

Hydrogeological studies and evaluation of surface and groundwater quality of Khyber Pakhtunkhwa, Pakistan

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ABSTRACT

The hydrochemistry and suitability of the groundwater for drinking and irrigation purposes in Haripur District, Pakistan, were investigated. The hydrogeological system, land use, and drainage areas have all been linked to identifying chemical compounds' sources in groundwater. Thirty-four (34) groundwater samples and eight (08) surface water samples were collected in the research area to determine the physico-chemical parameters of the groundwater and surface water. The results were compared with Pakistan Standard Quality Control Authority (PSQCA) and World Health Organization (WHO) standards for suitability. The spatial distribution map of the major ions (cations and anions) has been prepared, including calcium (Ca^{2+}), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}). The irrigation water quality has been assessed using the sodium adsorption ratio, residual sodium carbonate, magnesium hazard, electrical conductivity, and Kelly's ratio. Most of the samples fall within the permissible range of drinking water quality. However, in some samples, Cl^- and Na^+ concentrations exceed the permissible limits. By using the Piper Trilinear Diagram (1944), major hydrogeochemical facies were identified. All the field data showed that there existed three different groups of water. Ca-HCO_3 (52.38%), Na-Cl-SO_4 (21.42%), mixed type Ca-Mg-HCO_3 and Ca-Na-HCO_3 (26.19%) are dominant groups. Ca-HCO_3 type water is freshwater. Based on sodium adsorption ratio, four (4) samples were considered unsuitable for irrigation. Wilcox's classification shows that 90% of samples fall in the C_2S_1 category, which is permissible for irrigation purposes. There are two important parameters that suggest improvement of water prior to its use, that is, the sodium hazard and the magnesium hazard. The study furnished the fact that the hydrogeochemical facies and the constituents are mainly controlled by hydrogeology, water depth, land use and drainage.

Keywords: Groundwater; Hydrogeology; Physicochemical analysis; Hydrogeochemistry

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1. Introduction

Groundwater is the largest water resource and an extremely important commodity for the well-being of humans living around the globe [1]. Water shortage is a critical issue in many arid and semiarid regions where there is limited precipitation and surface water data available. In semi-arid and arid parts, groundwater is an essential source of freshwater for human welfare, irrigating crops, and industrial purposes. Man-made activities are deteriorating the groundwater quality greatly. Alarming population growth and migration, extensive industrial development, urbanization, and poor water management all put a strain on the world's water supply [2–5]. Drinking water quality is one of the main concerns of the world's population as it is directly related to human health [3,6].

Water is the most important natural resource for both living beings and biological diversity and economic development [7]. Overall, water demand is increasing day by day. All human beings rely on water for their survival. In many parts of the world, groundwater is an essential source of drinking water. The depletion of groundwater due to over-exploitation is a critical issue for the world now-a-days. Identification of the chemical composition of groundwater plays a key role. Understanding the quality of groundwater is vital for drinking, irrigation, and industrial purposes. The quality of groundwater varies from area to area and is controlled by the depth of aquifers. The hydrochemical facies are used to understand the type of groundwater in an aquifer.

Due to substantial built-up areas in megacities such as Karachi, Shanghai, Tokyo, and New Delhi, groundwater has received increasing attention for drinking, irrigation, and domestic purposes [8–10]. In many parts of the world, groundwater is the only source of freshwater to meet their everyday needs. However, it seems that saline water invasion has become a worldwide concern. Moreover, both trace elements and major ions can be a health concern for human beings [11]. The agriculture sector is heavily dependent upon pesticides and fertilizers, which also cause groundwater pollution [12]. The direct discharge of industrial complex effluents is also one of the major contributing agents to polluting water table [13].

Arsenic and heavy metal contamination of water have been reported in more than 70 countries [14–16]. Over 140 million people are affected by arsenic's surface and groundwater pollution in several countries around the globe [17,18]. Arsenic and fluoride are among the major groundwater pollutants which seriously affect human health and cause arsenicosis and fluorosis through drinking water intake. Therefore, assessment of the water quality is of the utmost importance for the health and the sustainable development of society [19–21]. Naturally, arsenic exists in the form of arsenates, sulfides, or metal arsenides within the earth [22]. Arsenicosis is a serious chemical disease in North America, South and Southeast Asia, South and Central America [23,24]. In arid and semiarid areas, water resources management and assessment of water quality are one of the major global challenges which are attracting researchers [4,25,26]. These water-deficient regions are facing severe groundwater pollution mainly due to anthropogenic

activities. For example, the Chinese Loess Plateau (the world's most water-deficient area) is at risk of serious water scarcity and security issues [27,28].

Pakistan is under stress regarding the deteriorating quality and quantity of water in most of the area. The rapid growth of the population demands more resources, and overexploitation of groundwater results in a declining water table. Pakistan is the sixth largest populated country and the third biggest consumer of groundwater. About 9% of the total extraction of groundwater in the world is performed in Pakistan [29–31]. Pakistan is included in those countries where the groundwater discharge surpasses recharge, and the groundwater is considered insufficient to meet the irrigation supply [32,33]. Additionally, there is a greater chance of a further decrease in the surface water supplies because the capacity of the primary reservoir is diminishing due to sedimentation [34].

Groundwater quality assessment is significantly important in densely populated areas. In the present research, a detailed physicochemical study was conducted to understand the geochemical processes occurring in the aquifers. The suitability of groundwater is evaluated through major cations and anions, pH, electrical conductivity (EC) and total dissolved solids (TDS). Groundwater is the only freshwater supply for their daily usage in the study area located in the Haripur District [35]. Therefore, information about the source of an aquifer is the primary focus of its safe utilization. Groundwater overexploitation leads to a loss in water quality because of higher salinity rises in groundwater flow lines [36].

The prime aim of the current study is to evaluate the hydrochemistry of the surface and groundwater. It is essential to study the hydrogeology and hydrochemistry of the surface and groundwater for the assessment of the safe yield. Additionally, an effort has been made to investigate the spatial extent of the aquifer, major ion chemistry, and hydrogeochemical processes that control the groundwater composition. This study will provide information about groundwater quality for drinking and irrigation purposes. It could also be helpful to adopt integrated water management schemes in the other districts of Khyber Pakhtunkhwa.

2. Location and geology of the study area

The study area (Haripur District) covers an area of 1,725 km² and it is situated in the northwestern corner of Pakistan, between latitude 33° 44' and 34° 18' N and longitude 72° 35' and 73° 15' E (Fig. 1). Haripur is the main city of the district that encompasses Haripur, Ghazi, and Khanpur tehsils. Haripur District is geographically significant as its boundaries coincide with five districts of Khyber Pakhtunkhwa and two districts of the Punjab Province, Pakistan. The total population of the district is more than one million, according to the 2017 census [37].

