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1 **Environmental Significance Statement**

2 The safety of drinking water and irrigation supplies greatly depends on groundwater quality,
3 but it is vulnerable to geogenic contaminants that are challenging to predict. Arsenic (As) is
4 one of the most toxic environmental pollutants of global concern. The concurrent release and
5 accumulation of geogenic As and iron (Fe) in freshwater systems pose significant global
6 environmental challenges, yet their co-occurrence dynamics and source linkages remain poorly
7 understood. This study investigates the spatial correlation and source apportionment of As and
8 Fe in shallow and deep aquifers of Shorkot, Punjab, Pakistan.



Co-occurrence, hydrogeochemical associations, and risk assessment of arsenic and iron in deep and shallow aquifers of Punjab, Pakistan

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Abstract

The safety of drinking water and irrigation supplies depends on groundwater quality but is vulnerable to geogenic contaminants that are challenging to predict. The concurrent release and accumulation of geogenic arsenic (As) and iron (Fe) in freshwater systems pose significant global environmental challenges, and their co-occurrence, dynamics and source linkages remain poorly understood. This study investigated the spatial distribution, co-occurrence, hydrogeochemical associations, and health risks of As and Fe in groundwater samples (n=74) collected from shallow (<19.8 m) and deep (>19.8 m) aquifers of Shorkot, Punjab, Pakistan. Results revealed that As concentrations (0.05 to 22.3 µg/L), with 19% of samples exceeded the WHO guideline (10 µg/L), while none of the samples surpassed the Pak-EPA threshold (50 µg/L). Iron levels varied between 0–218 µg/L, with higher mean concentrations (Fe: 74 µg/L) in deep aquifers compared to shallow ones (Fe: 66 µg/L). Health risk assessments demonstrated carcinogenic potential, with cancer risk (CR) values exceeding the acceptable threshold (CR > 0.0001) for both adults (0.0034) and children (0.005). Hazard quotient (HQ) and average daily dose (ADD) values further indicated non-carcinogenic risks, particularly for children (HQ: 0.5; ADD: 0.0002 mg/kg/day). A strong positive correlation ($r = 0.80$) between As and Fe highlighted the critical role of Fe-(hydr)oxide mineral dissolution in mobilizing As into groundwater. The study emphasizes to address chronic exposure risks and advocates for comprehensive source identification for sustainable groundwater management. This work advances the understanding of As-Fe synergies in alluvial aquifers and provides a framework for assessing similar geogenic contamination in vulnerable regions globally.

Keywords: Hydrogeochemistry; Iron oxides; Reduction; Health risk

1. Introduction

Water quality is very important for its utilization in different sectors such as drinking, irrigation and industry ¹. Groundwater is the main source of freshwater and the most easily available reservoir for drinking water, industrial and irrigation purposes. However, the recent industrial



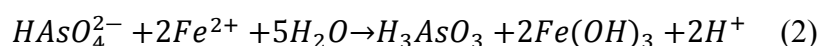
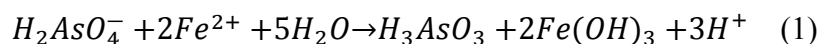
growth, population increase and climate change, along with natural processes have compromised the groundwater and environmental quality^{2,3}. Groundwater pollution is rapidly increasing at a global level^{4,5}. This enhanced groundwater contamination thus poses a severe hazard to environmental and human health^{6,7}.

Arsenic (As) is a ubiquitous element found in the natural environment (0.00005% crustal abundance) and known as a potential toxicant and carcinogenic agent⁸⁻¹⁰. Over 140 million people in > 70 countries worldwide are susceptible to As toxicity due to groundwater As contamination¹¹. Approximately 200-500 million people have been indicated to be at risk from exposure to As concentrations above the WHO drinking-water guidelines globally and about 270 million people in South Asia, with up to 30 million people in the Ganges River delta alone¹². Exposure to As containing groundwater induces toxic effects on public health if its level exceeds 10 µg/L¹¹. Using a machine learning approach,¹³ predicted that hundreds of thousands of residents in the Hetao Basin can experience arsenicosis due to high levels of As in groundwater. Arsenic exposure is attributed to multi-organ cancer, hyperkeratosis, black foot disease, and melanosis through potable water at certain concentrations^{14,15}. Recent studies have reported the elevated levels of As associated with international embodied trade across borders. Owing to the severe toxic effects associated with As exposure and poisoning, it is of pronounced significance to monitor its prevailing levels in different environmental compartments and associated health hazards.

The release of As into groundwater is a complex process influenced by the interplay of local hydrology, geology, and geochemistry^{16,17}. Arsenic geochemistry is governed by multiple factors, including aquifer mineralogy, adsorption-desorption dynamics, dissolution-precipitation reactions, redox conditions, organic matter content, and aquifer properties^{18,19}. Natural processes such as erosion, weathering, and the dissolution of As-bearing minerals, particularly Fe oxyhydroxides and sulfides, contribute to As mobilization in groundwater^{20,21}.



In groundwater, As exists in two inorganic forms: arsenite (As(III) under reducing conditions and arsenate (As(V) under oxidizing conditions. These species differ in their solubility across a wide range of pH and redox potential (Eh) conditions²². Redox reactions play a critical role in As mobilization. For instance, the reduction of As(V) to As(III) in the presence of Fe(II) can be described by the following reactions²³:



Under anoxic conditions, As(III) dominates due to the reductive dissolution of Fe-oxides and competitive adsorption-desorption processes^{24, 25}. Conversely, As(V) prevails in aerobic environments with arsenious acid (H_3AsO_3) and arsenic acid ($H_2AsO_4^-$, $HAsO_4^{2-}$) being the dominant species at moderate and high Eh values, respectively²². These redox-driven transformations significantly influence As concentration and its mobility in groundwater^{26, 27}.

The co-occurrence of As and Fe in groundwater is particularly significant as Fe minerals are often considered as both sources and sinks for As. Pyrite oxidation and the reductive dissolution of Fe oxyhydroxides are widely recognized As releasing mechanisms¹². This interplay between As and Fe not only affects As speciation and mobility but also has implications for remediation strategies. Understanding the spatial distribution and correlation of As and Fe in groundwater is therefore critical for assessing geochemical processes and associated health risks.

The present study is therefore focused on the co-occurrence, hydrogeochemical associations, and risk assessment of As and Fe in groundwater of deep and shallow aquifers in Punjab, Pakistan. The specific objectives are to: (i) spatially analyze groundwater quality in Tehsil Shorkot, (ii) evaluate the spatial distribution and correlation of As and Fe in groundwater; (iii) investigate the hydrogeochemical processes driving As and Fe mobilization; and (iv) assess the

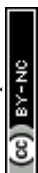


human health risks associated with the consumption of As and Fe containing groundwater. This study aims to provide a comprehensive understanding of As-Fe interactions and their implications for groundwater quality in urban and peri-urban areas.

