing the qualitative and hydrochemical properties of accessible groundwater is thus crucial for maintaining a sufficient supply for a variety of purposes.

The ability to evaluate water for drinking, irrigation, and other uses requires a thorough understanding of water hydrogeochemistry. Finally, a variety of factors affect groundwater quality, including rainfall, topographic relief, mineral dissolution, mineral solubility, ion exchange, oxidation, reduction, natural and anthropogenic activities such as geological structure and mineralogy of watersheds and aquifers, residence time, poor sanitary conditions, and the use of fertilizers and pesticides to increase crop yields (Nlend et al., 2021).

Many elements are capable of influencing human health, including main, minor, and trace elements, either by excessive intake or deficiency (Alam and Umar, 2013; Ali et al., 2019). As a result, water resource management requires a basic understanding of groundwater chemistry control procedures (Jehan et al., 2019; Sivapalan et al., 2003). It's crucial to keep an eye on the quality of water sources in Pakistan's arid and semiarid regions, especially groundwater, which is used for drinking and irrigation.

Pakistan faces severe shortages of water and is a water-stressed country. In the last few decades, both surface and groundwater availability have declined substantially (Talib, Tang et al. 2019). In Pakistan, groundwater is widely used for drinking and agricultural activities. The demand for domestic groundwater would then grow from 5.20 million acres to 9.70 million acres (Raza, Hussain et al. 2017). However, a significant rise in water quality problems due to over-exploitation in many areas of Pakistan. Arsenic and Fluoride contamination of groundwater sources is a serious health issue; however, data on the health effects on local communities is limited. Groundwater in Sindh Province

(Tharparker, Nagarparker, and Umarkot) is tainted with Arsenic, resulting in skin lesions on major body parts (arms, face, and feet), rough skin with black dots from dermal and oral contact, and dental and skeletal fluorosis from Arsenic and Fluoride contaminated water (Raza et al., 2017). As a result of high Fluoride concentration in groundwater, bone softening, and deformation problems have been identified in some areas of Punjab Province. A total of 124 children have been diagnosed with skeletal fluorosis as a result of elevated Fluoride levels in the groundwater in Lahore (Ahmad et al., 2003).

The lower Indus plain is divided into 14 irrigation regions that can be cultivated. The Rohri canal command area in central Sindh is vulnerable to surface and groundwater contamination, jeopardizing groundwater potability and agricultural use. In the study area, there is a paucity of literature on water quality assessment. The current research will be especially useful in identifying hydrogeochemical characteristics and groundwater evolution processes, as well as evaluating groundwater quality for domestic and irrigation purposes in southern Punjab. The findings can help to clarify how to resolve the negative effects, and the solution is to advocate for improved groundwater quality in Khanewal, Punjab. The aims of the research are (1) to investigate groundwater hydrochemistry and water quality, (2) to differentiate geogenic and anthropogenic causes of groundwater pollution by using cluster analysis (CA) and principal component analysis (PCA), and (3) to evaluate the groundwater suitability for drinking and irrigation.

2. Study area

Khanewal is a district in Pakistan's Punjab province, situated in the lower Bari of the river Doab (between Sutlej and Ravi rivers). In range, 43° N and 71, About 5° to 72. 47° F; Around 5° to 72. 47° E (Fig. 1). Groundwater is commonly used for domestic, agricultural, and commercial purposes in this area and water scarcity and shortages occur in the region. Four seasons, such as summer, winter, autumn, and spring, make up the climate of the region. The summer season begins in April and lasts until October. Winter began from October to February for a short time, then the spring and summer came. Autumn came at the end of summer and then went through a harsh winter season. The temperature ranges from 21°C to 51°C during the summer season, and from 1°C to 27 °C during the winter season. The Khanewal is 134 meters above sea level and has a desert climate with annual precipitation of about 166 millimeters. Furthermore, the Köppen-Geiger climate classification classifies the area's climate as BWh (Khwaja, 2020).

Pakistan has the world's largest canal irrigation system (based on the rivers Indus, Jhelum, Chenab, Ravi, and Sutlej (Zafar, 2019). A "doab" is described as the region between two rivers. Four famous doabs are separate doabs

between the Jhelum and Indus Rivers, the Chenab and Jhelum and Rivers, the Ravi and Chenab Rivers, and the Sutlej and Ravi Rivers (Hasan et al., 2017).

The river flow in the Khanewal district is given the predominant physical characteristics because it is situated in the upper Indus plains. Sand is commonly found in the subsurface of alluvial soils and is just a few feet deep. The soil is alluvial and slopes gently from northeast to southwest and northwest to southeast. In the entire country, the deposition of river sediment has resulted in. Overall, the irrigation system relies on groundwater and the canals that come from the rivers of Chenab and Ravi. The flow of groundwater recharge and water table depends on the water systems of the rivers (Akhter and Hasan, 2016). The geological formation, such as alluvium deposits overly on Precambrian soil, metamorphic igneous rocks, or semi-consolidated tertiary rock in the Khanewal district (Fig. 1).

Insert Fig.1 here

3. Materials and methods

3.1 Sampling and analysis

Sixty-eight groundwater samples were collected from wells, boreholes, and hand pumps in the Khanewal District to study the hydrochemical characteristics of groundwater. Wells were pumped to remove the effects of stagnant water for more than five minutes before sampling. In 120 mL plastic bottles, groundwater samples were collected and rinsed, and washed with 10% HCl solution. The bottles were soaked with double-deionized water after being rinsed. To collect samples from the area of study, a duplicate sampling technique was used. pH, temperature, depth, TDS, and EC were all measured in situ after sampling. 2-3 drops of HNO_3^- were then acidified with a sequence of duplicate samples. Following that, the water samples were examined at the Pakistan Council of Research in Water Resources laboratory (PCRWR). The pH, electrical conductivity (EC), and total dissolved solids were calculated using a pH meter and an electrochemical analyzer (Hac 44600-00, Loveland, CO, USA) (TDS). Significant anions such as nitrate (NO_3-N) and sulfate (SO_4^{2-}) were measured using an ultraviolet-visible (UV-VIS) spectrophotometer (Analytik Jena, Jena, Germany), while chloride (Cl^-) and bicarbonates (SO_4^{2-}) were measured using titration methods (HCO_3^-). The Flame photometer was used to calculate important cations like Na^+, K^+, and Fe^{2+} (PFP7, Cambridge shire, UK). With a 2% analytical error, Ca^{2+} and Mg^{2+} were calculated using volumetric titration with ethylene diamine tetraacetic acid (EDTA, 0.05 N). In samples containing methyl-orange, total alkalinity was measured by acid titration.

The Charge Balance Error (CBE) was calculated to confirm the authenticity of the water sample analysis. Positive CBE is associated with higher cation concentrations in these water samples, while negative CBE is associated with higher anion concentrations (Bozdağ, 2015). The equation (1) was used to calculate the CBE.

$$CBE = [\textstyle\sum cations - \sum anions] / [\sum cations - \sum anions] * 100 \tag{1}$$

Ionic levels were measured in milliequivalents per liter (meq/L) in this study. For water samples, the standard protocols were approved only with a CBE of ±5 % (Rashid et al., 2020b; Singh et al., 2015). The charge balance error of all ions viz. cation and anion strength were measured in (meq/L) and reported to be ± 5%.

3.2 Statistical analysis

In evaluating the data set for the different operations, statistical analysis plays an integral role (Su et al., 2013). To evaluate the relationship between various water quality parameters Regression, Pearson correlation analysis, and Correlation analysis were done with the help of (V23, SPSS Inc, Armonk, NY, U.S). Saturation indices have been computed by using a geochemical simulation program called PHREEQC Interactive (version 3.4) to find the trend towards dissolving or precipitating a certain mineral (Talib et al., 2019). Durov diagram was prepared by the help of Grapher (version 14 Golden Software, LLC, Golden, Colorado, U.S.A.) to interpret hydrochemical facies. For making maps, Arcgis 10.7.1 was used. Additionally, to define and assess the suitability of groundwater for irrigation, Grapher Software was used to construct a U.S. Salinity Laboratory diagram and a Wilcox diagram by correlating sodium absorption ratio/electrical conductivity and percent sodium/electrical conductivity, respectively. The WQI was calculated by using World Health Organization (WHO) guidelines. The WQI was determined by using the weighted arithmetic index (Brown and Dalton, 1970).

3.3 Groundwater suitability assessment

The Water Quality Index (WQI) values were computed to evaluate the suitability of groundwater for drinking (Cotruvo, 2017). Calculating WQI in three computing steps: First, the weights (ω_i) were given to all of the nine parameters (TDS, pH, Ca, Na, SO$_4$, Mg, HCO$_3$, K and Cl) with respect to the importance of the quality of groundwater (Table 1). Due to their significant measuring role, potassium, bicarbonate, iron, and fluoride are given a maximum weight of 5, while calcium is considered less essential and at least 1 weight is allocated.