The study area is part of the Haripur basin, which lies within the lesser Himalayan region and is bounded in the east to the northeast by Nathiagali Thrust and Margalla Hills, in the south by Haripur Plain and in the west by Gandghar Ranges. The areas in the Haripur basin are mostly plains containing both alluvial and fluvial deposits [38]. Hazara slates act as a basement rock for overlying fluvial

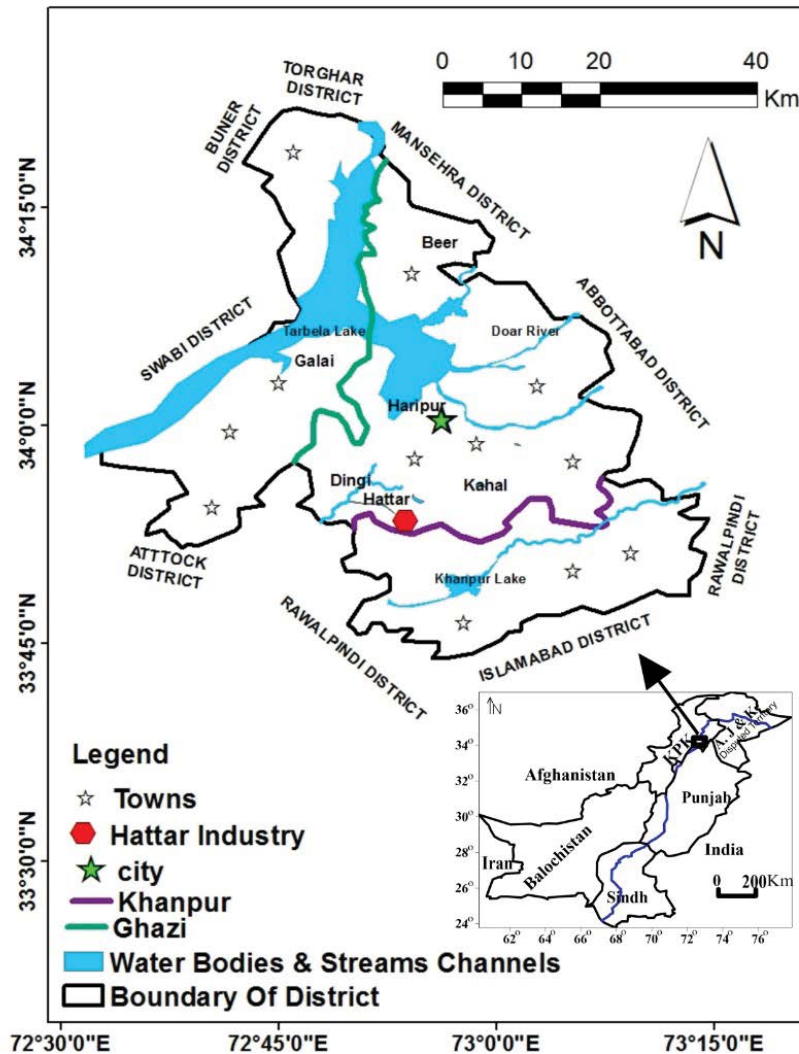


Fig. 1. Location of the study area with groundwater sampling and field locations.

and alluvial deposits. The mountains of the Haripur area consist of Pre-Cambrian to Eocene rock units. The Tanawal Formation of Cambrian consists mostly of quartzite and quartzose schists. The Hazara Formation is composed of metamorphosed shales, limestone with minor graphitic intercalation, slates, and phyllites. The Abbottabad Formation is also exposed in the Haripur area and consists of the arenaceous and dolomitic units [39].

An initial investigation into the groundwater of Haripur was carried out in 1975 by the Water & Power Development Authority (WAPDA) hydrogeology department in Peshawar. Two test holes were drilled in 1966 by Water and Soil Investigations Division of WAPDA for groundwater investigation. In Dor valley aquifer is unconfined. In most of the zones, the depth of the water table was less than 30 m below the land surface. Therefore, the transmissivity value must be reasonably high because most wells drilled in the area yield 150 m³/h [40]. WAPDA drilled twelve test holes between 1978 and 1981 for hydrogeological investigation, in which six well step tests were

performed. The main water-bearing zone is an alluvial fill in the area. The aquifer formed by the lower part of the alluvial fill consists of gravel, boulders, and sand layers. Deep confined or semi-confined aquifers lying in the south of Haripur have their top at a depth of between 55–120 m, and their piezometric levels fluctuate from 20 to nearly 80 m. The shallow perched aquifer has been formed near the surface in gravel lenses inserted in unsaturated clay. In the middle part, alluvial fill is thinner near the mountains, while bedrock was reached at 97 m depth in the test hole. Seasonal fluctuations in water level are sometimes more than 10 m near Tarbela Lake and close to mountains; elsewhere it usually ranges between 1.5–2.5 m. WAPDA regularly measured the water levels in open wells [41,42].

3. Materials and methods

Various techniques were used to develop a clear understanding of the hydrogeology and quality of groundwater in the current study. These techniques include field

measurements and the preparation of different maps and diagrams, such as the geological map [43], rainfall map, land use map, and a fence diagram.

The techniques opted for the present study included a collection of data from various departments. Furthermore, using the Arc GIS software, these data were interpolated to determine their relationship with the study area's various groundwater and surface water results. The geologic map has been reproduced using the data [43] (Fig. 2). The strata charts were procured from the Public Health Engineering Department (PHED) to develop the fence diagram to assess the nature of aquifers in the Haripur area (Fig. 3). Similarly, the rainfall data has also been interpolated to assess the effect on the groundwater (Fig. 4). The land use map has also been developed with the help of satellite data (Fig. 5).

3.1. Sampling

The fieldwork includes field measurements, sample collection, and preservation. A total of forty-two different sites in Haripur District were selected using a random sampling technique to collect water samples during December 2018 to March 2019 (Fig. 1). After pumping the water from a tube well for 5 min, the water samples were collected in sterilized bottles (1.5 L) for physical and chemical analyses. The bottles used for collecting samples were rinsed 2–3 times thoroughly with the same water to avoid unpredictable changes in the characteristics. The water well information was gathered from local people which includes water table depth, total depth of the well, and daily discharge. Physical tests such as pH, electrical conductivity (EC), total dissolved solids (TDS), and turbidity were measured in fields using a digital

probe meter. The water samples from each bottle were then labeled with an appropriate code that would help to identify the water sample's location and water type as well as type, that is, surface water and groundwater. These samples were shifted to the Chemistry Laboratory of Bahria University Islamabad and were kept in a refrigerator at a temperature of 4°C until further analysis.

3.2. Laboratory analyses

Lab work includes analysis of arsenic, calcium, magnesium, sodium, potassium, chloride, carbonate, bicarbonate, sulphate, fluoride, and iron. All these parameters were analyzed by using standard methods by the American Public Health Association (APHA 22nd edition). Following the standard operational procedures, replications and standardized adjustments as quality control methods and standard laboratory measures to ensure the quality of the results. The kit-based test was performed for arsenic and fluoride. Sodium and chloride were analyzed by titrating against silver nitrate (AgNO_3). Magnesium, calcium, carbonate, and bicarbonate contents were determined by volumetric titration in the water samples. The flame photometry method was used for the analysis of potassium and sulfate content.

