



## Hydrogeochemical and health risk evaluation of arsenic in shallow and deep aquifers along the different floodplains of Punjab, Pakistan

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### ABSTRACT

The current study delineated the distribution, (hydro)geochemical behavior and health risk of arsenic (As) in shallow (depth < 35 m; handpumps and electric pumps) and deep (depth > 35 m; tube wells) aquifers in five areas along the Indus River (Bhakar, Kallur Kot), Jhelum River (Jhelum) and Chenab River (Hafizabad, Gujranwala) floodplains of Punjab, Pakistan. Relatively, greater As concentration was observed in deep wells (mean: 24.3  $\mu\text{g L}^{-1}$ ) compared to shallow wells (19.4  $\mu\text{g L}^{-1}$ ), with groundwater As spanning 0.1–121.7  $\mu\text{g L}^{-1}$  ( $n = 133$ ) in three floodplains. Groundwater from Hafizabad (Chenab River floodplain) possessed the highest As (121.7  $\mu\text{g L}^{-1}$ ),  $\text{Na}^+$  (180  $\text{mg L}^{-1}$ ),  $\text{Ca}^{2+}$  (95  $\text{mg L}^{-1}$ ),  $\text{Cl}^-$  (101  $\text{mg L}^{-1}$ ) and  $\text{SO}_4^{2-}$  (1353  $\text{mg L}^{-1}$ ) concentrations. Arsenic health risk modeling indicated the potential carcinogenic (value >  $10^{-4}$ ) and non-carcinogenic (hazard quotient > 1.0) risks for groundwater of all areas, with the utmost risk estimated for Chenab floodplain and deep aquifers. Positive saturation index values for Fe oxide mineral phases may suggest their potential role in As mobilization/release in these aquifer environments. This study provides critically-important and baseline knowledge for a widespread groundwater As examination along these three floodplains, which is vital for launching suitable As mitigation and remediation programs to reduce the potential health risk.

### 1. Introduction

Medical geology is a growing interdisciplinary scientific field investigating the impact of natural geological factors and their effects on human, animal and plant health. It deals with the influence of environmental factors on the geographical distribution of health problems particularly in humans, which is a complicated subject and requires interdisciplinary contributions to resolve problems (Selinus et al., 2013).

Medical geology is considered to be an emerging field in Pakistan, especially for assessment of the groundwater quality and its suitability for consumption which requires multidisciplinary focus by researchers. A major focus is being given to arsenic (As) induced environmental, agricultural and public health issues, globally and nationally (Disanayake et al., 2010).

The International Agency for Research on Cancer (IARC) has classified As and some of As compounds as Class-I human carcinogen (IARC,

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2012). Considering the severe carcinogenic risk of As, in 1993 World Health Organization (WHO) has reduced the standard for As in drinking water to  $10 \mu\text{g L}^{-1}$  by replacing old standard value of  $50 \mu\text{g L}^{-1}$  (Yamamura et al., 2001). Moreover, on June 22, 2000, the US EPA (New Jersey) also recommended  $5 \mu\text{g L}^{-1}$  as a safe As limit in drinking water to adequately protect public health (US-EPA, 2017; WHO, 2004). However, in many developing countries including Pakistan, the earlier limit of  $50 \mu\text{g L}^{-1}$  guideline is established as a national safe standard for As in drinking water, which is pumped by millions of installed handpumps, electric pumps and tube wells at varying depths in alluvial sediments of the Indus Basin (Pak-EPA, 2008; Ghosh and Singh, 2009).