The second step is to calculate the relative weight (Wi) of an individual parameter (Equation (2)).

$$w_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad (2)$$

The relative weight of each parameter is denoted by W_i, the weight of each parameter is denoted by w_i, and

the number of parameters is denoted by n.

In the third step, the quality rating scale (q_i) will be determined for each parameter (equation (3)).

$$q_i = \frac{C_i}{S_i} \qquad (3)$$

The q_i is quality ranking, C_i is the quality of each parameter in milligrams per liter, and S_i is the WHO standard for

individual parameters in milliliters per liter in equation (3) Table 1.

Table 1 The weight and relative weight of all hydrochemical parameters

Chemical parameters	WHO Standards (mg/L)	Weight (wi)	Relative Weight (Wi)
TDS	1000	3	0.067
pH	8.5	3	0.067
Turbidity	5	4	0.089
Ca	200	1	0.023
Mg	150	2	0.045
Na	200	4	0.086
K	12	5	0.112
Cl	250	2	0.045
SO_4	250	4	0.089
HCO_3	250	5	0.112
NO_3	10	2	0.045
F	1.5	5	0.112
Fe	0.3	5	0.112
		$\sum w_i = 45$	$\sum W_i = 1$

For each parameter, the sub-index (SI) is determined first (equation (4)) to quantify the WQI required to summarize

all parameter sub-indices in a single sample equation (5)).

$$SI_i = W_i \times q_i \qquad (4)$$

$$WQI = \sum_{i=1}^{n} SI_i \qquad (5)$$

SI_i and W_i are the ith parameter's sub-indexes and relative weights, respectively, q_i on the other hand, is a rating

dependent on the concentration of the ith parameter.

4. Results and discussion

4.1 Groundwater quality and hydrochemical characteristics

In addition to pH, EC, turbidity, and TDS, the hydrochemical properties of groundwater have been statistically tested and the findings were compared to World Health Organization guidelines (Table 2). In the study region, the pH of the groundwater ranged from 6.9 to 9.2, with a mean of 7.79 (Table 2), which suggested that the groundwater was between neutral and slightly alkaline water. The permissible pH limit for drinking water is defined as 6.5 to 8.5 (WHO, 2011). The turbidity value varies between 0 and 7 NTUs (Nephelometric Turbidity Units) with the mean value of 2.52 NTU (Table 2), only 3 samples were showing high turbidity which is more than 5 NTU. The maximum turbidity allowed is 5 NTU according to (WHO, 2011). High turbidity can be caused by shallow and poorly built wells (Azis et al., 2015). In drinking water, the most acceptable EC limit is 1500 μmhos/cm (WHO: 2006). The EC values ranged from 350 μS/cm to 1525 μS/cm, with the mean value of 783.6 μS/cm (Table 2) in the study area. Groundwater ion concentrations are directly associated with EC, resulting in higher salinity and overall dissolved concentrations, respectively. Water with dissolved solids more than 1000 mg/L typically gives an unpleasant taste or renders the water unsuitable. The high TDS value affects the water's taste, hardness, and corrosive properties (Balakrishnan et al., 2011). TDS levels ranged from 137.0 to 1414 mg/L in the study area, with a mean of 707.3 mg/L (Table 2), the maximum permissible guideline value for drinking TDS recommended is 1000 mg/L (WHO, 2011).

Table 2 Statistical physicochemical parameters of groundwater samples (n=68) collected from the Khanewal district

Parameters	Minimum	Maximum	Mean	Standard Deviation	WHO Standards	NSBL*	NSBL %
Turbidity (NTU)	0	7	2.52	1.66	5	3	4.41
pH	6.96	9.2	7.79	0.36	6.5-8.5	2	0.02
EC (μS/cm)	350	1525	783.6	280.2	1000	12	17.65
TDS (mg/L)	137	1414	507.28	209.24	1000	3	0.04
TH (mg/L)	35	530	215.7	97.13	300	10	0.15
Na^+ (mg/L)	15	324	90.87	65.04	200	4	0.05
K^+ (mg/L)	0.2	34	6.42	5.07	12	6	0.08
Mg^{2+} (mg/L)	1.0	73	20.78	13.53	150	0	0
Ca^{2+} (mg/L)	16	34	52.93	13.53	200	0	0
Fe^{2+} (mg/L)	<0.1	4.16	0.54	0.66	0.3	38	55.8
F^- (mg/L)	0.01	3.95	0.54	0.52	1.5	2	0.02
Cl^- (mg/L)	9.6	167	46.78	29.25	250	0	0
SO_4^- (mg/L)	22	498	117.5	86.32	250	4	0.05
HCO_3^- (mg/L)	100	510	243.65	90.93	250	26	38.23
NO_3-N (mg/L)	<0.1	4.2	0.30	0.55	10	0	0

* Number of samples beyond (WHO) limits.

The suitable total hardness (TH) limit (as $CaCO_3$) in the absence of any other source of water is 600 mg/L, and in a normal situation, the allowable limit of TH is 300 mg/L (WHO, 2011). In groundwater, TH ranged from 35.0 to 530 mg/L, with the mean value 215.0 (Table 2). According to McCarty's (1967) classification, ten samples of groundwater fell into the "hard" category, making them unfit for human consumption (Table 2).

Iron concentrations ranged from 0.1-0.54 mg/L, with a mean of 0.54 mg/L (Table 2). The maximum concentration of iron allowed in groundwater, according to the WHO is 0.3 mg/L. The acceptable limit was exceeded in 54% of samples in the Khanewal district. The dominance of ferruginous minerals in the earth's crust determines the higher Fe^{2+} concentration in groundwater of the earth (Raju, 2006).

Groundwater sodium (Na^+) concentrations range from 15.0 mg/L to 324.0 mg/L, with a mean of 90.87 mg/L. (Table 2). The maximum permissible limit for Na^+ is 200 mg/L, according to (WHO, 2011). The permissible limit was exceeded in four samples in the study region (WHO, 2011). The most common causes of elevated levels of Na^+ in groundwater are salt deposit erosion and Na-bearing rock minerals. Natural brackish water from some aquifers is also absorbed by halite mineral water (Salama et al., 1999). Agricultural by-products may be another source of sodium in groundwater in the study region (Hem, 1989; Sultana, 2009).

Potassium (K^+) concentrations in groundwater range from 0.2 to 34 mg/L, with a mean of 6.42 mg/L (Table 2). According to the World Health Organization, a maximum potassium concentration of 12 mg/L is considered normal (1990). In the study area, six samples exceeded the permissible limits (WHO, 2011). K^+ is produced in groundwater by the weathering of potassium-bearing rocks such as sylvite (KCl) and silicates, especially clay minerals (Basak et al., 2017). K^+ may also be added to groundwater by fertilizers and the breakdown of waste materials (Spitz and Moreno, 1996). The concentrations of Mg^{2+} and Ca^{2+} were found to be 1-73 mg/L and 16-34 mg/L, respectively, with mean values of 20.78 mg/L and 46.78 mg/L Table 2 Statistical physicochemical parameters of groundwater samples (n=68) collected from the Khanewal district, the majority of which can be traced to mineral carbonates. The permissible limit for Mg^{2+} is 150mg/L and for Ca^{2+} is 200mg/L. According to the (WHO, 2011) guidelines, both Mg^{2+} and Ca^{2+} are within acceptable limits.

The most dominant anion in the study area was HCO_3^-, with values ranging from 100 to 510 mg/L and a mean of 243.7 mg/L (Table 2). Bicarbonate has a permissible limit of 250 mg/L (WHO, 2011). In our study area, 38% of samples exceeded the permissible limits. The presence of organic matter in the aquifer that is oxidized to produce

carbon dioxide, promoting mineral dissolution, is one cause of bicarbonate (El Maghraby, 2014; Jehan et al., 2019; Rashid et al., 2020b).

In the study area, SO_4^{2-} concentrations ranged from 22.0 to 498.0 mg/L, with a mean of 117.55 mg/L (Table 2). The permissible limit for SO_4^{2-} is 250 mg/L (WHO, 2011), 5.9% of the samples were found above the permissible limits. In KL-4 and KL-7 samples, the SO_4^{2-} content was found higher. In addition to water-rock interaction, high SO_4^{2-} content may also be contributed by anthropogenic sources in the study region (Jehan et al., 2020; Mohamed et al., 2017; Talpur et al.; Talpur et al., 2020).