The chemical composition of groundwater was compared with the standard values of WHO [44] and Pakistan Standards and Quality Control Authority [45] to show its suitability for drinking and irrigation purposes (Table 1). All the parameters have been used to assess their facies using the piper trilinear diagram for hydrogeochemistry. Apart from that, the statistical relationship between various parameters was established using the Pearson's correlation coefficients (Table 2).

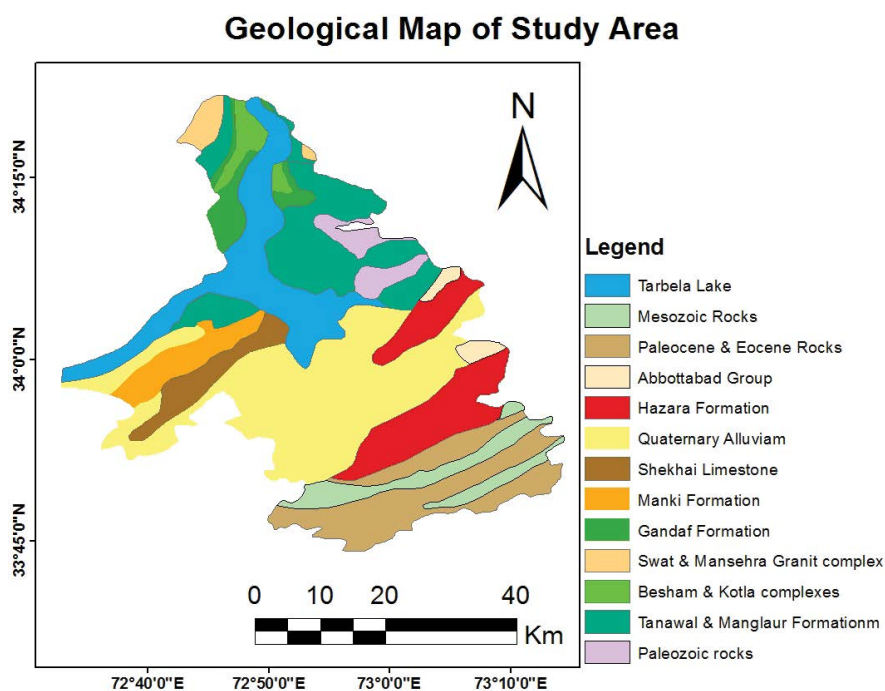


Fig. 2. Geological map of Haripur with localities of major rock units exposed in the area digitize after [43].

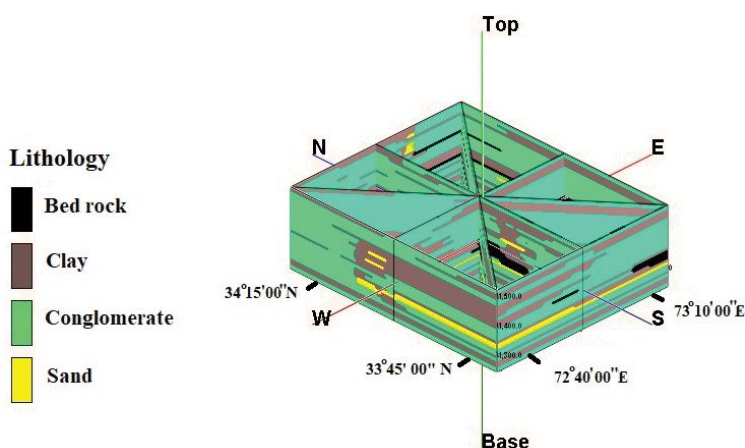


Fig. 3. Fence diagram showing the spatial lithological variation in the study area.

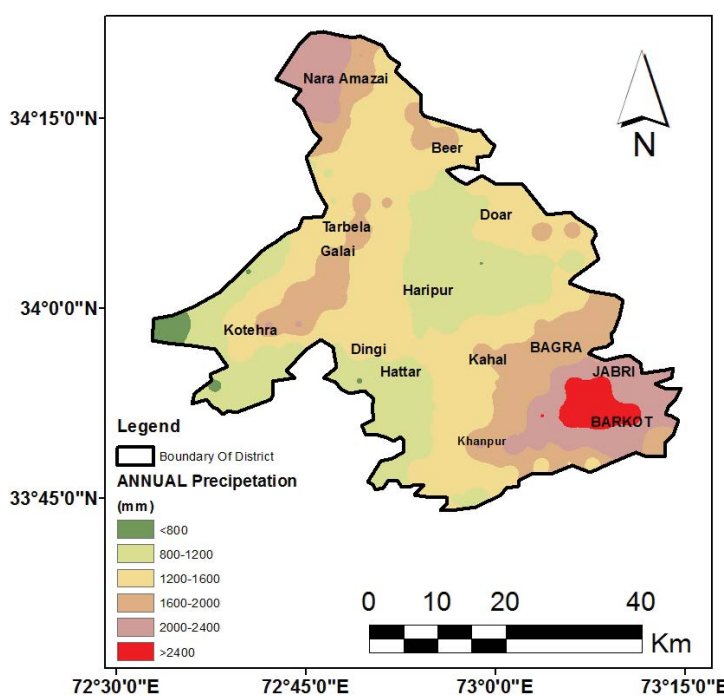


Fig. 4. Map displaying annual precipitation of District, Haripur.

3.3. Irrigation water quality

The good quality of water is essential for plant growth and achieving the maximum production of crops. Sodium and electrical conductivity play a vital role in the suitability of water for agricultural purposes. An excess of sodium in water produces adverse effects by changing the permeability and properties of soil, whereas an excess of EC will affect the root zone. Therefore, groundwater suitability for irrigation purposes of the study area was assessed using residual sodium carbonate (RSC), magnesium hazard (MH), Kelley's ratio (KR) and sodium adsorption ratio (SAR) classification. The standard guideline established by the USDA Salinity Laboratory to examine the water quality for irrigation practices is based on the EC [46].

For the determination of irrigation water, sodium adsorption ratio is an important parameter. All the concentrations are in meq/L and measure the sodium hazard to crops. The formula used for sodium adsorption ratio is following:

$$SAR = \frac{Na^+}{\sqrt{((Ca^{2+} + Mg^{2+}) / 2)}} \quad (1)$$

For the calculation of residual sodium carbonate, the following formula is used:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (2)$$

Table 1
Statistical summary of major ions and trace elements in groundwater and surface water of Haripur area

Parameter	Minimum	Maximum	Mean	PSQCA	WHO
pH	7.2	8.5	7.7	6.5–8.5	6.5–8.5
EC, $\mu\text{S}/\text{cm}$	265	1,753	590		1,000
TDS, mg/L	185	1,026	429.19	1,000	1,000
Turbidity, NTU	0	16	4.7	10	05
Calcium, mg/L	11	72	32.9	200	200
Magnesium, mg/L	19	114	59	100	150
Sodium, mg/L	29	771	70.1	200	200
Potassium, mg/L	0.5	22	8.4	30	12
Bicarbonate, mg/L	150	400	255		500
Chloride, mg/L	17.1	469.1	101.41	500	250
Sulphate, mg/L	14	141	61.2	400	250
Iron, mg/L	0.02	0.93	0.06	0.3	0.3
Fluoride, mg/L	0	6.7	3.9	1.5	04
Arsenic, mg/L	0	0.1	0.0007	0.01	0.01