2. Methodology

2.1 Study area

Jhang district is located 72 km from Faisalabad District in the Punjab province in Pakistan's centre (Figure 1). It is located on the Chenab River's eastern bank. It is the 18th most highly populated city in Pakistan, with latitudes ranging from 31.317475° and 72.347382° to 31.222351° and 72.326846° North and East, respectively. The topography of Tehsil Shorkot is flat, and it extends over an area of 2013 km² with 0.67 million residents. The major crops of the sampling area are wheat, sugarcane, chickpea, and rice. The groundwater composition depends on the local geology and contamination of the surface water bodies. The study area is surrounded by the Chenab River, which passes by industrial and urban cities like Sialkot, Gujrat, Gujranwala, Jhang, Faisalabad, and Multan. The majority of these cities discharge their agricultural, industrial, and other waste effluents into the river²⁸. This river serves as the main source of groundwater recharge in the study area. Residents of Shorkot tehsil rely heavily on groundwater for domestic, drinking, and crop irrigation activities. Fine silty mixed hyperthermic fluventic halpocambid soils with considerable aeolian deposits are found close to Shorkot, Punjab, Pakistan. Due to the unconfined aquifer and groundwater storage, streams create discontinuous, lenticular strata with variable, fine- and coarse-grained sediments.



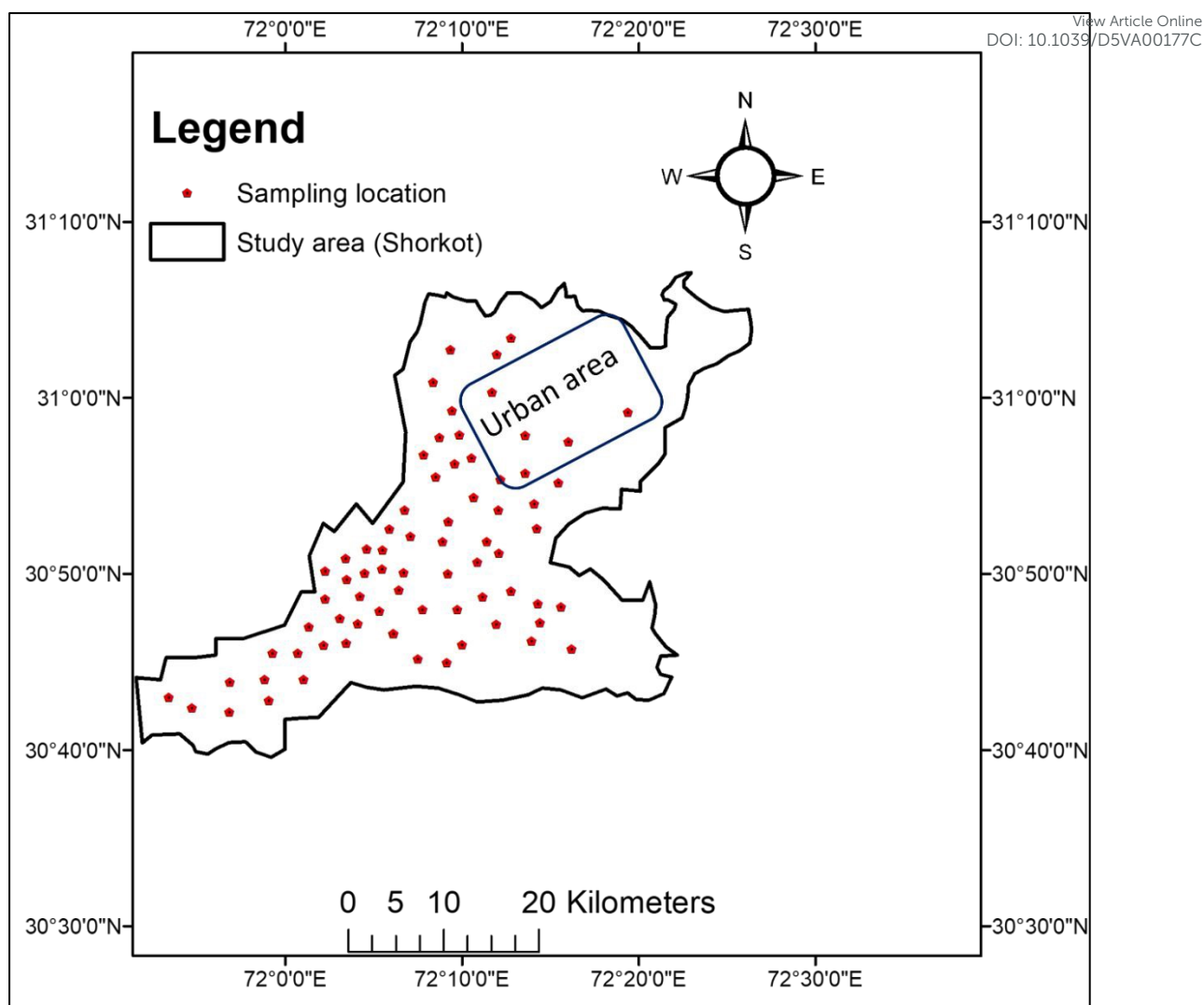


Fig. 1: The sampling locations in the study area of Shorkot.

2.2 Water sampling and storage

Groundwater samples ($n=74$) were collected using standard protocols to represent the whole study area²⁹. The water samples were obtained from hand pumps, electric pumps, and tubewells installed at varying depths (5-120 feet). Before collection, the water was purged for 5-6 minutes³⁰. Groundwater samples were collected from 74 peri-urban and sub-urban locations in Tehsil Shorkot, targeting four different water sources: canals (6 samples), tube wells (14 samples), hand pumps (42 samples), and electric pumps (12 samples). From each site, 5-6 water samples (100 mL each) were collected and their composite was used to indicate site variability. All the sample bottles were safely sealed, labeled with site ID, put in an ice bath, and delivered to the



laboratory. To avoid exposure to direct sunlight, the samples were kept at 4°C in the dark and examined within seven days of sampling to avoid physicochemical changes during storage. Based on previous research in Pakistan, the well depth was classified as deep (> 19.8 m) or shallow (<19.8 m)³¹.

2.3 Analytical procedures

All the water samples were filtered via Whatman filter paper No. 42 and kept in plastic bottles for further analysis. All the water samples were analyzed for physicochemical variables. All the chemicals used were acquired from Merck Chemicals, Germany. During solution preparation and analysis, double-distilled water was used to ensure the results' reliability.