The chloride (Cl^-) ion, which is stable in water, is the chlorine element's most significant natural type. Groundwater chloride depends on many variables, such as weathering, sedimentary leaching of rocks and anthropogenic sources (Jehan et al., 2019; Prasanth et al., 2012). 250 mg/L is the permissible chloride limit (WHO, 2011) for groundwater. The chloride content in the study area varies from 9.6 to 167 mg/L, with a mean of 46.7 mg/L (Table 2). All samples were found to be within the permissible limits (WHO, 2011). Nitrates in groundwater were between 0-4.2 mg/L and 0.30 mg/L with a mean value of 0.30 mg/L in study (Table 2). The primary cause of nitrate in groundwater is nitrate leaching from percolating water (Vincy et al., 2015). All water samples meet the permissible limits (WHO, 2011). Anthropogenic sources cause the pollution of NO_3-N.

F^- concentration in groundwater of study area ranged from 0.01 to 3.95 mg/L, with a mean of 0.54 mg/L (Table 2). The F^- is primarily attributed to the oxidation of minerals and the weathering of granite and igneous rocks. Fluoride is a vital component of the human body and fluoride content of potable water should not reach 1.5 mg/L (WHO, 2011). Long-term exposure to fluoride-contaminated water causes dental and skeletal fluorosis (Fordyce et al., 2007; Rashid et al., 2018; Rashid et al., 2020c). In KL-3 and KL-7 groundwater samples the fluoride concentration was beyond the permitted limits (WHO, 2011). Fluoride concentrations are induced by the dissolution of fluorides comprising minerals from granite and gneiss-rock (Naseem et al., 2010; Rashid et al., 2018).

As shown in Fig. 2, a helpful graphical method for representing hydrogeochemical data is the Durov diagram (Chen et al., 2019). In the groundwater, the mixed type was the most prevalent. Just a few samples were plotted in the field of D (sodium form in Fig. 2), indicating that (Na+K) predominates in groundwater. On the other hand, there was a noticeable difference in groundwater anions. The E field samples belonged to the bicarbonate type, suggesting the HCO_3 dominant anion. Those samples were primarily characterized by freshwater (TDS < 1000 mg/L) located in the

aquifer recharge region. The other belonged to brackish water's sulfate and mixed water types, suggesting the combined effects of evaporation, water-rock contact, and/or human activities.

Insert Fig.2 here

4.2 Hydrogeochemical Evolutional Processes

4.2.1 Source of hydrochemical components of groundwater

The Fig. 3a and Fig. 3b present the relation of TDS with major ions, the concentration of ions increases with the increase in TDS value.

Insert Fig.3 here

4.2.2 Water-rock interaction

The Gibbs diagram is a common tool for determining and analyzing the relationship between lithology and hydrochemistry in aquifers (Gibbs, 1970). According to this diagram, due to their chemical composition, the dissolved chemical elements are divided into 3 distinct areas. Both cation and anion ratios, viz. TDS was plotted against $Na^+/(Na^+ + Ca^{2+})$ and $Cl/(Cl + HCO_3)$ (Fig. 4). The Gibbs diagram depicts three variables that influence groundwater chemistry. These variables include the dominance of evaporation, precipitation dominance, and weathering dominance (Salem et al., 2015). According to Fig. 4, most of the samples are in the rock dominance region, indicating that rock dominance has influenced most groundwater samples. The main contributor to the enrichment of mineral groundwater is also the weathering of rock. The process by which groundwater mixes dissolvable salts and minerals promotes the weathering of the parent rock. In addition, long rock-water contact residence time also allows mineral dissolution (Selvakumar et al., 2017). Aquifer lithology and groundwater bedrock mineralogy have therefore been highlighted as geochemical processes of importance in the study area. As a result, both cations and anions have been enriched as halite and silicate minerals that lead to groundwater pollution and weathering processes in the area of study.

Insert Fig.4 here

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According to Pearson correlation matrix Table 3 Correlation matrix of the study area's physiochemical parameters for groundwater, It was found that TDS has strong correlation with Na^+ (0.83) HCO_3^- (0.74) Cl^- (0.60) and SO_4^{2-} (0.60) and SO_4^{2-} (0.86). With the increase in TDS value, all ionic concentrations increase (Fig. 3a and Fig. 3b). These ions were indicated to be primarily intended for sedimentary rock weathering. A poor correlation between Na^+ and Cl^- may be due to their genetic association with low evaporation Table 3 Correlation matrix of the study area's physiochemical parameters for groundwater. The moderate to low SO_4^{2-} and Ca^{2+} correlation suggests that gypsum dissolution does not occur, but that the excess Ca^{2+} is due to carbonate and the cation exchange (Lawal et al., 2015). Maybe a positive association between Ca^{2+} and K^+ is due to the exchange in the study region of ions and clay minerals.

Table 3 Correlation matrix of the study area's physiochemical parameters for groundwater

Parameter	pH	EC	TDS	Na	K	Ca	Mg	Fe	HCO₃	Cl	SO₄	F	NO₃
pH	1												
EC	-0.10	1											
TDS	-0.11	0.95	1										
Na⁺	0.00	0.80	0.83	1									
K⁺	-0.04	0.33	0.31	0.20	1								
Ca	-0.13	0.35	0.38	-0.09	0.22	1							
Mg	-0.13	0.43	0.48	0.054	0.19	0.40	1						
Fe	0.14	0.28	0.45	0.33	0.11	0.30	0.31	1					
HCO₃	-0.01	0.72	0.74	0.62	0.40	0.26	0.46	0.39	1				
Cl	0.00	0.52	0.60	0.56	0.12	0.07	0.22	0.38	0.23	1			
SO₄	-0.11	0.79	0.86	0.67	0.22	0.47	0.45	0.40	0.42	0.43	1		
F	-0.01	0.53	0.49	0.58	0.06	0.01	0.02	0.08	0.51	0.07	0.36	1	
NO₃	-0.10	-0.01	-0.02	0.05	-0.10	-0.14	-0.06	-0.04	-0.08	0.25	-0.09	-0.10	1

Note: Correlation is significant at the 0.01 level (2-tailed). Bold = strong correlation (>0.90).

In groundwater samples, Na^+ is responsible for ionizing halite minerals; if the Na/Cl mole ratio is ≥ 1, Na^+ is generated in the groundwater system as a result of silicate mineral weathering. (Rashid et al., 2020b; Rashid et al., 2018). In igneous rock, silicate minerals have mostly occurred, 95% of the earth's crust is composed of silicate minerals and the mantle. Silicon and oxygen are the primary components of silicate. Silicates are around 25% of all known minerals and 40% of common minerals. The composition of groundwater in our analysis showed that 85.3% of samples had a Na/Cl molar ratio of ≥ 1, and 14.7% showed Na/Cl <1. Therefore, the molar ratio Na/Cl is≥ 1, denoted silicate weathering in the groundwater samples of our analysis, and the ratio less than 1 showed non-silicate weathering. In addition, the groundwater Na/Cl ratio for this study varied between (0.45-8.1 and 2.16) respectively. However, in this analysis, the range and average results of silicate minerals were observed (1.03-8.10 and 2.42) and non-silicate minerals were identified (0.45-0.93 and 0.70), respectively. As a result, the findings of this analysis indicate that groundwater contamination in the study region is caused by both halite and silicate minerals. These findings are therefore consistent with the above-mentioned studies carried out in Pakistan (Rashid et al., 2020b; Rashid et al., 2018).

Saturation indices reflect the mechanism of groundwater enrichment and thermodynamic pattern in which the mineral dissolves/precipitates in water by computing groundwater information in the PHREEQ program (Deutsch, 1997; Rashid et al., 2020a). The high temperature, the lack of rainfall, and the arid-semiarid atmosphere increase the precipitation of calcite in the water system. Mineral phases/saturation indices for groundwater (n=68) and their mineralogical results for three minerals, viz., have therefore been determined. Calcite, gypsum, and dolomite are seen in (Fig. 5). In addition, the measurement of the mineral balance is useful in predicting dissolved mineral reactivity in water (Rojas et al., 2014). Measurements of and saturation can be used to estimate subsurface mineralogy. Some minerals, such as calcite and dolomite, are typically present in equilibrium in both subsurface and surface waters. Calculations have shown in this analysis that carbonate minerals have varying degrees of saturation. SI of the dolomite ranged from -1.19 to $+2.66$, as shown in Fig. 5, and that of calcite ranged from 0.57 to 1.54. The SI ranges from -2.69 to -0.92 for gypsum. These findings showed that in different samples the dolomite and calcite vary and there is both supersaturation and unsaturation level, these minerals may precipitate (SI> 1) and further dissolution (if SI< 0) is also possible. Gypsum value, on the other hand, is below 0; indicating an unsaturation condition and findings also indicating that Na^+ and Cl^- may not be the primary source of halite. The results of this research show that silicate minerals lead to groundwater pollution in the study region (Meybeck, 1987).