Table 2
Correlation analysis of different parameters

	pH	EC	TDS	Turbidity	F ⁻	Na ⁺	Cl ⁻	Fe	Ca ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	K ⁺	Mg ²⁺
pH	1												
EC	-0.284	1											
TDS	-0.419	0.939	1										
Turbidity	-0.160	0.259	0.273	1									
F ⁻	0.102	0.397	0.380	0.204	1								
Na ⁺	-0.197	0.674	0.642	-0.037	0.285	1							
Cl ⁻	-0.175	0.672	0.641	-0.031	0.306	0.996	1						
Fe	-0.120	0.403	0.341	0.969	0.286	-0.034	-0.028	1					
Ca ²⁺	0.403	-0.010	-0.016	0.115	0.098	0.012	0.011	0.192	1				
HCO ₃ ⁻	-0.156	0.085	0.145	0.054	0.161	0.148	0.163	0.086	-0.189	1			
SO ₄ ²⁻	-0.034	0.481	0.484	0.271	0.314	0.324	0.331	0.298	-0.064	0.225	1		
K ⁺	-0.178	-0.044	0.025	-0.024	-0.076	-0.078	-0.075	-0.020	0.072	0.111	-0.010	1	
Mg ²⁺	-0.288	0.212	0.282	0.054	-0.026	0.322	0.309	0.017	0.224	0.143	-0.050	0.180	1

Magnesium hazard can be assessed by using Eq. (3) [47]. All the concentrations are expressed in meq/L.

$$\text{MH} = \frac{\text{Mg}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}} \times 100 \quad (3)$$

Kelley's ratio can assess the sodium present in the water, which can be used to check its quality for irrigation usage. In this method, sodium measured against calcium and magnesium for KR.

$$\text{KR} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}} \quad (4)$$

4. Results and discussions

The fence diagram in Fig. 3 shows the overall lithological view of the study area. The green color in the diagram

shows the amalgamated channel bodies that serve as aquifers in the area. The channel staking with time shows the development of a prominent aquifer system that varies from strictly confined at deeper levels to unconfined at shallower depths. The thicker units of the channel fill are present in the northwestern areas, whereas the thinner channel fill deposits are in the southwestern zone. Small sand bodies are also incorporated in the south to the southwestern side. Clay and conglomerate are the dominant lithologies in the section. The quaternary sediments are underlain by the metamorphic bedrock present in the southeastern corner area, as evident from the well (Fig. 2). In general, it may be assumed that initially during the quaternary age there were thinner channel fill deposits, but with the vertical change it is marked by a well-developed increase in the thickness of channel fills that furnishes the intensity of processes with time. The aquifer material is conglomerate and bedrock with the clay units serving as the confining layers.

The areas with the highest precipitation are those of the south-eastern quadrants of Haripur which are near to Islamabad (Fig. 4). The rainfall in these areas is 3036–3477 mm/y with an average of 3256.5 mm/y. The probable cause of heavy rainfall in these areas is the high-altitude mountainous catchment and thick forest cover. On the contrary, the lowest rainfall recorded in Haripur is from the western corners of the district, which is about 831–1,272 mm/y with an average of 1050 mm/y.

Land use maps are essential to monitor social, environmental changes, activities, and arrangements such as landscape changes, ecological variations, urban planning, and management [30,48,49]. There are ten different types of land use labels in Fig. 5. The land use map of the Haripur District shows that it predominantly consists of agricultural land, comprising 42.3%, whereas forest cover involves 30.64%, followed by shrubs and bushes, which contain 2.57%. Labels of rangeland contribute 11.20%. Riverbeds, water bodies, and canals in the region cover 9.04% of the total and the settlements contribute 4.12%. Fruit orchards and barren land represent 0.11% and 0.02%, respectively. The map shows the localities of various water bodies present in the district as well as the cultivated areas for agricultural use, vegetation, and open lands [50].

4.1. Hydrogeochemistry

Hydro-chemical facies of the groundwater can be classified using the piper Trilinear diagram based on dominant ions. The information was presented on a Piper diagram [51], which is a graphical representation of hydrochemical facies based on the relative abundance of cations and anions in water samples (Fig. 6). A total of forty-two samples were studied in Haripur District and their groundwater and surface water facies were identified according to the concentration of various cations and anions present in the water. The TDS values of surface and groundwater are 444 and 365 mg/L, respectively. In the study area, cations are dominated by $Na > Mg > Ca > K$, while the main anion is HCO_3^- , with an abundance order of $HCO_3^- > Cl^- > SO_4^{2-}$. Piper diagram illustrates three main types of waters in the area $Ca-HCO_3^-$ (52.38%), $Na-Cl-SO_4$ (21.42%) and mixed type $Ca-Na-HCO_3^-$, $Ca-Mg-HCO_3^-$ (26.19%). The dominant water type in the present study area is $Ca-HCO_3^-$. $Ca-HCO_3^-$ type water is low mineralized, freshwater, and this type of water is distributed over more than half of the area, indicating active recharge [52]. The composition of water and changes in its flow path and water-rock interaction are the primary sources of major ion concentration. The dissolution

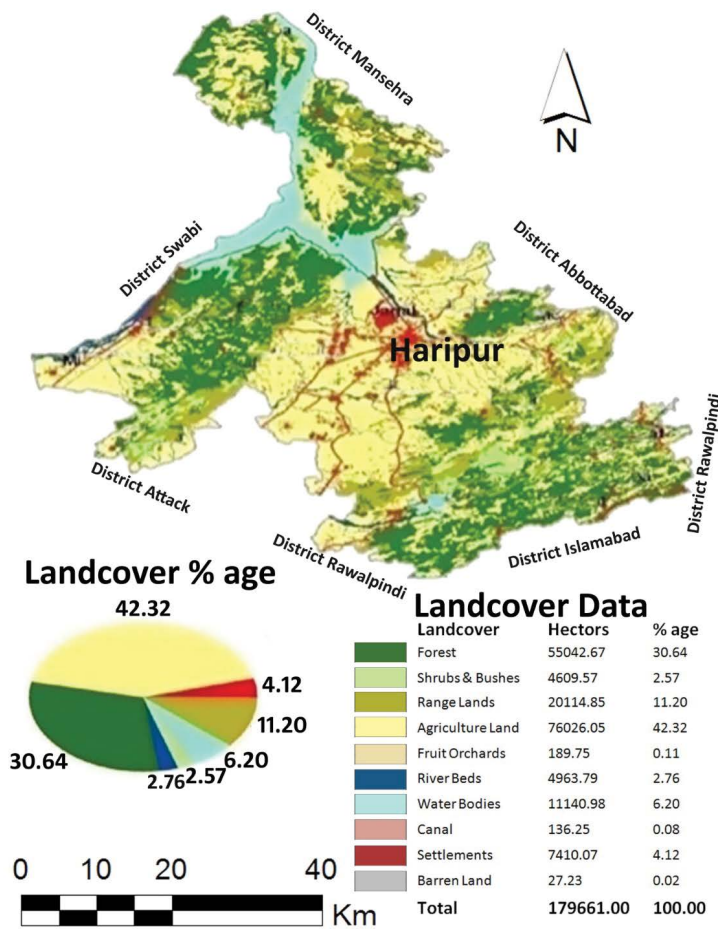


Fig. 5. Land use map of district Haripur showing water bodies, cultivated lands and buildup areas after [50].