2.4 Physicochemical analysis of groundwater

The portable pH meter (Jenway, Model-370), and EC/TDS meter (Jenway, Model-470) were used to evaluate water samples for pH, EC, and TDS. A flame photometer (BWB Technologies, Berkshire, UK) was used to measure the concentrations of Ca, K, and Na in water samples at analytical wavelengths of 422.7 nm, 589.0 nm, and 766.5 nm, respectively. The barium sulphate (BaSO₄) precipitation method was used to determine the SO₄ concentration in groundwater with calorimetric method. The major anions present in water, such as Cl, CO₃, and HCO₃, were measured following the previously described standard titration methods³².

2.5 Arsenic and iron analyses

The Fe content in water samples was analysed by atomic absorption spectrophotometer (AAS, PerkinElmer pinAAcle 900F, USA) at 372.0 nm wavelength. While the hydride generation AAS (HG-AAS) was used to measure As concentration at 193.7 nm wavelength. The water samples for As analysis were prepared with 1% NaOH, 3% NaBH₄, and 1.5% HCl³³.

2.6 Quality controls and analytical precision



For quality control/quality assurance (QC/QA), the AAS was calibrated using 1000 mg/L stock solution (CPAchem, Bulgaria), and working standards were prepared through dilution. For every twenty samples, standards of known As and Fe concentrations were run for QC/QA. The certified reference materials, namely As (A003.2NP.L5) and Fe (A019.2NP.L5), were used to authenticate the findings of the As and Fe analysis on AAS in water samples. The analytical accuracy was ensured through recovery, which ranged from 78 to 116%. Each sample's reading was replicated three times after the equipment was calibrated with standard solutions.

2.7 Exposure and cancer risk assessment

Health risk assessment parameters (Eq. 3-5) were quantified for the potential health risks related to As/Fe-contaminated water. The hazard quotient (HQ) is measured by dividing the chronic daily intake (*ADD*) with oral reference dose (*RfD*) of As/Fe.

$$ADD = \frac{C \times IR}{BW} \quad (3)$$

$$HQ = \frac{ADD}{RfD} \quad (4)$$

The cancer risk (CR) value for As/Fe was estimated as follows:

$$CR = ADD \times CSF \quad (5)$$

Here, C stands for the As and Fe level in water, IR for the volume of water consumed each day (2 L/day), BW for the average body weight of an adult (72 kg), *RfD* for Fe and As (0.007 and 0.0003 mg/kg/day, respectively), and CSF for As (1.5 mg/kg/day).

2.8 Statistical analysis



Microsoft Excel (2019) software was employed to perform descriptive statistics for all the factors. Utilising XLSTAT (ver. 2018), Pearson correlation and principal component analysis were performed. The Geographical Information System (GIS) (ver. 10.4.1) was used for interpolation of Fe and As data with the Inverse Distance Weighted (IDW) technique (Figure 1-2). In the Grapher (version 10.4), the Piper plots and Durov diagram are used to demonstrate the water hydrogeochemistry.

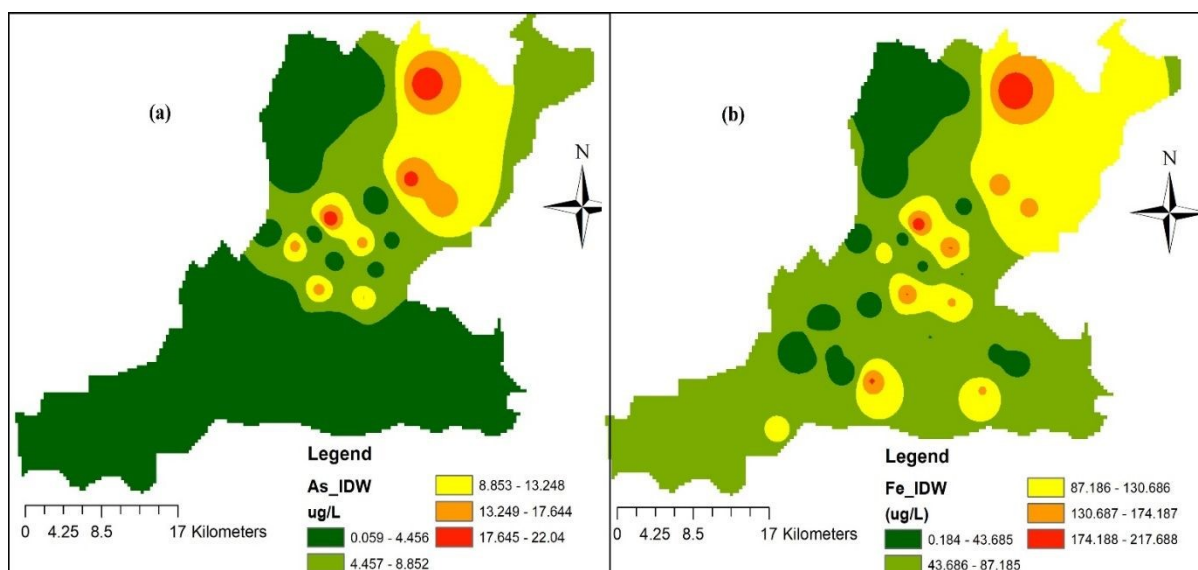
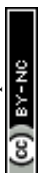


Fig. 2: The IDW map of As ($\mu\text{g/L}$) (a) and Fe ($\mu\text{g/L}$) (b) at 74 sites of tehsil Shorkot along River Chenab floodplains

3. Results and Discussions

3.1 Arsenic concentration in groundwater

In water samples, the mean As concentration was $4.1 \mu\text{g L}^{-1}$ ($0.05\text{-}22.4 \mu\text{g L}^{-1}$) (Figure 3). On average, 19% of groundwater samples exhibited an As level of $> 5 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$, respectively. Nevertheless, none of the water samples exceeded As limit of $50 \mu\text{g L}^{-1}$. The results showed that the water samples were within the Pak-EPA's safe limits. However, the WHO considers a concentration of more than $10 \mu\text{g L}^{-1}$ to be carcinogenic.