Insert Fig. 5 here

4.3 Major influencing factor responsible for water quality

Multivariate statistical means are widely used to solve environmental problems and provide evidence for understanding both natural and anthropogenic processes. In the analysis of water quality data, the principal components analysis (PCA) and correlation analysis (CA) have been widely used as impartial methods for extracting useful information (Singh et al., 2005). Pearson correlation analysis is a popular method for determining and describing the strength of a linear relationship between two variables.

Cluster analysis (CA) is an important multivariate statistical technique often used to better organize complex water data into various clusters. Ward's method, which often calculated the squared Euclidean distance between the water variable for the similarity index, used this technique. CA combined water observations that fall within the comparable cluster with most similar geochemical results (Chen et al., 2007). Thus, after the Wards method of measuring the Euclidean distance, three cluster groups were constructed. C1 less polluted, C2 moderately polluted, and C3 severely polluted were those three clusters.

The variability was 28.48% within the clusters and 71.52% between the clusters (Figure 6a). There are (n=43) groundwater samples in the less contaminated cluster C1, while C2 contains (n=5) and C3 contains (n=20). Cluster C1's percentage contribution was 63%, Cluster C2 was 7.3 % and Cluster C3 was 29.4%. Cluster C3 was thus regarded as a highly contaminated cluster, often reflecting the degradation in the quality of groundwater. The distance between the Cluster C1, C2 and C3 centroids was (0, 815.8836, and 473.5987), (815.8836, 0, and 1282.7403) and (473.5987, 1282.7403, and 0) respectively. The mean concentrations of the groundwater variables pH, EC, Tur, TDS, TH, Na, K, Ca, Mg, Fa, Cl, SO_4, F and NO_3 for the Clusters C1, C2 and C3 were (7.7, 858, 2.5, 548, 261, 213, 103, 7.6, 52, 21, 0.5, 52, 123, 0.5, and 0.34), (7.8, 1436, 4.4, 1027, 400, 368, 223, 7.5, 87, 36.4, 1.46, 79, 330, 1.6 and 0.14) and (7.9, 478, 2.14, 301, 170, 184, 33, 3.7, 46, 16.7, 0.44, 28, 50, 0.6 and 0.14, respectively).

Whereas, for clusters C1, C2, and C3, the distance between the central objects was (Observation 26, Observation 5, and Observation 57) respectively. In C1, C2, and C3, the distances for this observation were (0, 863, and 460.98), (863, 0, and 1317.56), and (460.98, 1317.56, and 0), respectively. Geochemistry of the central objects, however, viz. Observation 26, Observation 5, and Observation 57 for groundwater variables such as pH, EC, Tur, TDS, TH, Na, K,

Ca, Mg, Fe, Cl, SO_4, F, and NO_3 were (7.9, 850, 3, 544, 290, 210, 107, 48, 22, 0.3, 53, 121, 0.7, and 0.1), (7.5, 1525, 5, 976, 490, 380, 212, 9.2, 84, 41, 0.82, 44, 266, 1.09, and 0.2) and (7.6, 482, 2, 308, 195, 29, 2.6, 52, 16, 0.2, 52, 16, 0.2, 84, 41, 0.9, and 0.2) in the central objects for clusters C1, C1, C2 and C3, respectively. Groundwater variables were, however, clustered in (Fig. 6b).

Insert Fig.6 here

PCA is a statistical method for identifying sources of groundwater contamination. As shown in factor loadings (varimax normalize) after rotation representing the variability of groundwater parameters, four primary components (F1, F2, F3, and F4) defined (percent) of the total variance with an own value > 5.8 Table 4 Rotated factor loadings for the groundwater samples in the Khanewal district.

The first factor (F1) representing 36.60% of the total variance of the EC, 0.86, 0.87, 0.66, 0.72, 0.65, 0.54 or 0.84, 0.48, respectively, was 0.66, 0.72, 0,50, 0.60, 0.60, 0,56, 0.78, 0.56, 0.78 and 0.48 (Table 4). The dissolution of gypsum and calcium-carrying rocks, as well as the interaction of water and rock, genesis the source of SO_4^{2-} and HCO_3^-. F1 is also linked to water salinity, as determined by EC and major ion chemistry. Natural processes, such as carbonate ($CaCO_3$) and mineral bearing, contributed significantly to the F1 component. High levels of major ions like Ca^{2+}, Mg^{2+}, Na^+, and Cl^- may mean that anthropogenic activities affect mineral water reaction (Shanmugam et al., 2014).

Table 4 Rotated factor loadings for the groundwater samples in the Khanewal district

Loading factors	F1	F2	F3	F4
Depth	0.11	0.16	-0.39	-0.35
pH	-0.08	-0.12	-0.46	0.51
EC	0.91	-0.23	0.10	-0.18
Tur	0.47	0.21	-0.50	0.40
TDS	0.97	-0.18	0.09	-0.06
TH	0.66	0.69	0.19	-0.02
Na	0.72	-0.66	-0.03	-0.02
K	0.38	0.06	-0.18	-0.15
Ca	0.50	0.66	0.10	-0.06
Mg	0.60	0.53	0.19	-0.02
Fe	0.56	0.14	-0.20	0.63
HCO_3	0.78	-0.11	-0.18	-0.07
Cl	0.54	-0.30	0.40	0.39
SO_4	0.84	-0.01	0.09	-0.11
F	0.48	-0.46	-0.29	-0.31
NO_3	-0.07	-0.25	0.64	0.30
Eigenvalue	5.86	2.20	1.48	1.37

Variability (%)	36.60	13.75	9.24	8.54
Cumulative %	36.60	50.35	59.59	68.13

The second factor (F2) accounts for 13.75% of the overall variance, with an individual value of 1.84. Strong loading was observed for Mg^{2+} and Ca^{2+}, with correlation coefficients of 0.53 and 0.66, respectively. With water forms HCO_3^-·Ca.Mg, the percentage contribution of component F2 Table 4 Rotated factor loadings for the groundwater samples in the Khanewal district results in high concentrations of Mg^{2+} and Ca^{2+}, which recorded extreme evaporation, scarce precipitation, and a shallow watertable influenced by irrigation water, which reported extreme evaporation, scarce precipitation, and a shallow watertable influenced by irrigation water (Guo et al., 2017).

With an average value of 1.48 and a strong NO_3 load of 0.71, the third factor (F3) accounts for 9.2% of the overall variability. The components F1 and F2 showed an anthropogenic contamination source. NO_3^- contamination was caused by agricultural activities such as NO_3^- fertilizers in the form of KNO_3, urea, animal manure, and sewage waste.

Factor IV explained 8.54% of the general variance, with an average of 1.37. In groundwater, the pH and Fe^{2+} values of the significant coefficient of correlation (r) were estimated to be 0.51 and 0.63. In soils, rocks, and minerals, iron occurs naturally. Groundwater in the aquifer comes into contact with these strong dissolving materials, releasing their elements, including Fe^{2+}, depending on the degree of acidity, into mineral groundwater dissolution (Deutsch and Siegel, 1997).

4.4 Groundwater suitability evaluation

4.4.1 Assessment for Drinking Purpose

WQI is an important groundwater quality parameter that is used to decide whether water is appropriate for domestic use (Avvannavar et al., 2008). WQI is a method that calculates the effect of groundwater parameters on groundwater quality, and it is measured by using WHO drinking standards (Edition, 2011). There are five categories according to the WQI criteria: excellent (<50), good (>50), bad (>100), very poor (>200), and water not suitable for drinking (>300) (Sahu and Sikdar, 2008). Table 5 Water Quality Index (WQI) classification of the study area listed the different types of groundwater based on WQI references, and a spatial distribution map Fig. 7 provided more information about the different types of water in the study region. 2.94% samples are excellent for drinking, while 39.7% are Poor, 11.76% are good, and 27.94% are very poor for drinking. Furthermore, 17.64% are unsuitable for

drinking. Fig. 7 demonstrates that maximum number samples in groundwater of study area are not appropriate for drinking purposes.