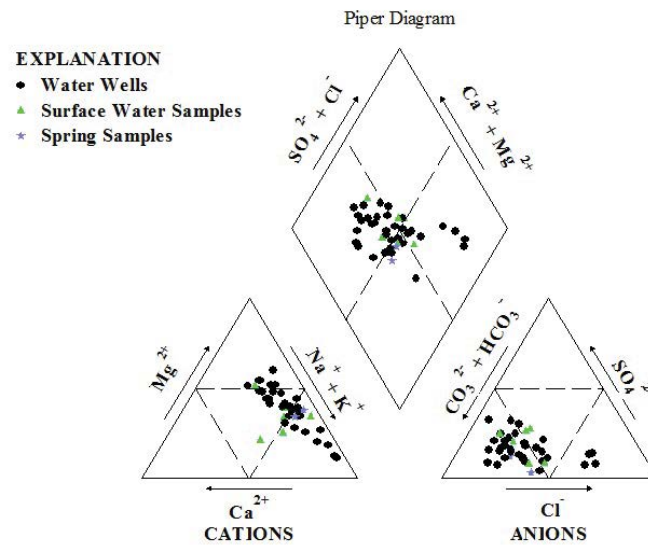


Fig. 6. Piper diagram showing the chemical composition of water.

of carbonate minerals, that is, dolomite and calcite, are the probable sources of Ca-HCO₃. The Na-Cl-SO₄ type of water has longer water-rock interaction and is mature water.

Correlation analysis is one of the most important methods for the interpretation of the hydrochemistry of water. It established the general relationship between measured chemical variables to show a multivariate pattern that helps classify data. The correlation analysis variables were pH, EC, TDS, Turbidity, Fe, Na⁺, Cl⁻, F⁻, Ca²⁺, HCO₃⁻, SO₄²⁻, K⁺, and Mg²⁺. TDS shows a good correlation with EC ($r = 0.93$) as the conduction of electrical current through the water depends on the dissolved constituents. TDS also shows a negative correlation with pH ($r = -0.42$) that points towards the alkalinity and acidity of groundwater is related to the total dissolved constituents. If in higher quantities, the dissolved constituents will lead to the acidity of the groundwater. TDS has a positive relationship with the F⁻ ($r = 0.38$), Cl⁻ ($r = 0.64$), Na⁺ ($r = 0.64$), Fe ($r = 0.34$), and SO₄²⁻ ($r = 0.48$), which supports the above relationship between TDS and pH. Furthermore, pH shows a fair relationship with the Ca²⁺ ($r = 0.40$) that represents the groundwater's mild to strongly alkaline nature with pH values above 7. Subsequently, a low concentration of HCO₃ in the groundwater system means less dissolution of carbonates, which indicates higher alkalinity of the groundwater system (Morse et al. 2007). Iron is also related to the turbidity of groundwater ($r = 0.97$). Fe is an abundant element on earth and it exists in the form of siderite, hematite, magnetite, limonite, and goethite etc. found in all types of rocks and sediments. Iron in the groundwater exists in two forms, that is, ferrous, and ferric iron. The ferrous iron is dissolved in water that is clear and colorless. Whenever this water is exposed to air, the water turns cloudy, and a reddish-brown substance begins to form that creates turbidity in the groundwater. This is the oxidized or ferric form of iron that will not dissolve in water. Cl⁻, SO₄²⁻ and F⁻ have a moderate correlation with TDS ($r = 0.64$, 0.48 , and 0.38 , respectively). In nature, the concentration of F⁻ in groundwater is controlled by many

factors [53]. The geochemistry and evolution mechanisms of F⁻ have been widely explored [54–57], and in most of these studies, the occurrence of F⁻ in groundwater is attributed to the geogenic factor. Cl⁻ is found to be strongly linked to the Na⁺ and Mg²⁺ with $r = 1$ and 0.31 , respectively. Na⁺ and Mg²⁺ are also found to have a fair correlation ($r = 0.32$). This shows the fact that sharing of these elements is gaining a salty load of groundwater in the zone [58].

4.2. Drinking water quality

The pH is a measure of the concentration of hydrogen ions. Generally, the pH value does not affect human health, though a low pH value increases the reactivity of water. The recommended guideline value for drinking water from the World Health Organization [44] for pH is 6.5–8.5. The pH of field water collected lies virtually around the value of 7.2–8.5 (Fig. 7a). The pH of all the samples lies within WHO's acceptable limit (2011) and thus satisfies the drinking purpose.

Electrical conductivity is exceedingly dependent on the number of solids present in the water (such as salts). Seawater has a higher conductivity than brackish waters because of it has higher amounts of dissolved ions of sodium and chloride ions. Most of the water sample values fall between 500 to 1,000 $\mu\text{S}/\text{cm}$ in the study area. According to WHO and drinking water quality regulatory authorities, the acceptable limit for EC is under 1,000 $\mu\text{S}/\text{cm}$. The Dingi-02 well shows an exceptionally high value for EC 1,758 $\mu\text{S}/\text{cm}$, which is an open well near the Hattar industrial waste line. The higher value of EC in Dingi-02 may be due to industrial disposed water from Hattar industries (Fig. 7b).

The measure of total dissolved constituents of organic and inorganic substances present in a liquid is called total dissolved solids (TDS). TDS is comprised chiefly of chlorides, sulfates, nitrates, carbonates, bicarbonates, phosphates, magnesium, calcium, potassium, sodium, manganese, iron, and a few others. According to WHO (2011) and drinking