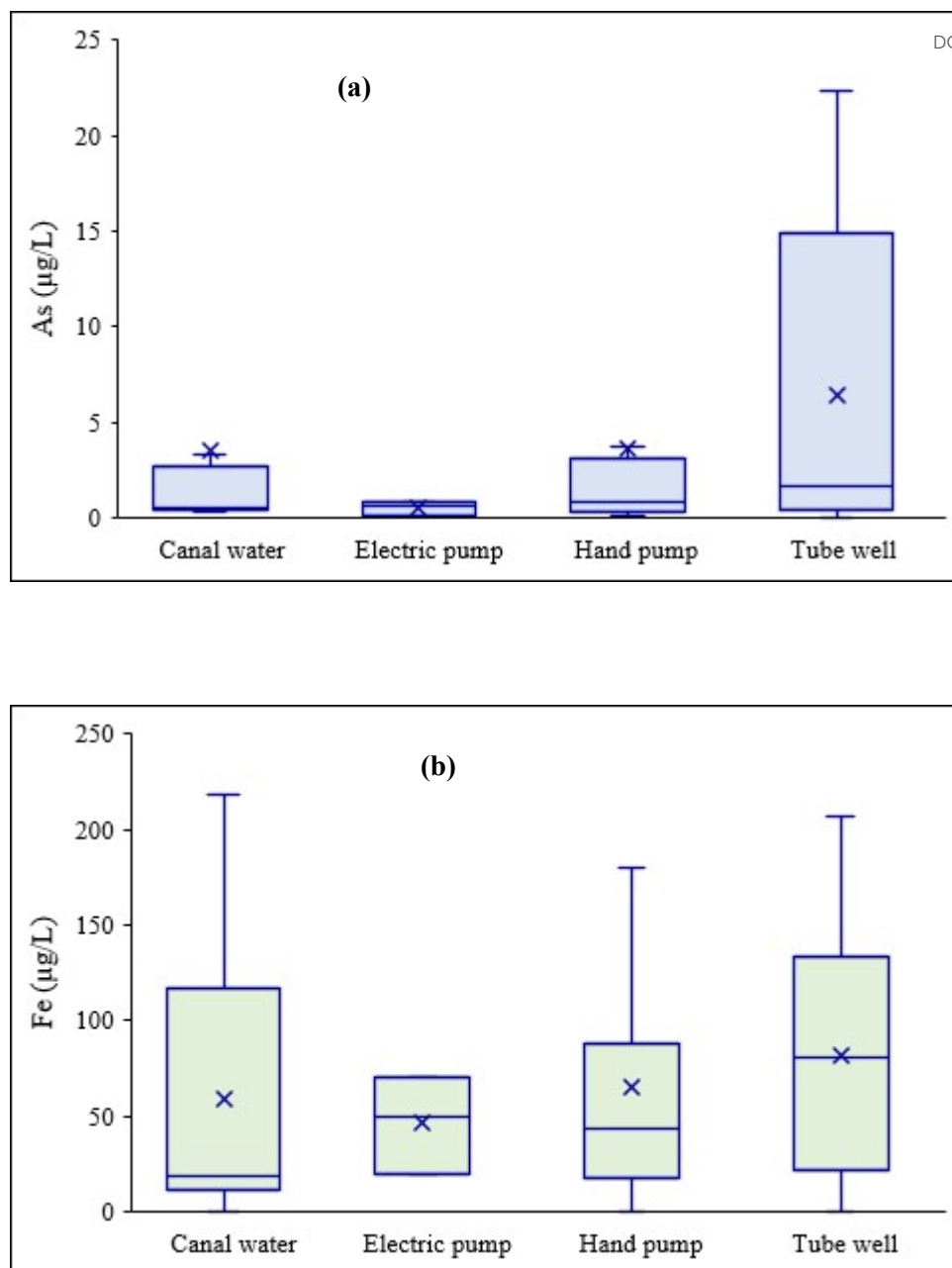
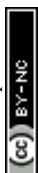


Fig. 3: Concentrations of As (a) and Fe (b) in water samples of tehsil Shorkot.

The data were evaluated with respect to differences in location, i.e., urban, peri-urban, and rural areas (Table 1). The average concentration of As was $5.2 > 4.3 > 1.3 \mu\text{g L}^{-1}$ respectively for peri-urban, rural, and urban areas, respectively. About 25% and 21% of water samples in peri-urban and rural areas, respectively, exceeded the WHO limit for As. This reveals that there is no major difference in As groundwater contamination among peri-urban, rural, and urban areas.



This can be due to possible common natural sources of As for all the three types of sampling areas.

Table 1: Arsenic contents ($\mu\text{g}/\text{L}$) in water samples with respect to area and well depth.

Statistics	Urban	Rural	Peri-urban	<19.8m	>19.8m
Mean	1.3	4.3	5.2	3.7	6.1
SD	1.3	6.7	8.3	6.2	8.6
Minimum	0.06	0.05	0.19	0.06	0.05
Maximum	3.3	22.3	21.3	21.3	22.4
Median	0.9	0.7	0.8	0.7	0.7
% > WHO limit	0.0	21	25	15.8	33.3

3.2 Distribution of arsenic as a function of depth and source

Average As contents increased from 3.7 to 6.1 $\mu\text{g L}^{-1}$ with increasing well-depth (<19.8 - >19.8 m) (Table 1, Figure 3). About 15.7% and 33.3% of water samples in shallow and deep wells, respectively, have higher As contents than the WHO safe limit. The increasing As concentration with depth is associated with the geochemical conditions of the aquifers. The redox reaction and pH variation govern the release of As from the mineral ores³⁰. Deep water wells (> 19.8 m) had a greater mean Fe content (74 $\mu\text{g L}^{-1}$) than shallow water wells (19.8 m) Fe content (66 $\mu\text{g L}^{-1}$). This could be ascribed to the dissociation of As-bearing pyrites³⁴. Moreover, the shallow groundwater is commonly replenished with the recharge due to its enhanced groundwater pumping for various applications. Contrarily, deep water stays in the Earth's crust for a longer time and has more contact with As/Fe-bearing minerals (FeS_2 , FeAsS , As_4S_4 , and As_2S_3) than shallow water. This can be a plausible reason for higher As/Fe levels



in deep water than shallow water. Of these, reductive dissolution of As-bearing host minerals (mainly Fe/Mn-(oxyhydr)oxides) is considered the dominant mechanism of As mobilization in contaminated aquifers³⁵. The As is dominant in shallow depth (<150 m) throughout the Cenozoic fluvial-deltaic sedimentary aquifers (Chatterjee 2024), while its elevated level is reported at higher depths (Sadiq et al. 2024). Moreover, wells in the Himalayan-sourced alluvial flood and delta plains of India, Bangladesh, Nepal, Pakistan, and Myanmar had very high levels of As, but adjacent groundwater well bores drilled to similar depths just a few meters apart have wide variation in dissolved As concentrations (<10 $\mu\text{g L}^{-1}$ to >1,000 $\mu\text{g L}^{-1}$). The As-concentration varied consistently across diverse water sources and well depths (Figure 3). A relatively greater level of As (6.9 $\mu\text{g L}^{-1}$) was found in tube wells because of the deep depth of the well as compared to other sources like hand pumps (3.6 $\mu\text{g L}^{-1}$), canal water (0.65 $\mu\text{g L}^{-1}$) and electric pumps (0.39 $\mu\text{g L}^{-1}$). More than 36% of tube well samples (depth > 19.8 m) had an As level of > 10 $\mu\text{g L}^{-1}$, and more than 16% of hand pump samples (depth > 10.6 m) had an As content of > 10 $\mu\text{g L}^{-1}$. However, none of the canal and electric pump water had As contents above the WHO limit³⁶. The present data showed that most of the hand pumps and tubewells are installed at deeper depths and showed higher As and Fe concentrations than electric pumps across the study area of Tehsil Shorkot.