Although geogenically released As is a major source of groundwater As contamination (Vithanage et al., 2017), many anthropogenic activities are also thought to be responsible for contamination of groundwater and surface water with As (Shahid, 2017; Tweed et al., 2020). It is a ubiquitous toxic element in the geothermal system (Wang et al., 2018; Herath et al., 2018; Amen et al., 2020) and present in about > 200 mineral forms, but the most common minerals are arsenical pyrite (FeAsS), orpiment (As<sub>2</sub>S<sub>3</sub>) and realgar (AsS). The geochemical alteration in underground sediments could possibly trigger As release in aquifers (Frohne et al., 2011). For example, water-rock interaction, sorption/desorption, oxidative/reductive dissolution processes of As-bearing FeAsS (Hussain et al., 2020) and/or Fe oxides can result in As contamination of groundwater systems (Kumar and Singh, 2020; Shakoor et al., 2018). The high As levels in groundwater might also be attributed to oxidative desorption with a rise in the evaporative concentration process with other physicochemical parameters (Natasha et al., 2020).

Exposure to As may cause skin lesions, pigmentation and hardening of hand palm and feet soles also termed as hyperkeratosis and multi-organ cancer (WHO, 2020; Radfard et al., 2019). Human exposure to As could be through multiple routes such as ingestion, inhalation and dermal contact. Among all these exposure pathways, drinking As-contaminated water poses one of the major threats to human health as reported by a large number of documented cases globally, and by some studies nationally (Tabassum et al., 2019; Greco et al., 2019; Wei et al., 2019; Rufz-Vera et al., 2019). Medical geology via human health risk assessment models has been recently implemented to examine whether exposure to toxic elements, like As, could increase incidence of the adverse effects on human health (Machado et al., 2020; Chandrajith et al., 2020; Rinklebe et al., 2019).

Previous research has focused to assess health risk of As from groundwater in a single area without comparing different river floodplains (Murtaza et al., 2020; Shahid et al., 2018; Rasool et al., 2016, 2017). Very limited research has been directed to examine the hydro-geochemical behavior and health risk of As in groundwater along different river floodplains in Pakistan. Also, it is intriguing to explore the distribution of As and other key groundwater parameters in shallow and deep wells, as well as understanding the (hydro)geochemical behavior of As in these aquifers along different river floodplains by using multivariate analysis and geochemical speciation modeling.

The overarching aim of the current research was to delineate As distribution, (hydro)geochemistry, As-induced potential health risk and geochemical speciation of groundwater along three different river floodplains of Punjab (Jhelum, Kallur Kot, Bhakkar, Gujranwala and Hafizabad), representing the Jhelum River (Jhelum), Indus River (Bhakkar, Kallur Kot), Chenab River (Hafizabad, Gujranwala) floodplains in the study area. We examined the groundwater As and other water quality parameters distribution and (hydro)geochemistry in two different depth zones, i.e., shallow well depth (< 35 m) and deep well depth (> 35 m).

## 2. Materials and methods

### 2.1. Description of the study area

Indus River is the longest river of Pakistan flowing from mountains of

the Karakoram Range to southward through Punjab and Sindh provinces and making its final fall into the Arabian Sea. Major tributaries of the Indus River in Punjab are Sutlej, Ravi, Chenab and Jhelum rivers (Fig. 1). Over a large part of the Indus Plain of Pakistan, the water wells have been reported to be contaminated with varying As concentration (Shahid et al., 2018), which are installed mainly in the alluvial and deltaic sediments (with the thickness of several hundred meters) (Shamsudduha et al., 2008; Naseem and McArthur, 2018). The sediments are comprised of mainly coarse sand, having a high percentage of fine to coarse sand and silt (Talib et al., 2019).

The arid and semi-arid climate in Punjab and Sindh provinces of Pakistan resulted in a high prevalence of Pleistocene (Quaternary) deposits. Hence the occurrence of high groundwater As is thought to be linked with the geology-geomorphology of alluvial and deltaic sediments throughout the Quaternary period (Shamsudduha and Uddin, 2007). These deposits are widely distributed in the western sedimentary basin with less reducing conditions and promoting oxidative environments in these areas (Shamsudduha and Uddin, 2007; Farooqi et al., 2007).