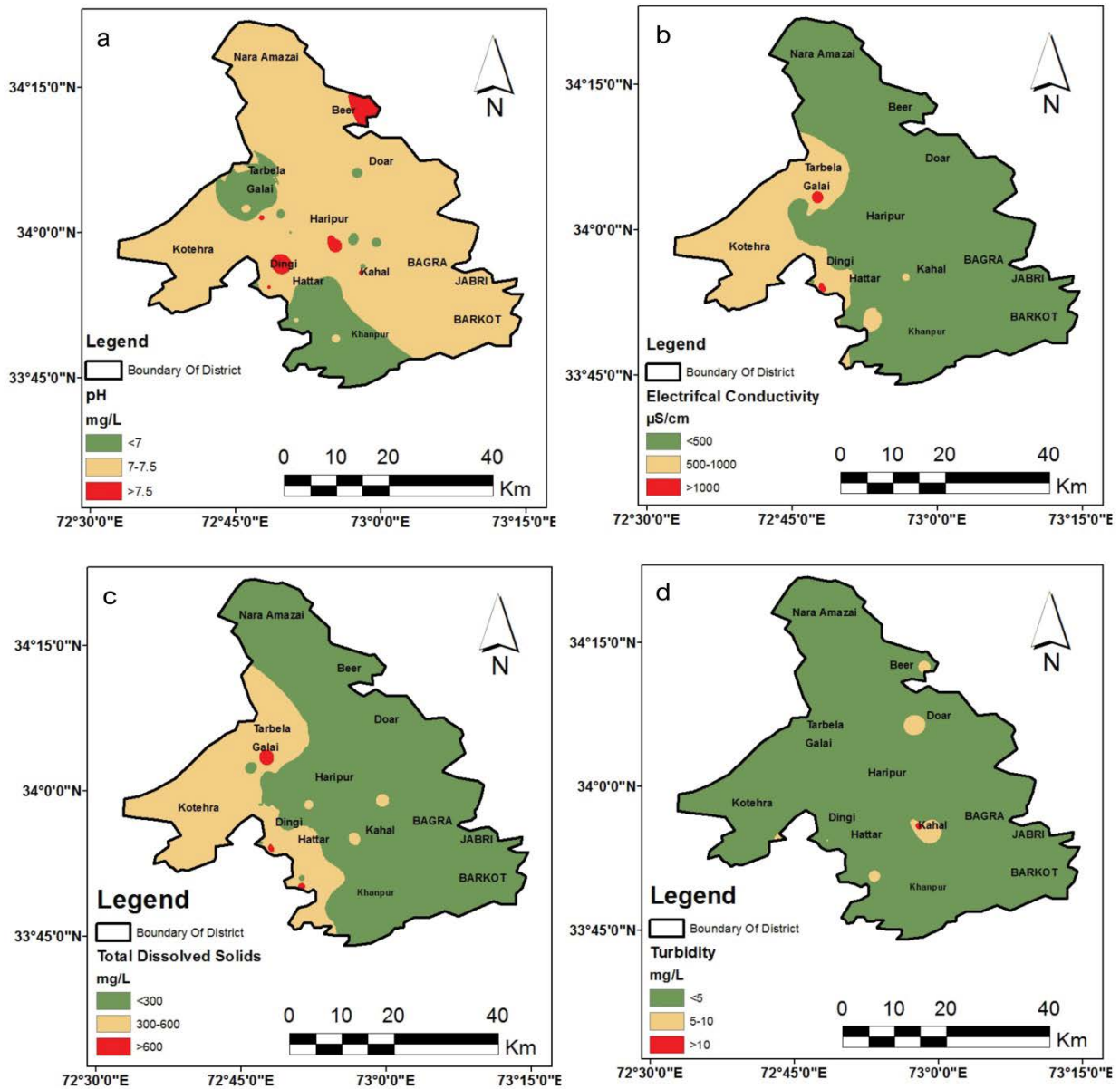


Fig. 7. The spatial distribution of (a) pH, (b) EC, (c) TDS, and (d) turbidity in Haripur area.

water quality regulatory authorities, the suggested limit is 500 mg/L. However, in the present study, TDS content values are below 500 mg/L for most samples. For example, Dingi-02 well has a value of over 1,000 mg/L, and Galai-02 has about 910 mg/L of TDS (Fig. 7c).

Haziness and cloudiness in water are mostly suspended, invisible particles, just like smoke in the air. It is called nephelometric turbidity units (NTU). The turbidity value in the study area ranges from 0 to 16 NTU, with an average of 4.7 NTU (Fig. 7d). The standard limit for turbidity is 10 NTU according to the Pakistan Standard Quality Control Authority (PSQCA), whereas the World Health Organization (WHO) allowable limit for turbidity is 5 NTU.

The assessment of sodium is critical because it is a major cation present in the water. The higher sodium

concentration causes several health problems for human health, like hypertension [59]. Overdosage of sodium causes kidney damage, edema, stroke, headaches, hypertension, stomach problems, and nausea, whereas sodium deficiency may appear as a blood pressure disorder, fatigue, mental apathy, and depression. The maximum limit for sodium in drinking water is 200 mg/L as per [44] standard. The average concentration of sodium in-field water samples was 170 mg/L. In few places, the sodium concentration was higher than in Fig. 8a. The Galai area contains a maximum concentration of sodium. It is a hilly area, and the probable cause is the dissolution of minerals.

Calcium and magnesium are interrelated in the water as both maintain an equilibrium state in most waters. Because of its higher solubility, calcium is commonly found in rocks