Table 5 Water Quality Index (WQI) classification of the study area

WQI	Water Type	No. of Samples	% of samples
(<50)	Excellent	2	2.94
(>50)	Good	8	11.76
(>100)	Poor	27	39.7
(>200)	Very poor	19	27.94
(>300)	Unsuitable for drinking	12	17.64

Insert Fig.7 here

4.4.2 Assessment for Irrigation Purpose

The suitability of the groundwater in the study area for irrigation was assessed by using Wilcox and USSL diagrams, as well as other agricultural indices such as sodium percentage (Na%), Sodium adsorption ratio (SAR), permeability index (PI), magnesium hazard (MH), and Kelly ratio (KR). Table 6 summarizes the irrigation indices of groundwater samples statistically. summarizes the irrigation indices of groundwater samples statistically. The primary parameter for the calculation of suitability is the sodium adsorption ratio (Odukoya and technology, 2015). According to SAR, the sodium hazard in groundwater can be rated as low (SAR10), medium (10-18), moderate (18-26), or very high (SAR>26). SAR ranges from 1.65-65.19 in the study area, with an average of 12.87 indicating a low, medium, and high risk of sodium. According to the USSL diagram (Fig. 8), 45 samples (45%) belong to the C_2S_1 and C_3S_1 groups, indicating that they can be used for irrigation with minimal Na^+ exchange. Nine samples belong to the C_3S_2 group, four to the C_3S_4 group, five to the C_2S_2 group, and five to the C_1S_1 group. These types of water are not suitable for agricultural use.

Table 6 summarizes the irrigation indices of groundwater samples statistically.

Indices	Minimum	Maximum	Mean	S.D	Permissible Limit	Unsuitable Samples	Suitable Samples
PI	34.78	113.5	70.29	18.13	>25	-	100

MH	9.44	68.96	38.43	13.47	50	13	80.88
KR	0.11	8.68	1.25	1.55	1	29	57.35
SAR	1.07	7.99	2.81	1.13	18	13	80
%Na	10.64	89.78	45.66	20.71	60	15	77.94

Insert Fig.8 here

The sodium percentage (Na%) also indicates how suitable the water is for irrigation purposes (Seth et al., 2016). As it reacts with the soil, high levels of sodium in groundwater are undesirable, resulting in its low permeability. In this way, plant growth is also decreased as a result. (Yahiaoui et al., 2015). The percentage of EC and Na^+ is critical in determining the suitability of groundwater for agricultural use. The sodium content of cropland is determined by the Na^+ level in agricultural water, and higher Na^+ levels in cropland cause a change in the permeability of the soil, making it difficult to plow and unsuitable for seed production (Jeevanandam et al., 2012). The formula for calculating percent sodium (%Na) is given.

$$\%Na^+ = \frac{(Na^+ + K^+)}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \qquad (6)$$

The Na^+% varies from 15.6% to 92.3% with a mean value of 52.8%. Deflocculation, soil tilt, and permeability impairment are caused by a high percentage of Na^+ (Selvaraj et al., 2012). For irrigation usage, groundwater containing less than 60% Na^+ is considered acceptable. The percent Na value has a mean value of 45.66 and ranges from 10.64 to 89.78. 77.94 % of the samples are falling in the excellent to acceptable category. To further define groundwater for irrigation, Wilcox's diagram, where EC is graphed against percent Na^+ is used. As in Fig. 9, Approximately 36.7% of the samples were good to permissible, followed by 22% percent belonging to doubtful permissible and 22% of the samples falling into doubtful categories for irrigation use and 11.7% are unfit for irrigation.

Insert Fig.9 here

The Permeability Index is a primary factor for assessing water appropriateness for irrigation. According to (Doneen and Engineering, 1964). Class 1 (>75%, suitable), class 2 (25-75%, good), and class 3 (less than 25%, unsuitable) are the three classifications for PI.

$$\text{PI} = \text{Na} + {} + \sqrt{HCO_3/Ca} + \text{Mg} + \text{Na} * 100 \tag{7}$$

The study area findings are in the range of 34.7 to 70.3 with a mean value of 70.3. Most samples fall in Class I under the Deneen classification sampling programs, suggesting that groundwater is suitable for irrigation.

Magnesium Hazard analysis is another approach suggested by Szabolcs and Darab for determining the agricultural suitability of groundwater (Szabolcs, 1964). Soil modification increases as Mg^{2+} content relative to Ca^{2+} grows, allowing clay particles to scatter and causing damage to the soil structure by reducing hydraulic conductivity. For irrigation purposes, magnesium risk less than 50 is considered acceptable, while greater than 50 is unfit for irrigation and crop yield declines as soils become more alkaline (Bhat et al., 2018). With a mean value of 38.42, the magnesium value for the study area varies from 9.4-68.95. In 13 samples, Magnesium Hazard was more than 50 and these are unsuitable for irrigation, while others are good for irrigation.

The Kelly Ratio is a key requirement for determining the quality of groundwater used in agriculture (Brooks et al., 2005). For all groundwater samples from the study area, Kelly's Ratio (KR) was computed with the following Equation 8.

$$\text{K.R} = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \tag{8}$$

If the Kelly ratio is greater than 1, higher sodium content in groundwater is found, while a ratio of less than 1 Kelly is considered ideal for irrigation purposes (Bouderbala and Health, 2015). In the study area, the Kelly ratio ranges from 0.12 to 8.6, with a mean value of 1.29. Kelly's ratio is lower in 39 samples, which means that the water sample is suitable for irrigation, whereas 29 samples that have a ratio greater than 1, are not suitable for irrigation.

5. Conclusion

The groundwater of Khanewal district is slightly alkaline. The groundwater variables such as pH, total hardness, turbidity, EC, TDS, Na^+, K^+, Fe^{2+}, and F^- in groundwater samples exceeded WHO guidelines for drinking water. The hydrogeochemical characteristic are controlled by weathering of rocks, ion exchange and known mineral prospects of the area.

 The increasing order of cation and anion abundance has been observed in the following sequence: $Na^+>Ca^{2+}>Mg^{2+}>K^+$ and $HCO_3^->SO_4^{2-}>Cl^-$. The mixed water type such as Na·Ca- HCO_3 and Na·Ca (Mg)-HCO_3·SO_4 are main facies in the study area. The abundance of Na^+ and HCO_3^- in the study region reveals that silicate

weathering is the primary source of hydrochemical compositions of groundwater. Ion exchange and rock weathering processes, such as the dissolution of albite, carbonate and gypsum minerals, are important rock-water interactions that regulate the evolution of groundwater hydrochemistry, according to correlation analysis and graphical relationships between ions.Gibbs diagrams showing rock dominancy governing groundwater evolution. The geochemical modeling saturation indices shows the aqueous phase is under-saturated in comparison to evaporites like gypsum (negative values), while carbonates like calcite and dolomite are in equilibrium in comparison to the over-saturated phase (positive values).

The water quality index (WQI) shows that 17.64% of the groundwater samples are unsuitable to drink. However, according to the agricultural indices approximately 68% of the groundwater samples are suitable for irrigation. Anthropogenic activities and sedimentary rock weathering play a significant role in the depletion of the groundwater system in the study area.

Declarations

The authors declare complete compliance with the ethics of publishing and, thus, approved by all the authors. All the authors consented the prospective publication of the article and adhere to the availability of data and material as per journal's policy and requirements. The authors have no conflicting interests to disclose. The authors have not received any financial support for this research article.

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Authors' contribution

Javed Iqbal: Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing - original draft. **Chunli Su**: Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Abdur Rashid, Nan Yang, Muhammad Yousuf Jat Baloch**: Formal analysis, Writing - review & editing. **Shakeel Ahmad Talpur, Gohar Rahman, Earjh**: Software, Resources, Writing - review & editing, Visualization.