3.3 Distribution of iron as a function of depth and source

The maximum Fe concentration (218 $\mu\text{g L}^{-1}$) in water samples was obtained at <19.8 m depth (Table 2). The concentration of Fe was 72.2 > 62.6 > 54.3 $\mu\text{g L}^{-1}$ in rural > peri-urban > urban areas, respectively. The level of Fe (90.1 $\mu\text{g L}^{-1}$) in tube wells is higher than in hand pumps (62.8 $\mu\text{g L}^{-1}$), electric pumps (0.5 $\mu\text{g L}^{-1}$) and canal water (21.2 $\mu\text{g L}^{-1}$). Furthermore, Fe concentration (66-74 $\mu\text{g L}^{-1}$) increased with well depth (< 19.8 to > 19.8 m), just like As.³⁷ reported that Fe increased with depth, suggesting that the reduction dissolution of Fe (III)



minerals was promoted in a reductive environment and Fe(II) became the dominant form of total pore water soluble Fe concentration. Except for some Fe (III) minerals, As is also soluble in all rock types and flows downward with groundwater ³⁸.

Table 2: Iron concentration ($\mu\text{g/L}$) in water samples with respect to area and well depth.

Statistics	Urban	Rural	Peri-urban	<19.8m	>19.8 m
Mean	54.3	72.2	62.6	66	74
SD	47.0	59.8	71.1	59.1	69.7
Minimum	16	10	0	0	0
Maximum	138	207	218	218	207
Median	39	54	35	48	81

3.4 Correlation of As and Fe

Results revealed that the Fe concentration increased with As concentration, which reflects a strong correlation ($r=0.80$) between As and Fe in the aquifers (Table 3). Furthermore, high As concentrations are associated with elevated Fe concentrations in groundwater ³⁹. The mechanisms that are involved in As release in groundwater are: i) oxidation and dissolution of minerals containing As and Fe; ii) weathering of As-containing minerals ²⁶; and iii) Fe reduction increases As mobility in the aquifer ⁴⁰, iv) and competitive ion exchange process using dissolved phosphate fertilizers ³⁵.

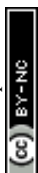


Table 3: Pearson correlation of all the water variables of sampling area.View Article Online
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Variables	As	Fe	pH	EC	TDS	Cl ⁻	Na ⁺	K ⁺	Li ⁺	Ba ²⁺	Ca ²⁺	Ca ²⁺ + Mg ²⁺	HCO ₃ ⁻
Fe	0.8												
pH	0.1	-0.2											
EC	- 0.1	0.1	-0.3										
TDS	- 0.1	0.1	-0.3	1.0									
Cl ⁻	0.1	0.2	-0.1	-0.1	-0.1								
Na ⁺	- 0.1	0.0	-0.2	0.8	0.8	-0.3							
K ⁺	- 0.1	0.2	-0.4	0.6	0.6	-0.1	0.3						
Li ⁺	- 0.1	0.2	-0.4	0.9	0.9	-0.1	0.7	0.8					
Ba ²⁺	0.0	0.2	-0.3	0.3	0.3	0.1	0.1	0.6	0.4				
Ca ²⁺	0.0	0.0	-0.2	0.6	0.6	-0.2	0.8	0.1	0.5	-0.1			
Ca ²⁺ + Mg ²⁺	0.1	0.1	-0.1	-0.4	-0.4	0.3	-0.5	0.0	-0.3	-0.1	-0.2		
HCO ₃ ⁻	0.0	0.0	0.0	0.4	0.4	0.1	0.2	0.2	0.2	0.2	0.1	-0.1	
CO ₃ ²⁻	0.2	0.1	0.2	0.1	0.1	-0.2	0.1	0.0	0.0	-0.1	0.2	-0.2	0.3

In fact, both As and Fe coexist in the minerals, and As is released from the dissociation/dissolution/desorption of these rocks and sediments^{24,41}. Since As is mainly found in S- and Fe-bearing mineral deposits, the most common As-S/As-Fe minerals are FeAsS, As₂S₃, and AsS/As₄S₄, which are found primarily in hydrothermal and magmatic ore deposits³⁰. Typically, the concentration and correlation of As and Fe are studied in natural environments. However, the detailed mechanism of the interaction, adsorption, desorption, and coprecipitation of As and Fe in natural environments is poorly understood⁴². The sampling area of the current study lies between the Chenab, Indus, and Ravi rivers. Therefore, the elevated concentration of As near river floodplains might be because of As-bearing sediments, the Himalayan flows, and the climatic conditions¹⁶. Since alluvial sediments are brought from the Himalayan peaks by the Indus River system, this would be one possible source for the



existence of As, Fe, and other contaminants in the soils of Central Punjab that may infiltrate the shallow and deep aquifers ⁴⁰.

3.5 Physicochemical variables and hydrogeochemistry of groundwater

The summary of physicochemical variables of water samples is presented in Table 4, Table S1-S2. The WHO drinking water standards were used to compare water quality parameters ¹¹. The pH of water in the study area ranged from 6.8 to 8.5, which lies within the threshold limit (6.5 to 8.5). However, the water samples had different salt concentrations with an EC value range of 0.34-4.43 dS m⁻¹ and TDS remained 217-2835 mg/L. About 15% of water samples have an EC higher than 2 dS m⁻¹, while none of the samples have a TDS greater than 1000 mg/L. The Ca has shown a maximum value of 357 mg/L with 4% of water samples having a Ca level of >100 mg/L (WHO limit). The mean Na level was 135 mg/L in groundwater samples (Table 1), and 21% of water samples revealed a concentration above the WHO permissible value (200 mg/L). The other physicochemical attributes remained within the WHO threshold limit. The water quality assessment results match those used in recent regional studies. ⁴³ proved that combining spatial analysis with ecotoxicological risk assessment is useful across different watershed sizes. ⁴⁴ also found integrating biological and physicochemical parameters gives a stronger assessment of water quality in areas affected by human activities.

Table 4: Physicochemical properties of water sample of tehsil Shorkot.