The Punjab province of Pakistan has a semi-arid climate with an average annual precipitation of  $3.2 \text{ mm year}^{-1}$  (Khattak and Ali, 2015). The rivers of Indus Basin are about 50–80% fed by snow and glacier melt in the Hindu-Kush Karakoram (HKK) part of the Himalayas, with the remainder coming from monsoon rain in the plains. In Pakistan, Indus River and its tributaries support many heavy industries and agriculture and provide the main supply of groundwater for industrial, potable water, irrigation water and other domestic uses. Relatively abundant water and fertile soils of the Indus Plain have encouraged a major proportion of the population to settle in the nearby regions, which can be a potential source of high exposure to the people by As-contaminated groundwater, primarily via drinking well water. The groundwater sampling sites were selected randomly to represent the different floodplains, including the River Chenab (Gujranwala, Hafizabad), River Indus (Bhakkar, Kallur Kot) and River Jhelum (Jhelum) (Fig. 1).

### 2.2. Groundwater sampling and preservation

Groundwater sampling points were randomly selected considering their spatial distribution in the area to obtain an approximate representation of As and groundwater composition in the area. The privately-owned wells were sampled that are actively used to pump groundwater for drinking, irrigation and other domestic purposes. Groundwater samples were collected using the pumps already installed in the privately-owned three types of bores (tube wells, handpumps and electric pumps).

Before the collection of groundwater samples, water was purged for 5–6 min through the tap in order to eliminate the impact of any kind of impurity from pipes and stagnant water (Tabassum et al., 2019). The depths for the groundwater bores were recorded from their owners in the study area, which ranged from 23 to 82 m. Typically, in Pakistan, the average depth of different wells (tube wells, electric pumps, hand-pumps) ranged from 3 to 85 m (Shakoor et al., 2017; Qureshi et al., 2003). However, the well depth highly depends on the water table of a specific area. In this study, we have categorized the well depth as shallow well (< 35 m) and deep well (> 35 m) based on the earlier research in Pakistan (Shakoor et al., 2018; Farooqi et al., 2007).

Two sets of groundwater samples (100 mL each) were collected in 100 mL plastic bottles for As, Fe, cations and anions analysis. Based on the qualitative observation, the groundwater samples were clear with no suspended particles and were not filtered. For the first set, groundwater samples were acidified in the field with concentrated HNO<sub>3</sub> to bring the pH < 2. The second set of water samples was not acidified and used for ions and other water quality parameters analysis. All the water samples were kept in an ice bath to prevent it from direct sunlight and immediately brought to the laboratory and stored at 4 °C in dark and analyzed within seven days of sampling (US-EPA, 2016).