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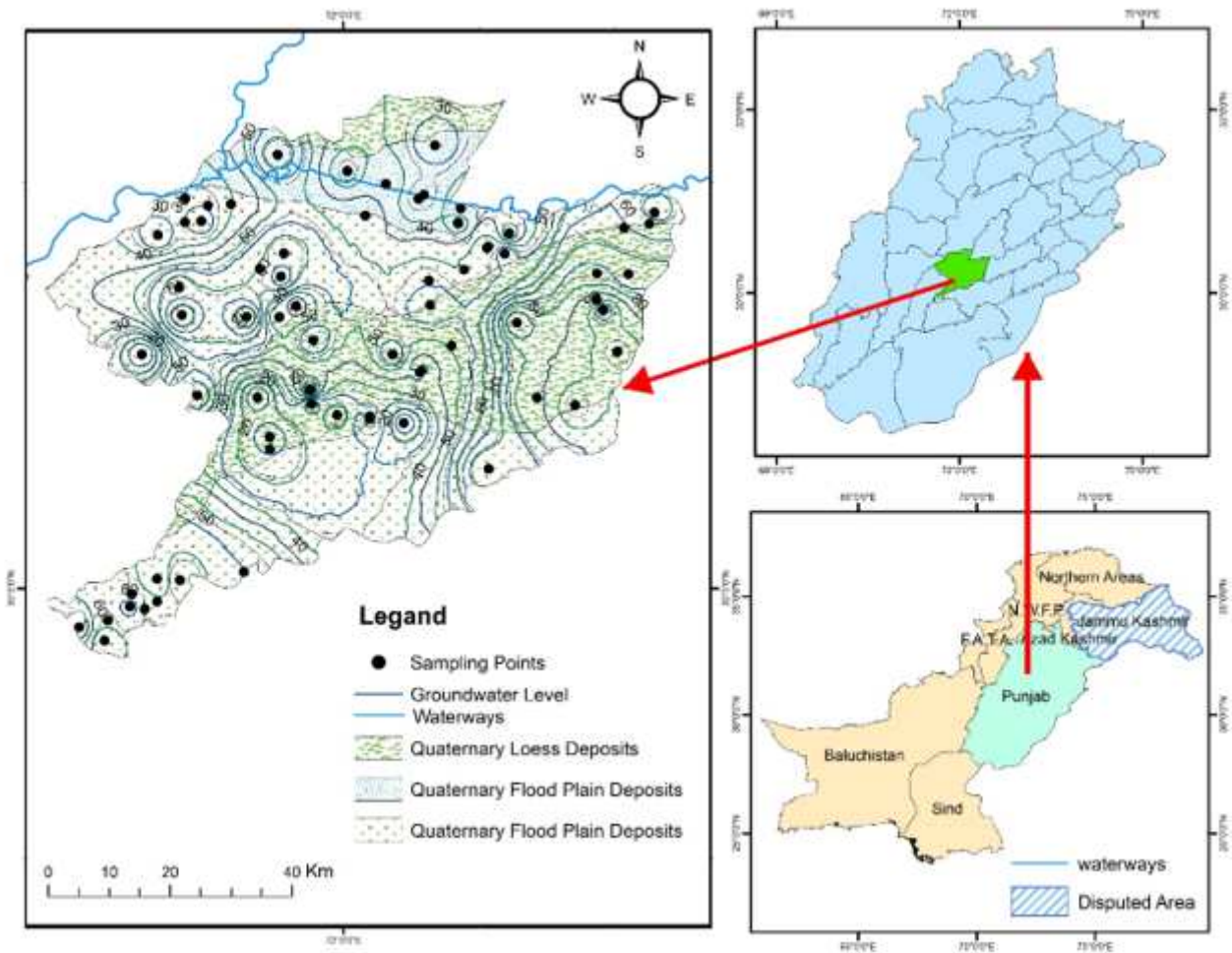
Figures

Figure 1

Groundwater sampling points and geological formation of Khanewal district. For creating study area map, Arcgis 10.7.1 was used
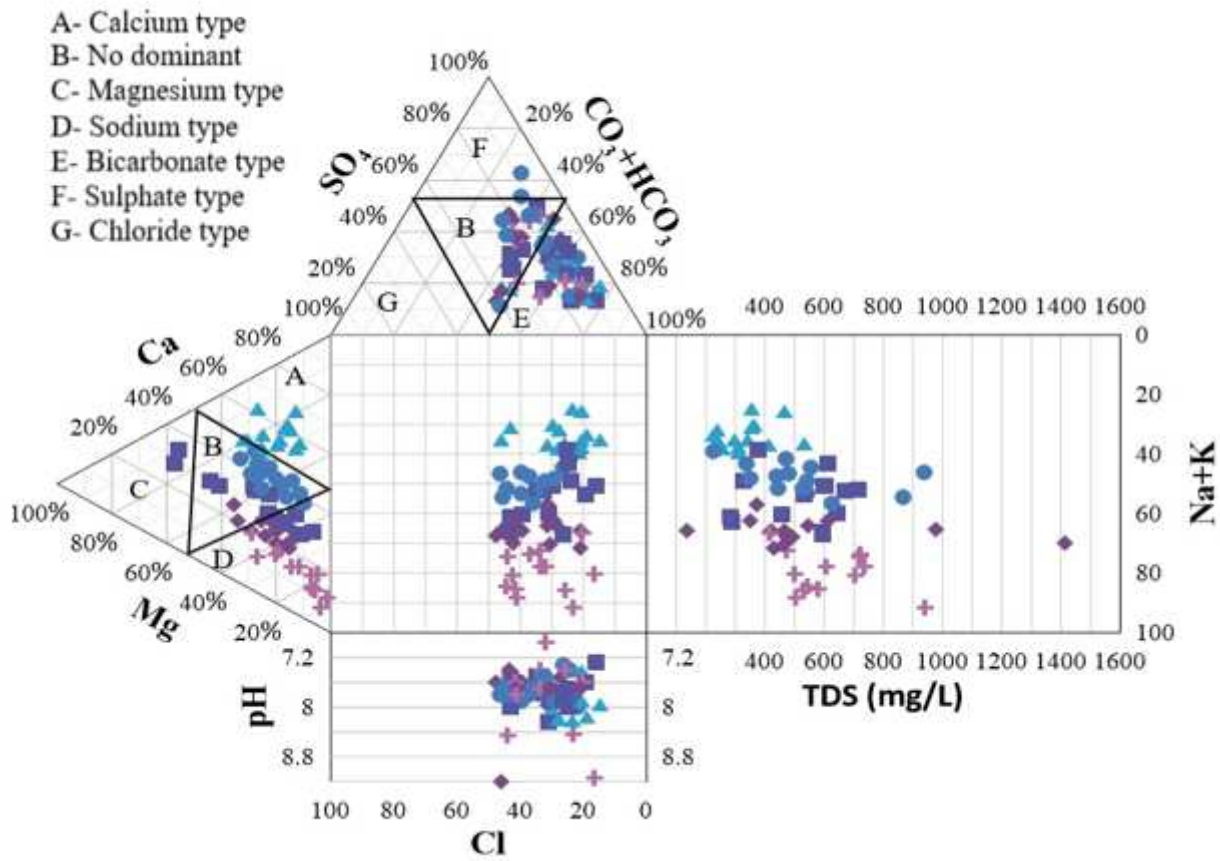
Figure 2

The Durov diagram of groundwater in the Khanewal district. Durov diagram was prepared using Grapher (version 14 Golden Software, LLC, Golden, Colorado, U.S.A) to interpret hydrochemical facies.
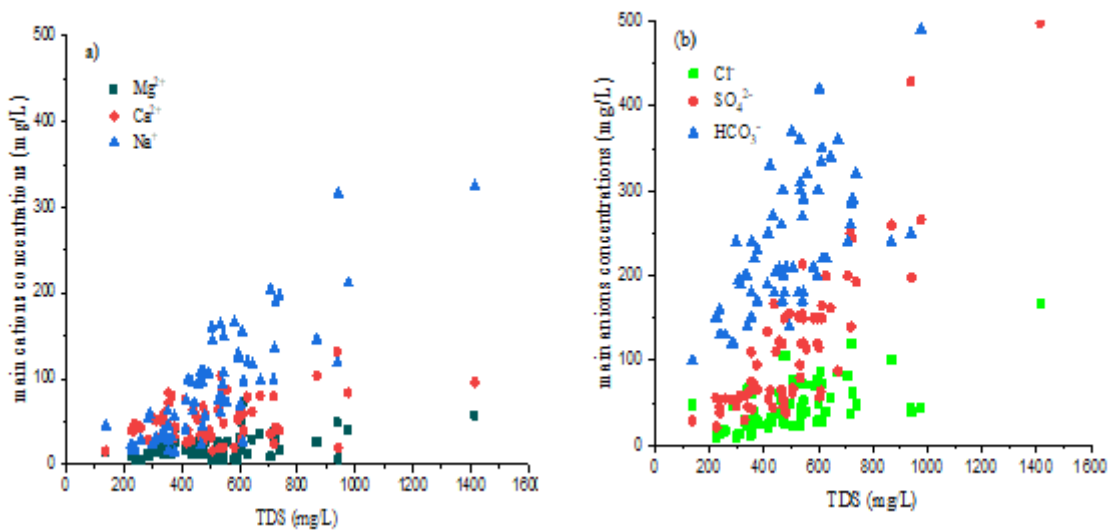