Parameters	Statistics	Shorkot	Urban	Rural	Peri-urban	WHO
pH	Range	6.8-8.5	7.2-8.4	6.8-8.5	7.6-8.5	6.5-8.5
	Mean ± SD	7.79 ± 0.33	7.7 ± 0.41	7.76 ± 0.36	7.86 ± 0.2	
EC (dS m ⁻¹)	Range	0.34-4.43	0.36-3.46	0.38-4.43	0.34-3.05	2 dS m ⁻¹
	Mean ± SD	0.99 ± 0.76	0.83 ± 0.85	1.234 ± 0.86	0.76 ± 0.49	
TDS (mg L ⁻¹)	Range	217-2835	230-2214	243-2835	218-1952	1000

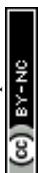
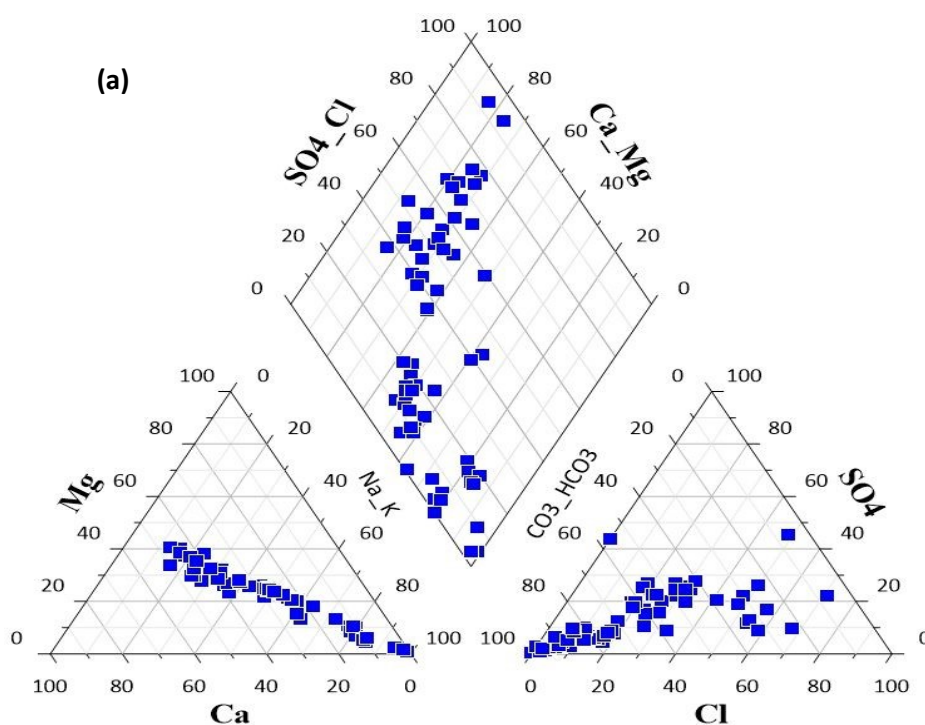


	Mean ± SD	634 ± 486	531 ± 544	790 ± 550	486 ± 314	500
CO ₃ ²⁻ (mg L ⁻¹)	Range	0-96	0-60	0-96	0-78	500
	Mean ± SD	40.5 ± 21.6	37.5 ± 16.8	45.9 ± 21.9	35.1 ± 21.9	
HCO ₃ ⁻ (mg L ⁻¹)	Range	36.6-878.4	67.1-469.7	97.6-878.4	36.6-732	500
	Mean ± SD	328.8 ± 150	250.1±128.1	356.85 ± 2.48	326.96±149.4	
Cl ⁻ (mg L ⁻¹)	Range	0-923	0-781	0-923	0-532.5	250
	Mean ± SD	372.8±230.8	332.9±287.5	390.5 ± 250.9	301 ± 161.5	
Mg ²⁺ (mg L ⁻¹)	Range	0.4-119	4.7-29	0.5-119	0.4-79.3	-----
	Mean ± SD	13.22 ± 16.92	13.5 ± 8.75	14.4 ± 20.5	11.6 ± 14.8	
Na ⁺ (mg L ⁻¹)	Range	1.2-1840	5-335	1.2-1235	2-1840	200
	Mean ± SD	135.34 ± 276.33	73.34±103.9	170.07±249.59	119.1 ± 352.4	
K ⁺ (mg L ⁻¹)	Range	1.4-108	2.4-108	2.6-56	1.4-21	200
	Mean ± SD	9.28 ± 15.03	17.35±29.07	10.17 ± 12.56	4.563 ± 3.74	
Li ⁺ (mg L ⁻¹)	Range	0.3-1.3	0.3-1.3	0.3-0.9	0.3-1.2	0.7
	Mean ± SD	0.41 ± 0.19	0.44 ± 0.28	0.438 ± 0.182	0.37 ± 0.17	
Ca ²⁺ (mg L ⁻¹)	Range	1.3-357	14.1-87.1	1.7-357	1.3-238	100
	Mean ± SD	39.68 ± 50.67	40.04±26.25	43.23 ± 61.46	35.05 ± 44.55	
Ca ²⁺ (mg L ⁻¹)	Range	10.5-273	17.5-147.7	11.7-273	10.5-58.9	----
	Mean ± SD	38.8 ± 36.27	48.6 ± 44.8	40.99 ± 44.03	31.73 ± 15.11	

Plotting the primary anions and cations contents on the Piper and Durov plots reveals water chemical composition (Figure 4 (a, b)). It is worthwhile to depict the hydrogeochemistry of water using the relative concentration of the selected anions and cations. Plotting TDS concentration on the Durov diagram revealed that most water samples had TDS lower than 15 g L⁻¹ with HCO₃ and Cl as the predominant anions, confirming the chemical characteristics of water. Results showed that significant cations and anions predominated in the water in the research area in the following proportional order: Na > K > Ca > Mg, and HCO₃ > Cl > SO₄.



A Na-HCO₃-Ca water type was indicated by the piper diagram, which also revealed the abundance of Na over K, Ca, and SO₄ and HCO₃ over Cl and SO₄. The graph also demonstrated that HCO₃, Cl, and then SO₄ were the three major ions. Low SO₄/Cl indicated low SO₄ water compared to Cl, hence the ratio was low. The most prevalent kind of water's hydrochemistry was Na-HCO₃-Ca, with less SO₄ than Cl and a mixture of Ca-Mg-Cl and Na-Cl^{45,46}. According to the Durov and Piper plots, the prevailing geochemical settings, water-mineral interactions, the mineral dissolution containing Na, K, and Ca, and the usage of salts in various industries all contribute to the chemical composition of water. The Piper diagram showed that weak acid anions (HCO₃ and CO₃) were greater than strong acid anions (Cl and SO₄), but alkaline ions (Ca and Mg) were lower than the alkalis (K and Na).