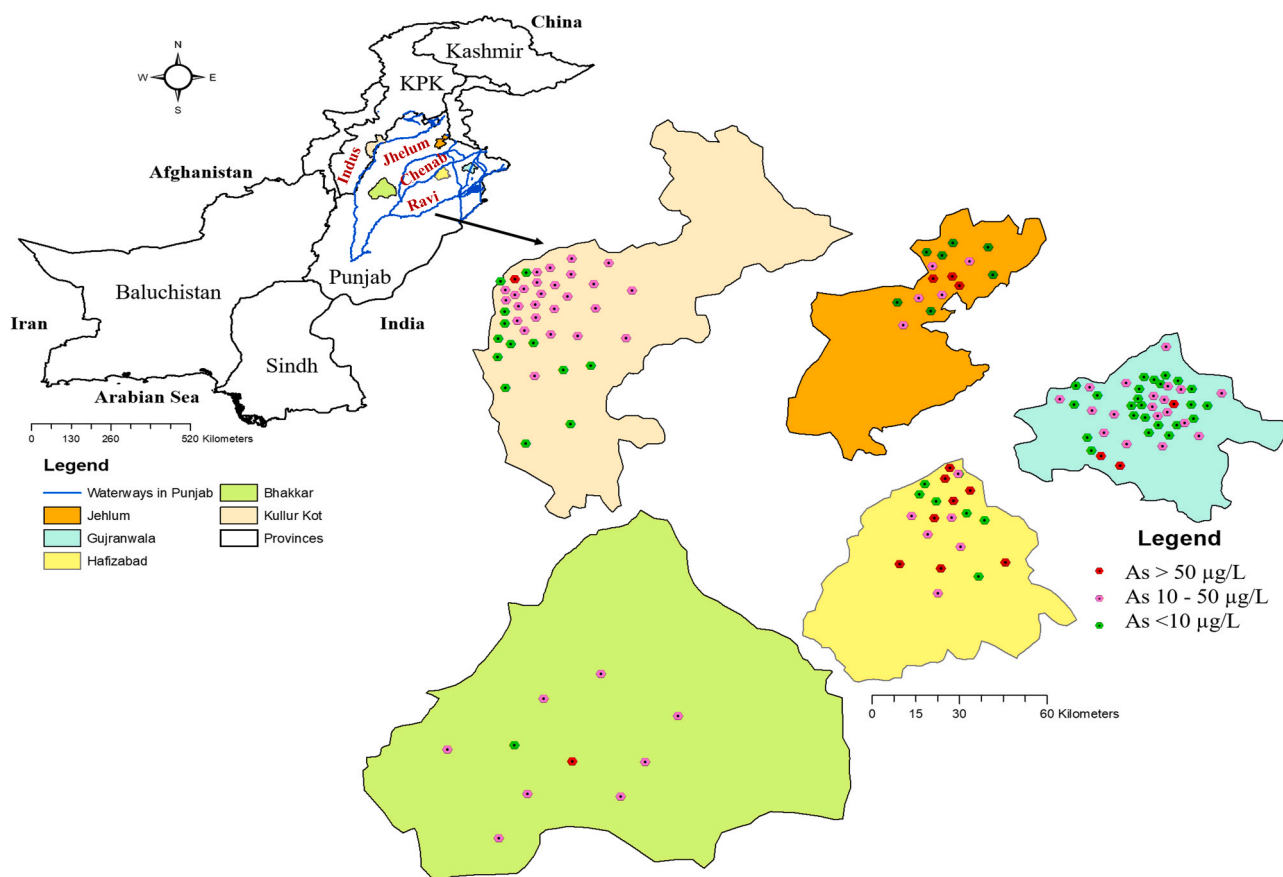


Fig. 1. The GIS map of the five study areas indicating sampling points along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

### 2.3. Field analysis of groundwater

During the collection of groundwater samples, various physical and chemical parameters such as temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO) were measured in the field. The EC, TDS, pH and DO of groundwater samples were recorded using the portable pH (Model 370, Jenway), EC/TDS (Model 470, Jenway, Stone, Staffordshire, U.K.), and DO (OHAUS, USA; model ST300) meters.

### 2.4. Total arsenic and other elemental/analytical determinations

The analytical analysis of As at a wavelength of 193.7 nm was carried out using a hydride generation atomic absorption spectrophotometer (HG-AAS; Agilent, model No. 200 series AA) as described by Niazi et al. (2018).

Total Fe concentration was analyzed in groundwater using a flame atomic absorption spectrophotometer (F-AAS; PerkinElmer, PinAacle 900F) at an analytical wavelength of 372.0 nm. The concentrations of calcium (Ca), potassium (K) and sodium (Na) in groundwater were determined by using a Flame Photometer (BWB-XP, BWB technologies). The analytical wavelengths used were: 422.7 nm (Ca), 589.0 nm (Na) and 766.5 nm (K).

The  $\text{SO}_4$  in groundwater was determined by barium sulfate ( $\text{BaSO}_4$ ) precipitation method. The 1 N stock solution of barium chloride ( $\text{BaCl}_2$ ) was prepared and added into groundwater samples, then allowed to precipitate  $\text{SO}_4$ -S as  $\text{BaSO}_4$  following the method described elsewhere (Ryan et al., 2007). The major anions ( $\text{CO}_3$ ,  $\text{HCO}_3$ , and  $\text{Cl}^-$ ) were determined using the standard titration method as described elsewhere (Estefan et al., 2013).