Figure 3

Scatter plots of major cations (a) and anions (b) versus TDS. Scatter Plot graphs for major cations and anions were made using Grapher (version 14 Golden Software, LLC, Golden, Colorado, U.S.A)
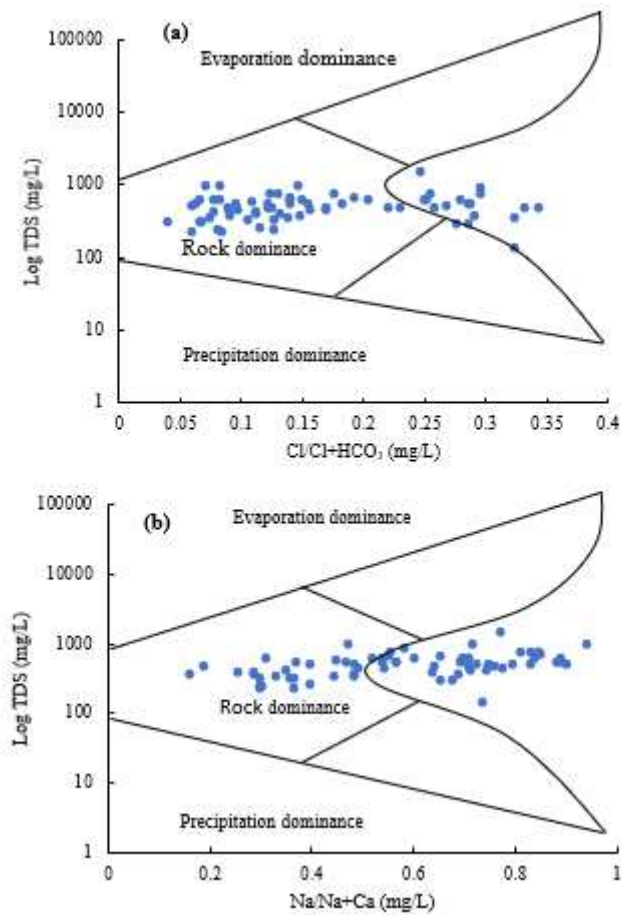
Figure 4

The Gibbs diagram demonstrates the ionic composition of the samples of groundwater. (a) Cl/Cl + HCO3 mg/L verses Log TDS, and (b) Na/Na + Ca mg/L versus Log TDS. Microsoft Excel 2019 was used to draw the Gibbs diagram to determine and analyze the relationship between lithology and hydrochemistry in aquifers.
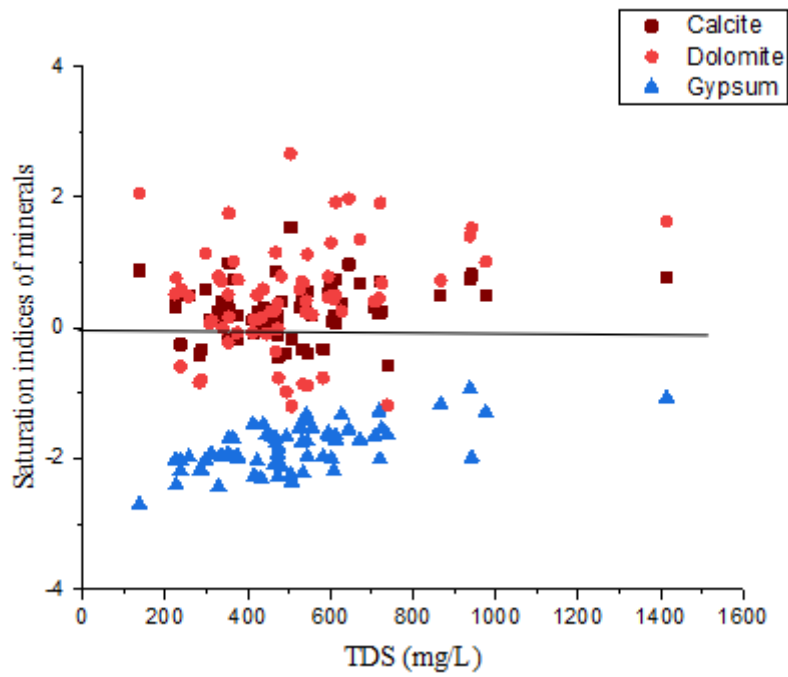
Figure 5

The variation of saturation indices of the selected minerals. Saturation indices have been computed by using a geochemical simulation program called PHREEQC Interactive (version 3.4) to find the trend towards dissolving or precipitating a certain mineral
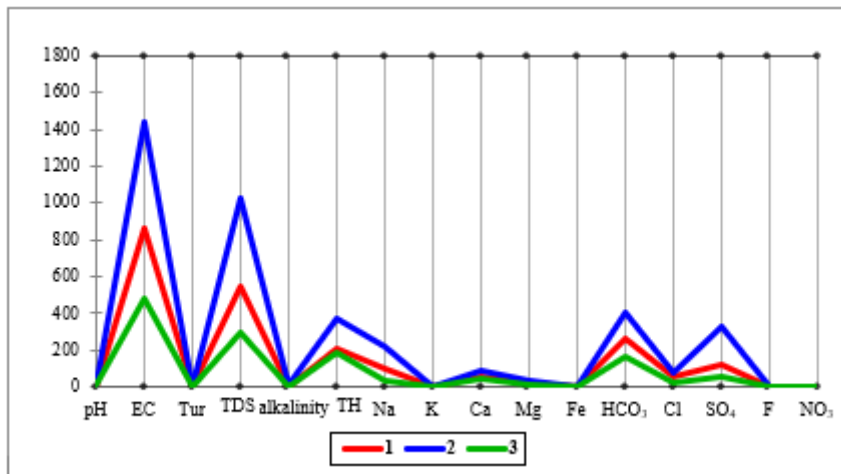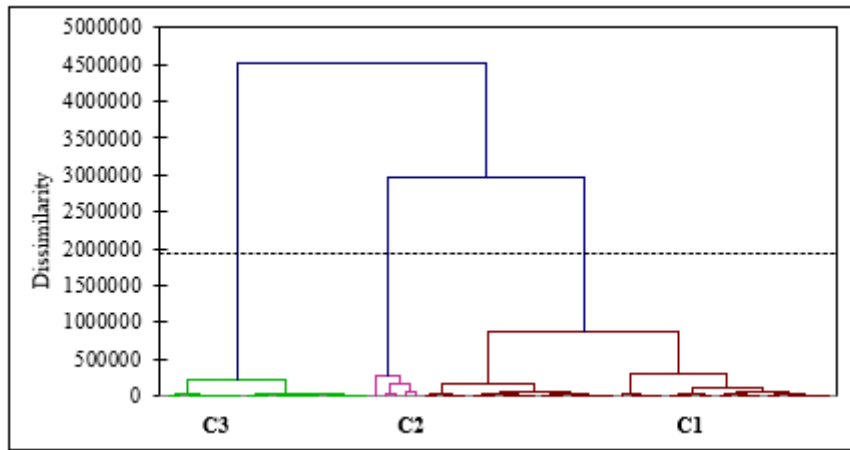
Figure 6

a Clustering of groundwater samples based on dissimilarity. b Khanewal District groundwater variables. Correlation analysis was done with the help of (V23, SPSS Inc, Armonk, NY, U.S).
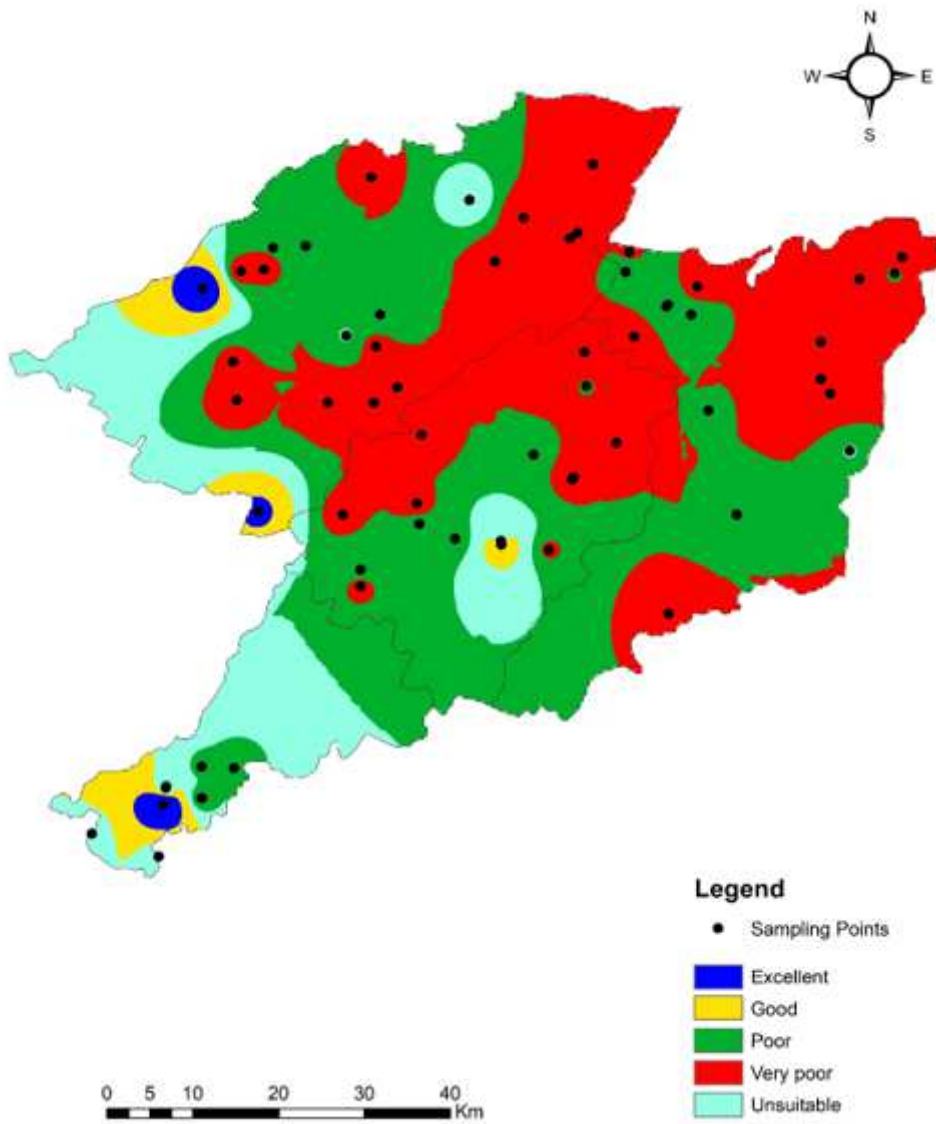
Figure 7