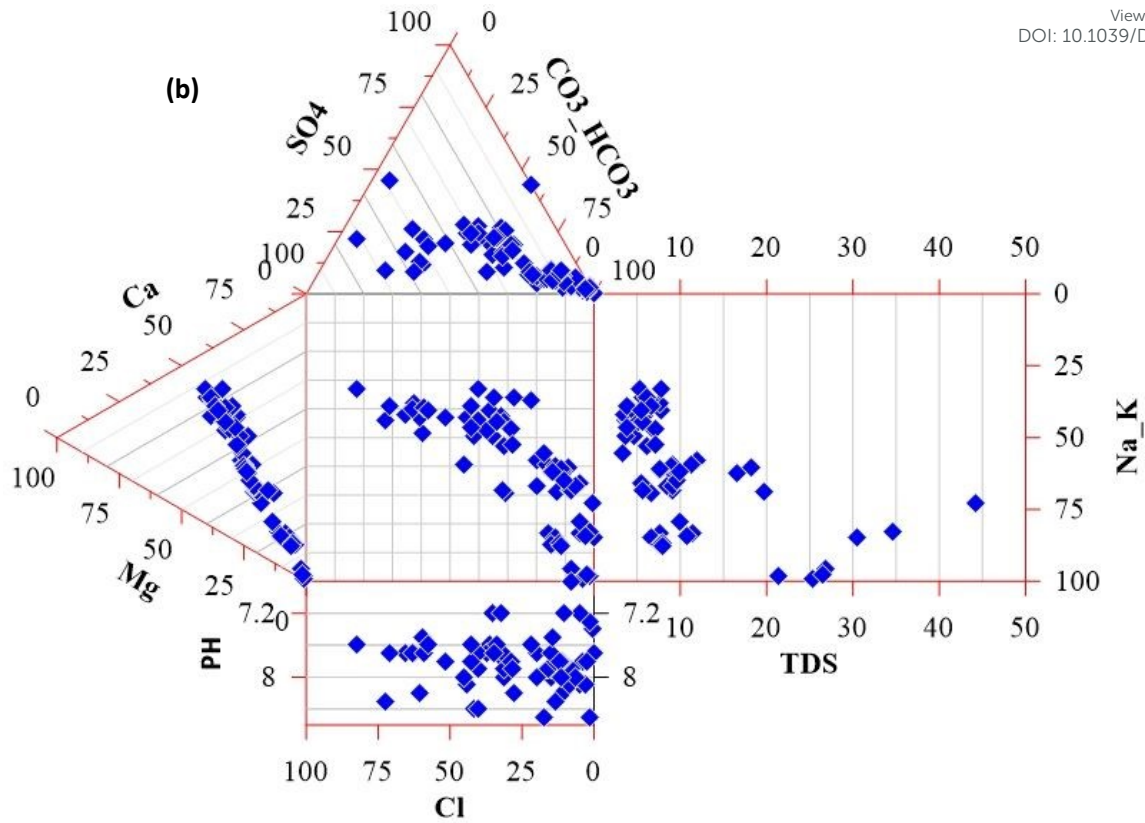


Fig. 4: Piper (a) and Durov (b) plots showing the groundwater chemistry with pH and TDS collected from tehsil Shorkot, Punjab, Pakistan.



3.6 Hydrogeochemical control on As-Fe behaviour

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The occurrence pattern of association between As and Fe is aligned with redox-controlled dissolution processes in alluvial floodplain aquifers. The increase in Fe with respect to depth indicates stronger reducing conditions that enhance the reductive dissolution of Fe-bearing minerals, a process that can desorb As previously sorbed or co-precipitated with Fe-minerals into porewater⁴⁷. This interpretation is consistent with the depth-dependent trends and describes that groundwater–mineral interactions, coupled with site-specific redox environments, are key indicators of the spatial and vertical variability in Fe and As⁴⁸. Furthermore, the hydrochemical facies stated by Piper and Durov diagrams further suggests ongoing mineral weathering and ion-exchange reactions that elucidate groundwater composition⁴⁹. Variability in recharge conditions in the Chenab floodplain, together with potential anthropogenic inputs along the river basin, may also contribute to the observed heterogeneity⁵⁰.

3.7 Human health risk assessment

Risk assessment indices predict potential hazards associated with the prevailing levels of a contaminant in the environment⁵¹. The possibility of HQ and CR associated with As-laced water has been shown in Table 5. For adults, the ADD value of As varied from 0.0000 to 0.0006 mg/kg/day with a mean concentration of 0.0001 mg/kg/day. The mean values of HQ and CR were 0.4 and 0.003, respectively. Similarly, average values of HQ, ADD, and CR for children were 0.5, 0.0002 mg/kg/day, and 0.005, respectively. The values of CR exceeded the limit value of 0.0001 for both adults and children. The results indicated a potential carcinogenic risk in local inhabitants due to drinking As-rich water for a long period. In addition to As, several other pollutants and contaminants also persist in the groundwater of the Sub-Continent, posing serious health risks to humans. Groundwater contaminated with As in both shallow and deep wells is risky for communities that don't treat their water^{52,53}. Hence, it is important to monitor



the groundwater, support families in removing As from their water at home, enforce national standards for safe drinking water, and run awareness programs in high-risk zones^{43, 44}.

Table 5: Arsenic health risk assessment of water samples for human adults and child.

Parameter	Variables	ADD	HQ	CR
Child	Range	0.0000-0.0009	0.0-2.9	0.00001-0.03
	Mean \pm SD	0.0002 \pm 0.0003	0.5 \pm 0.9	0.005 \pm 0.009
Adult	Range	0.0000-0.0006	0.0-2.1	0.00001-0.028
	Mean \pm SD	0.0001 \pm 0.0002	0.4 \pm 0.64	0.0034 \pm 0.006

3.8 Multivariate analysis

The Pearson correlation matrix has shown a strong correlation between variables in water samples of the study area (Table 5). A positive and strong correlation was present between As-Fe ($r = 0.8$), Li⁺-Na⁺ ($r = 0.7$), Ca²⁺-Na⁺ ($r = 0.8$), and Li⁺-K⁺ ($r = 0.8$). Moreover, the strong correlation between As and Fe indicates that As has been released due to the dissolution of As/Fe-bearing minerals in the groundwater.

The PCA is a classical technique used in hydrogeochemical research to identify the components (Table S3) which maximise variance³⁰. Six major principal components (F1-F6) were recognized that affect the water quality, indicating 86% cumulative variance (Table S3). In F1, the major contributions were by pH, TDS, EC, K⁺, Na⁺, and Ca²⁺ (variance: 35%), which might be linked with the presence of related minerals such as CaCO₃ that released their respective ions in the groundwater. The other significant contributors (F2) were Fe and Ba (variance: 15%), which might be present in the groundwater due to Fe-containing minerals. The other major contributors were As and CO₃²⁻ (F3) (variance: 12%), HCO₃⁻ (F4), Cl⁻ (F5), and Ca²⁺ + Mg²⁺ (F6), which might be associated with CO₃²⁻ minerals that affect the water quality.