### 2.5. Exposure assessment of arsenic

Two health risk assessment models were evaluated for As considering the As-induced carcinogenic and non-carcinogenic health hazards by estimating chronic daily intake (CDI) (Eq. (1)) via exposure route. The non-carcinogenic risk was estimated by calculating hazard quotient (HQ) (Eq. (2)), and the carcinogenic risk was calculated by evaluating cancer risk (CR) (Eq. (3)) (Shah et al., 2020).

$$CDI = \frac{C \times IR}{BW} \quad (1)$$

$$HQ = \frac{CDI}{RfD} \quad (2)$$

$$CR = CDI \times CSF \quad (3)$$

In these equations,  $C$  refers to As concentration ( $\mu\text{g L}^{-1}$ ) in groundwater,  $IR$  is ingestion rate ( $2 \text{ L day}^{-1}$ ),  $BW$  is body weight ( $70 \text{ kg}$ ),  $RfD$  is oral reference dose ( $0.3 \mu\text{g kg day}^{-1}$ ),  $CSF$  refers to cancer slope factor ( $1500 (\mu\text{g kg day}^{-1})^{-1}$ ) (USEPA, 2011; US-EPA, 1986).

### 2.6. Quality control and analytical precision

To validate the results of As analysis on HG-AAS in groundwater, a standard NIST reference material (SRM; 1640) was used. On an average, As concentration analyzed in SRM 1640 was close to the certified As concentration ( $26.67 \pm 0.41 \mu\text{g L}^{-1}$ ) provided in NIST SRM 1640 with a recovery of 105.3%.

## 2.7. Geochemical modeling

To estimate the equilibrium conditions of various mineral-like phases/salts controlling the geochemistry of sediments, saturation index (SI) values were calculated using geochemical speciation modeling software, PHREEQC (Parkhurst and Appelo, 1999). The SI values for a specified mineral phase are expressed as: oversaturated/precipitation ( $SI > 0$ ), unsaturation/dissolution ( $SI < 0$ ) and equilibrium ( $SI = 0$ ) (Bibi et al., 2011).

## 2.8. Statistical analysis

Descriptive statistical analyses were performed using Microsoft Excel (2019). Pearson correlation and principal component analysis (PCA) were carried out using the XLSTAT (2018) software. The locations map to show the distribution of As was developed using ArcGIS 10.4.1 software. Piper plots were designed using Grapher version 13.

## 3. Results and discussion

### 3.1. Arsenic distribution in groundwater

Fig. 2A indicates the average concentration of As in groundwater of five study areas in the three different river floodplains, i.e., Jhelum, Kallur Kot, Bhakar, Gujranwala and Hafizabad, in Punjab, Pakistan. Elevated concentration of As in groundwater samples was observed (range: 0.1–121.7  $\mu\text{g L}^{-1}$ ). On an average, 83%, 61%, 13% and 3% of groundwater samples from five areas have As concentration above the safe limits of 5  $\mu\text{g L}^{-1}$  (DEP-NJ, 2006), 10  $\mu\text{g L}^{-1}$  (WHO, 2011), 50  $\mu\text{g L}^{-1}$  (Pak-EPA, 2008) and 100  $\mu\text{g L}^{-1}$ , respectively (Bhattacharya et al., 2017) (Table S1, Supplementary information). The 100  $\mu\text{g L}^{-1}$  As limit is considered as the threshold of different types of cancers from As in drinking water (Bhattacharya et al., 2017). The high As concentration ( $> 100 \mu\text{g L}^{-1}$ ) was found in four out of the five sampling regions except for Bhakar.