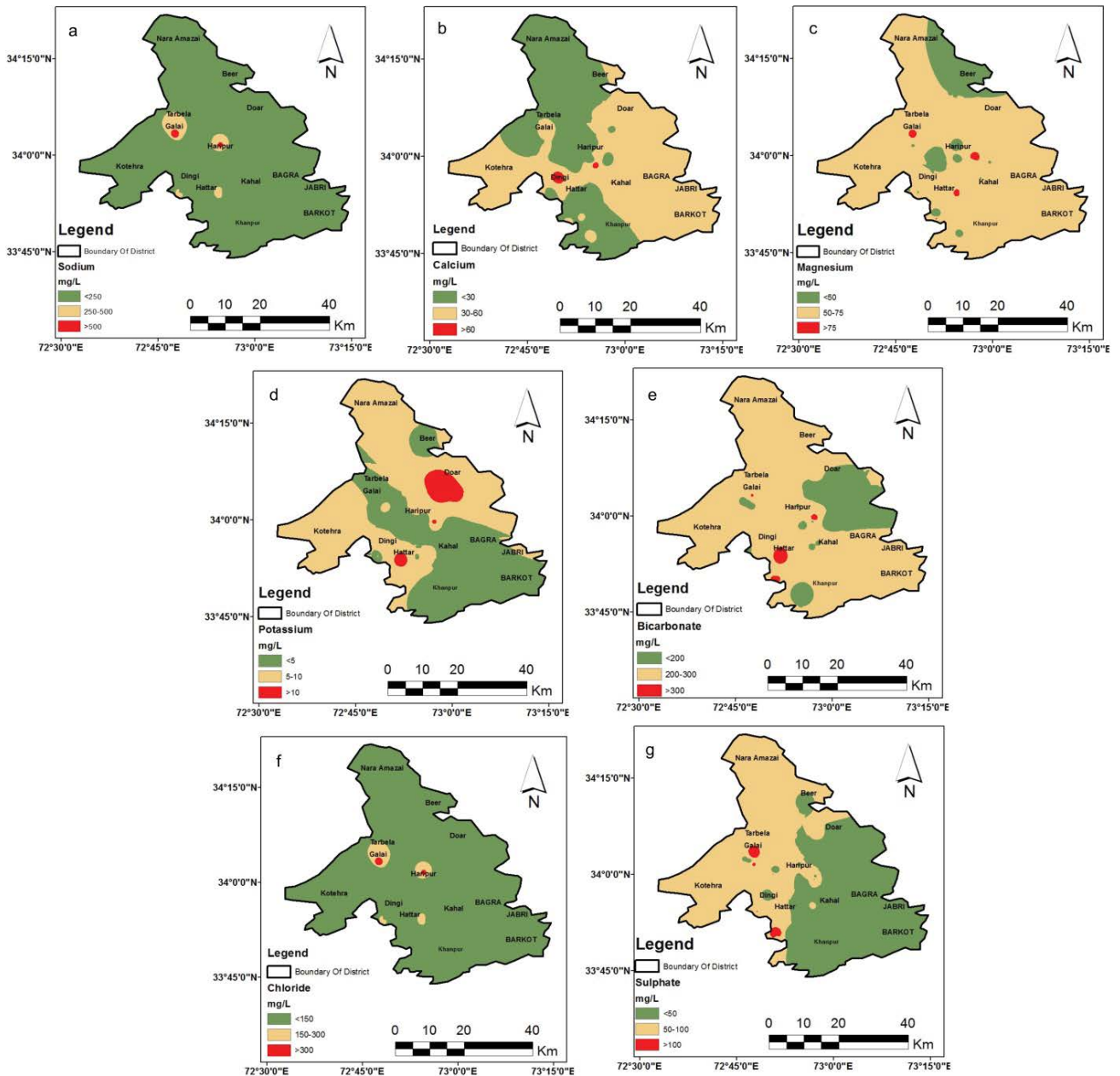


Fig. 8. Spatial distributions of major ions (a) Na^+ , (b) Ca^{2+} , (c) Mg^{2+} , (d) K^+ , (e) HCO_3^- , (f) Cl^- and (g) SO_4^{2-} in Haripur area.

and thus abundantly available in groundwater (Fig. 8b). The calcium content in the present study area ranges from 11 to 72 mg/L and the average value is 32.9 mg/L. The desirable limit for calcium is 200 mg/L [44] and PSQCA. Therefore, the entire sample in the research area falls within the desirable limit for drinking purposes.

Magnesium is one of the most important parameters for determining water quality. The magnesium values in field points ranged from 26 to 127 mg/L, with an average of 59.3 mg/L. The maximum limit for magnesium in water is 150 mg/L as per the WHO standard. All the field samples in the study area lie within the acceptable range (Fig. 8c). Excess

intake of magnesium in water causes an unpleasant taste in water. However, magnesium is helpful for the functioning of cells in enzyme activation [60].

Potassium is an essential element for humans, as it maintains a balance in the fluid in the human body but is not found in high concentrations in water. According to the WHO, the permissible limit for potassium is 12 mg/L [44]. In the present study area, the average concentration of potassium is 8.4 mg/L. Therefore, most of the area in the study area shows allowable limits for potassium, whereas eight samples shown in Fig. 8d exceed the permissible limit.

Bicarbonate is an important anion present in the groundwater. The concentration of bicarbonate in water depends mostly upon the geology of the area. Carbonate rocks, calcite, and dolomites are the primary sources of bicarbonates. In the present study, the range of HCO_3^- is from 160 to 400 mg/L with an average of 255 mg/L, which is shown in Fig. 8e. All the samples fall under the allowable limit. The permissible limit for HCO_3^- is 500 mg/L.

Chloride is broadly spread in nature as a salt of calcium chloride (CaCl_2), potassium chloride (KCl) and sodium chloride (NaCl). Chloride ions are highly mobile and leached from various rocks into the soil and water by weathering [61]. Chloride is widely used in the chemical industry, snow ice control and the production of fertilizers. In the present study area, range of chloride was from 17 to 469 mg/L with an average of 101 mg/L. The permissible limit for chloride is 200 mg/L [44]. Some of the samples exceed the permissible limit of Cl^- (Fig. 8f). The maximum value of Cl^- reported in Galai-02 sample, which is 469 mg/L.

Sulfate ions are also present in natural water. These are derived from gypsum and the soluble sulfide minerals added into groundwater through oxidation. An excess dosage of sulfate in water causes respiratory problems [62]. In the present study, the sulfate concentration ranged from 14 to 141 mg/L, with an average of 61 mg/L. The permissible limit for sulfate is 200–250 mg/L according to the World Health Organization [44]. Fig. 8g indicates that the field samples are falling within the allowable limit for drinking purposes.

The presence of arsenic in water may be due to the erosion of rocks. The type of arsenic depends upon its source. Usually, it is toxic and harmful. In our research area, almost all the samples are free from arsenic except for two localities, Dingi, and Jarikas, shown in Fig. 9a. The prominent cause of arsenic in this area is industrial discharges that are being disposed of directly into Jarikas and Dojal Nala untreated. It has been reported that Hattar Industrial Estate discharges 20,000 gallons of wastewater into various Nalas (natural streams). Hattar Industrial Estate houses many chemical units, the textile industry, heavy electrical, and vegetable oil production units. As a result, people living near Hattar Industrial Estate suffer from kidney disorders, respiratory problems, skin allergies, and eye diseases [63].

Fluoride is also found in trace amounts in water. The sea, rivers, and lakes contain less than 0.5 mg/L fluoride through a higher fluoride concentration associated with the groundwater sources. The small amount of fluoride in drinking water is beneficial [64]. Fluoride is also significant against cavities and tooth decay, according to [65]. Most of the population in Pakistan is affected due to fluoride contamination in drinking water [66]. The fluoride in the study area ranges from 0 to 6.7 mg/L, with an average of 3.8 mg/L. The standard limit for fluoride is 20 mg/L according to the National Environmental Quality Standard (NEQS) by EPA, whereas the World Health Organization [44] allowable limit for fluoride is 4 mg/L. The maximum reported value of fluoride in the study area is 6.7 mg/L in the Dingi-02 area, which is shown in Fig. 9b.

The fourth most abundant element in the earth's crust is iron. Iron solubility in natural water is dependent upon oxidation-reduction potential and pH. Iron is an essential element containing significant biological proteins [61]. The WHO recommended guidelines for iron value in drinking water is 0.3 mg/L. The range of iron in the study area is from 0 to 0.93 mg/L as shown in Fig. 9c.

According to the spatial distribution maps of the hydrochemical constituents in groundwater, a wide variation was found in the Dingi-02 and Galai-02 locations. The rest of the localities are within the permissible range and thus fit for domestic purposes. The following parameters exceed the permissible limits in Dingi-02 locations: EC, TDS, arsenic, fluoride, chloride, and iron. According to the geological map of the district, Dingi-02 area is mostly covered with recent alluvium deposits. The annual precipitation rate at this area is also very low compared with other areas, and the area lies at lowest elevation point in the district. The Dingi-02 area is the main discharge point where Hattar industrial waste exhausts directly into Jarikas nala, suggesting the mixing of untreated discharge into water and causes anthropogenic contamination in the zone. The parameters exceeded in the Galai area are TDS, arsenic, and sodium. Topographically, the Galai area lies at the high-altitude location and the area receives moderate to high rainfall compared with the adjacent locations. The Tanawal Formation (Metamorphic) is present in the