Groundwater suitability assessment for drinking purpose of the study area. IDW, spatial analysis tool available in ArcGIS 10.7.1 was used to draw the groundwater suitability map
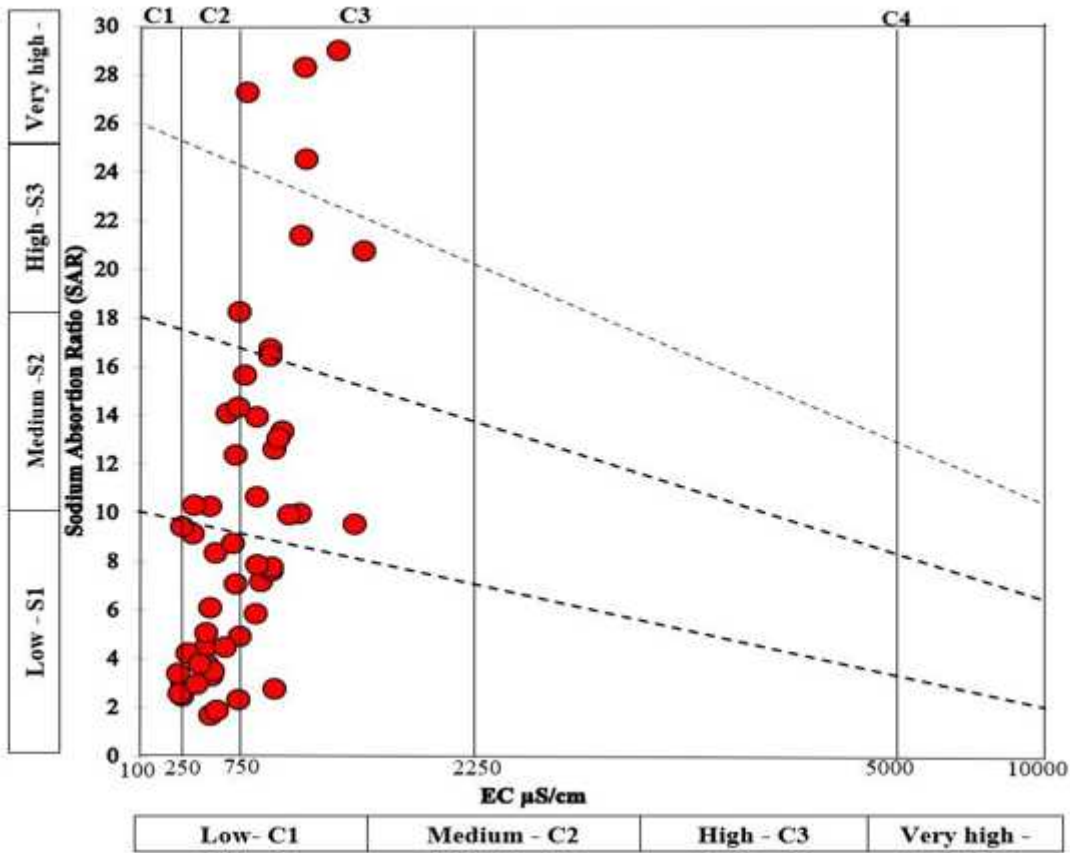
Figure 8

Diagram of United States Salinity Laboratory (USSL)1954 for the classification of irrigation water. To define and assess the suitability of groundwater for irrigation, Grapher Software was used to construct U.S. Salinity Laboratory diagram
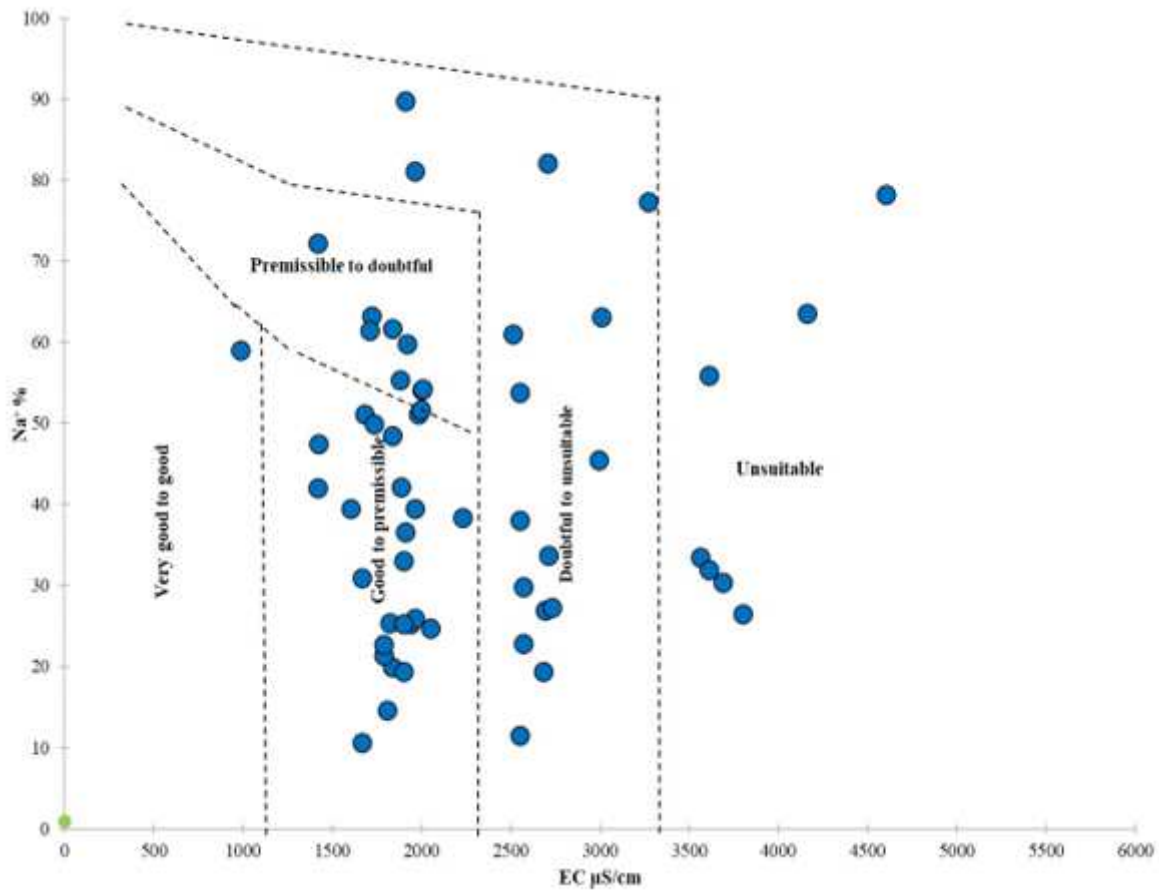
Figure 9

The Plot of %Na versus EC (Wilcax 1948). To assess the suitability of groundwater for irrigation, Grapher Software was used to draw Wilcox diagram