Our data showed that the mean groundwater As concentration in five areas was in the order of: 40.7  $>$  30.9  $>$  30.8  $>$  17.4  $>$  15.0  $\mu\text{g L}^{-1}$  for Hafizabad  $>$  Jhelum  $>$  Bhakar  $>$  Kallur Kot  $>$  Gujranwala, respectively (Fig. 2A; Table S1, Supplementary information). Based on the WHO As limit in drinking water (10  $\mu\text{g L}^{-1}$ ), 53%, 67%, 68%, 90% and 48% wells contained As above this limit and 20%, 38%, 3%, 10% and 9% of wells had As content  $>$  50  $\mu\text{g L}^{-1}$  (i.e., Pak-EPA limit), in Jhelum, Hafizabad, Kallur Kot, Bhakar and Gujranwala, respectively (Table S1, Supplementary information). It was observed that, out of 133 total groundwater samples, four samples had As content  $>$  100  $\mu\text{g L}^{-1}$  from Jhelum, Hafizabad, Kallur Kot and Gujranwala (Table S1, Supplementary information). Noticeably, 17% of all the groundwater samples had As content less than 5  $\mu\text{g L}^{-1}$  (Table S1, Supplementary information).

High As concentration in groundwater samples of the study area could be associated with the geochemical conditions of aquifers which can release As into groundwater, such as reducing conditions (Raven-scroft et al., 2009), oxidizing situations with elevated pH (Jacks, 2017) and/or sulfide oxidation pathway (Herath et al., 2016). Rabbani et al. (2017) reported that increasing As contamination situation of groundwater near the Indus River floodplain could be due to As release from As-bearing minerals in sediments. These authors evaluated As contamination of groundwater in 216 villages along the bank of River Indus in Sindh, Pakistan (mean As: 15  $\mu\text{g L}^{-1}$ , SD(+/-): 30  $\mu\text{g L}^{-1}$ ), and about 13 million of the population was estimated to be at risk of As exposure. The groundwater As contamination in the three floodplains could possibly be ascribed to the high pumping of groundwater and as such As release by oxidation/reduction and dissolution pathways (Shakoor et al., 2018; Kumar et al., 2020). Also, the saline type of water and alkaline pH ( $>$  8) might be responsible for the dissolution of As-containing sediments and groundwater As contamination (Stuckey et al., 2016; Iftikhar et al., 2020) (see further discussion below in Section 3.2). Lone et al. (2020)