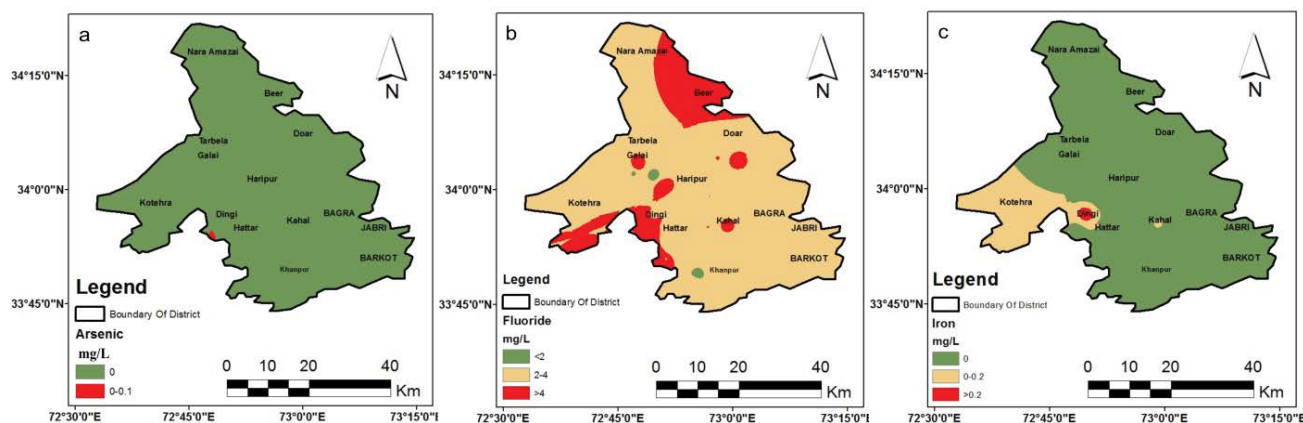


Fig. 9. Spatial distribution of (a) arsenic (As), (b) F^- and (c) Fe in the water of Haripur area.

region, and the probable cause of the higher concentration is the dissolution of particular minerals in the region.

4.3. Irrigation water quality

A high concentration of sodium affects the physical properties of the soil. Sodium enriched water reduces the permeability of the soil and causes the soil to disperse [67]. SAR is an important parameter. Its value from 0 to 3 is considered good, while greater than 9 is unsuitable [68]. The SAR value in the study area ranges from 1 to 17 with an average of 4. Four samples in the study area exceeded the permissible limit and were found unsuitable for irrigation.

All the samples are plotted in Wilcox's diagram [69] to classify the water in Fig. 10. Sodium is plotted against EC. Based on Wilcox's diagram classification, the majority of the studied water samples are classified as C_2S_1 (90%) (medium salinity with low sodium), which is permissible for irrigation. The rest of the samples (04) are classified as C_3S_2 (10%) (High salinity with medium sodium) which is good for irrigation purposes.

If the concentration of calcium and magnesium is lower than the concentration of bicarbonate and carbonate, then soil fertility and plant growth are affected. A sample with an RSC value above 2.5 meq/L is not suitable for irrigation, whereas less than 2.5 meq/L values are suitable (Richards, 1954). All the observed water samples are within the permissible range of RSC and fit for irrigation usage.

Magnesium hazard values exceeding 50 mg/L are unsuitable for irrigation. Water samples reflect that 95% of the locations exceeded the magnesium hazard value and thus are unfit for irrigation.

Water having a KR range greater than 1 is considered unsuitable for irrigation [70]. In the study area, 84% of the samples are within the KR value range, indicating good quality for irrigation, whereas 16% of the samples exceed the KR value range and are unfit for irrigation.

5. Conclusions

The current research provides significant information on groundwater quality for drinking and irrigation usage in Haripur District, Khyber Pakhtunkhwa, Pakistan.

The physicochemical results of the present study revealed that pH, turbidity, calcium, magnesium, sulfate, iron and bicarbonate in the groundwater samples lie within the permissible range of the World Health Organization.

Chlorides, arsenic, fluoride, electrical conductivity (EC) and total dissolved solids (TDS) concentrations exceed the permissible limit in the Dingi-02 locality. Apart from this the arsenic also shows a higher concentration in the Jarikas area. The sodium, chloride and potassium concentration exceed in the Galai-02, Bandi Seeran and Pind Munim localities. Potassium concentration have also been found higher in several parts of the Haripur area. Two plausible sources of groundwater pollution are delineated in this study that is the anthropogenic and the geogenic. The Dingi 02 area and its surroundings are infested by the anthropogenic influence whereas the Galai area is found to be influenced by the natural processes leading to the higher concentration of various constituents.

Three major types of water were identified, including the dominant water type is $Ca-HCO_3$ (52.38%), $Na-Cl-SO_4$ (21.42%) and a mixed type, $Ca-Na-HCO_3$, and $Ca-Mg-HCO_3$ (26.19%). $Ca-HCO_3$ type water is low mineralized, freshwater, and it is distributed over more than fifty percent (50%) of the area, indicating active recharge and young groundwater. The rest of the area shows different stages of maturity of groundwater, that is, from hydrochemically intermediate to mature groundwater. The irrigation water quality has been assessed by using the sodium adsorption ratio, residual sodium carbonate, magnesium hazard, electrical conductivity, and Kelly's ratio. Most of the groundwater fall into the safe category for irrigation practices. Wilcox's classification shows that 90% of samples fall into the C_2S_1 zone, which is permissible for irrigation. However, two important parameters

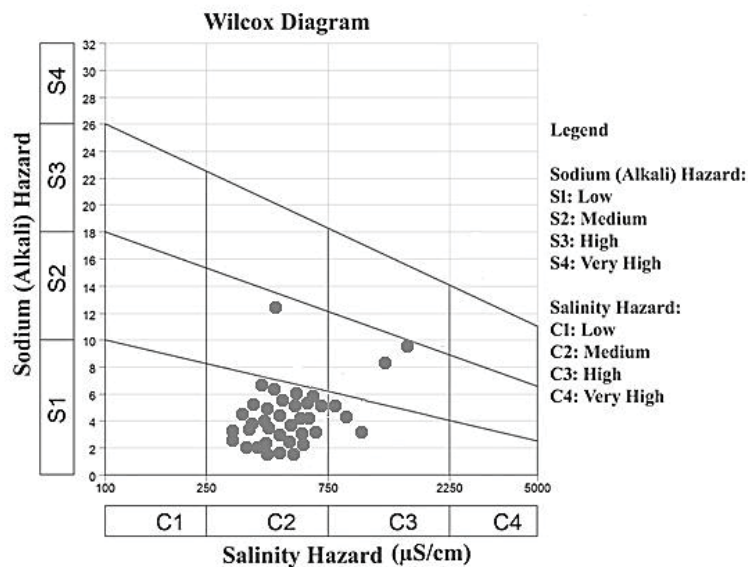


Fig. 10. Wilcox diagram for water of the Haripur area.

suggest improving water before its use, that is, the sodium and the magnesium hazard for irrigation purposes.

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Authors contributions

Atif Mehmood contributes literature review, software, and formal analysis. Muhsan Ehsan and Anwar Qadir contribute to conceptualization and methodology. Abid Ali, Danish Raza, and Haroon Aziz contribute the Writing – Review and Editing section of the paper.

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