The PCA graph showed two major groups in the dataset (Figure 5). Evidently, As, Cl⁻ and Ca²⁺-Mg²⁺ were assembled on the left side of the plot, indicating covariance, and their correlation might support the As mobility/sorption from rocks in the study area. The EC, TDS, Ca²⁺, Na⁺, Li⁺, K⁺, and HCO₃⁻ were grouped on the right side, having strong covariance that might be linked to calcite and dolomite dissolution. However, variation in pH showed that lower pH values cause the release of ions in the groundwater by reducing ferric ion (Fe³⁺) (insoluble form) to the ferrous ion (Fe²⁺) (soluble form) and arsenite As (III) to As⁰ (non-toxic form) ⁵⁴. The findings (close grouping of As and Fe) proposed that the sources of As and Fe origin can be the same, the dissolution of Fe- and As-bearing minerals.

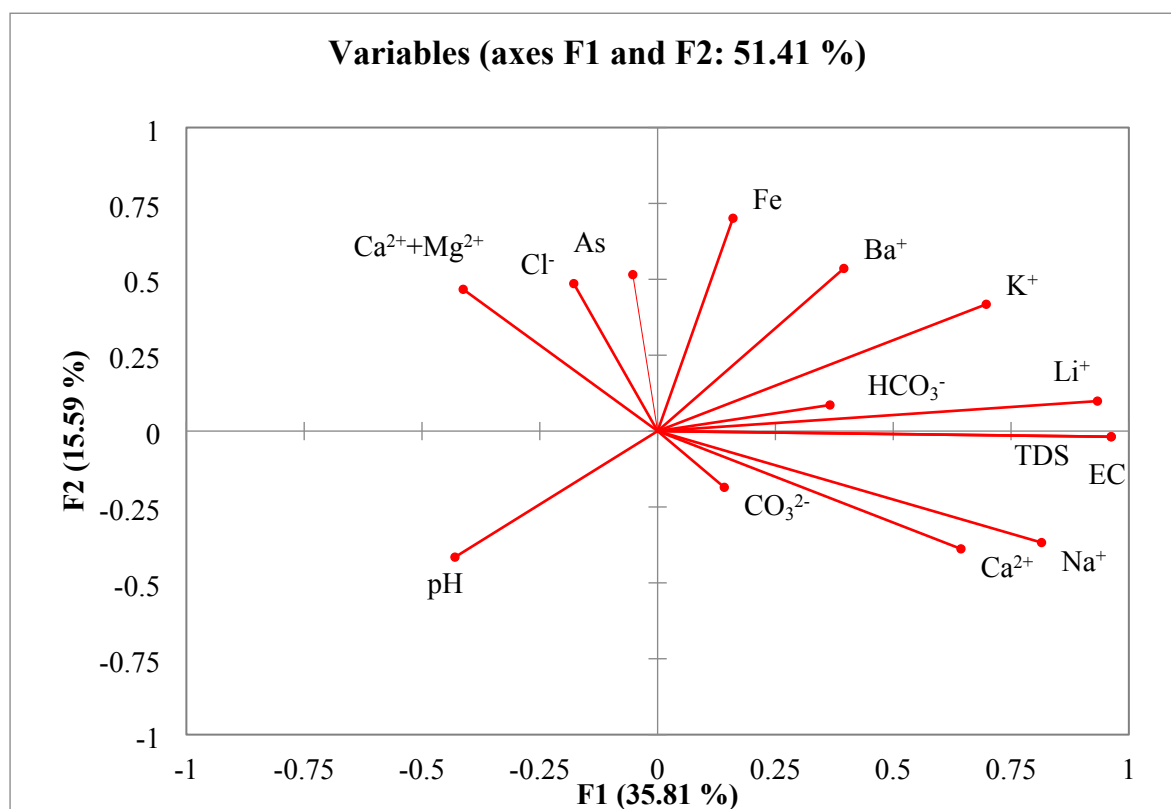
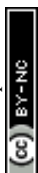


Fig. 5: Principal component analysis of As contents and other variables.

4. Conclusions

The present study reveals that As and Fe concentrations in groundwater samples from Tehsil Shorkot ranged from 0.05 to 22.3 µg/L and 0 to 218 µg/L, respectively. About 19% of the



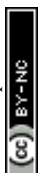
samples exceeded the WHO guideline value of 10 µg/L for As, rendering them unsafe for drinking, although all samples remained within the permissible limit set by Pak-EPA (50 µg/L). Risk assessment indices highlighted potential carcinogenic risks associated with the long-term consumption of As-contaminated water, underscoring the urgency for mitigation measures. A strong correlation ($r = 0.8$) was observed between As and Fe concentrations, suggesting that their co-occurrence is linked to the dissolution of As- and Fe-bearing minerals in the aquifer. Deeper tubewells (>19.8 m) exhibited higher concentrations of both As and Fe compared to shallow ones (<19.8 m), indicating that depth plays a critical role in the distribution of metal(loid)s. These findings emphasize the need for further research to explore the mechanisms governing the sorption, dissolution, and co-precipitation of As and Fe in groundwater systems. A detailed geochemical characterization of aquifer sediments is essential to advance the understanding of As and Fe mobilization. This includes investigating mineralogy, redox conditions, and the influence of competing ions under varying pH and Eh conditions. Additionally, studying the sorption-desorption behaviour of As and Fe on aquifer materials will provide critical insights into their mobility and retention. It is concluded that public awareness programs should be implemented to educate communities about the dangers of contaminated water and promote the adoption of safe water practices. The integration of scientific research with community engagement will pave a way for developing effective strategies to mitigate health risks and ensure safer groundwater resources for the population.

Declarations

Ethical approval: All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Compliances with ethical standards

Conflicts of interest: There is no known potential conflicts of interest



Competing instrests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Consent to participate: NA

Consent to publish: NA

Availability of data and materials: The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

During the preparation of this work the author(s) have not used any Generative AI and AI-assisted technologies in the writing process.

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Credit authorship contribution statement

B Murtaza: Study planning and execution, sample preparation and analyses, study supervisions, original draft write-up. N Farooq: sample preparation and analyses, methodology, writing - original draft. M Imran: Participated in conceptualizing the idea, writing - review & editing. M Shahid: Supervision, statistical analyses, manuscript write-up and editing, correspondence, G Abbas: Data analyses, writing - review and improvement, T Hussain: Data analyses, editing, N Masood: Review, editing, improvement, S Ahmad: Review, editing, improvement, and HF Bakhat: final review, editing, improvement. N. K. Niazi: manuscript write-up, editing, and intellectual contribution.



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Data Availability Statement

All the associated data have been presented in supplementary data.

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