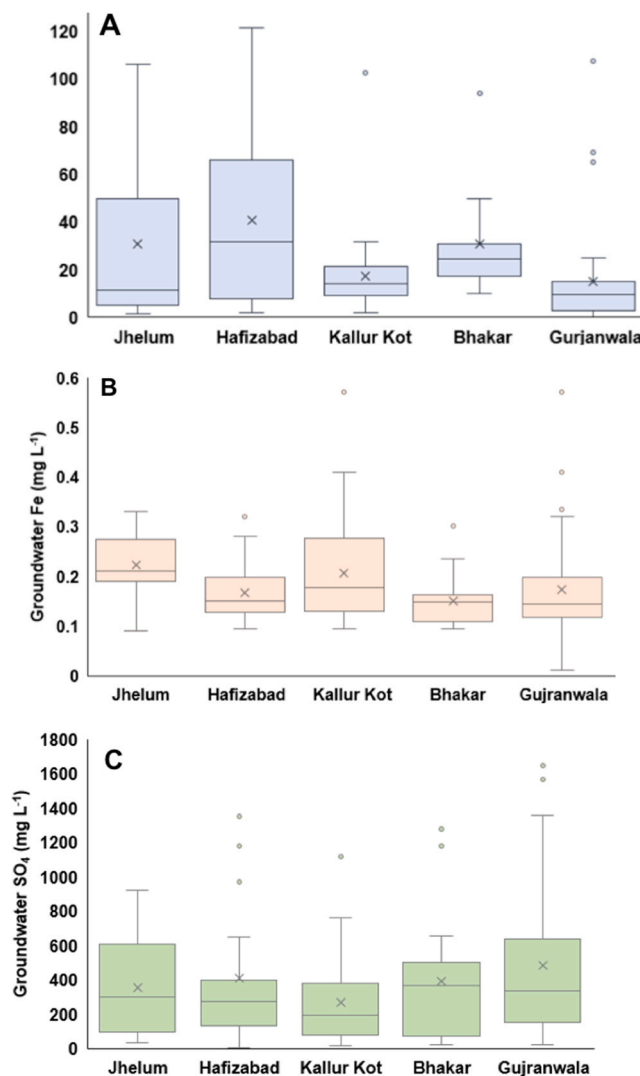


Fig. 2. Boxplots representing the mean and quartiles of the measured (A) As, (B) Fe and (C)  $\text{SO}_4$  values along with the minimum, maximum and median values from the groundwater of five study regions along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

studied the upper Indus River Basin to evaluate the hydrogeochemical processes responsible for groundwater As mobilization. The authors reported the possible influence of high pH, Fe and  $\text{SO}_4^{2-}$  in groundwater As release indicating that metal oxides/hydroxides are predominantly controlling the groundwater As mobilization. In the current study, high As concentration in groundwater was observed along the Chenab River floodplain in Hafizabad area, which might be due the high As content in underground sediments developed in the floodplain by Chenab River (Nickson et al., 2005). However, this aspect needs further investigation in future studies where comprehensive drilling of sediments should be taken to characterize As and mineralogical composition (Kumar et al., 2020).

### 3.2. Arsenic concentration in shallow vs. deep wells and from different pumping sources

Table 1 shows descriptive statistics for As concentration in the groundwater from shallow and deep wells and as a function of pumping source of groundwater. The well depth spanned 23–82 m and categorized into shallow well depth ( $<$  35 m) and deep well depth ( $>$  35 m) as described above. The deep and shallow aquifers showed some difference

**Table 1**

Arsenic concentration in groundwater as a function of pumping source and well depth from five study areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab in Pakistan.

Arsenic content ( $\mu\text{g L}^{-1}$ ) variation with pumping source and well depth

Pumping source	HP	EP	TW
Sample #	36	31	66
Depth (m)	27.4–51.8	22.9–61	27.4–82.3
Mean $\pm$ SD	13.8 $\pm$ 8.4	21.9 $\pm$ 22.5	28.3 $\pm$ 32.7
Range	1.5–31.9	1.3–102.5	0.1–121.7
Median	12.7	16.2	12.1
Well Depth	< 35 m	> 35 m	–
Sample #	39	94	–
Mean $\pm$ SD	19.4 $\pm$ 22.8	24.3 $\pm$ 27.7	–
Range	1.3–102.5	0.1–121.7	–
Median	12.5	13.6	–

HP: Handpump, EP: Electric pump, TW: Tube well.

in As content, although it was slight in this study (Table 1; Fig. S1A, Supplementary information). For deep and shallow wells, the mean As concentration was 24.3 and 19.4  $\mu\text{g As L}^{-1}$ , respectively, showing the possible influence of well depth on As distribution. Relatively, higher As concentration in deep wells might be associated with the oxidative dissolution of As-bearing mineral phases, such as FeAsS,  $\text{As}_2\text{S}_3$  in the deep underneath sediments, which can release high As and associated sulfide-S to  $\text{SO}_4$ . The principal source of As is FeAsS that undergoes oxidation releasing inorganic As into aquatic systems. The depth profiles

of Fe and  $\text{SO}_4$  showed their high concentration in deep well water compared to shallow well water (Fig. S2, Supplementary information) that might be attributed to the release of slightly higher As in deep groundwater.

A greater  $\text{SO}_4^{2-}$  concentration in most of the deep wells, as observed in our study (up to 1656  $\text{mg L}^{-1}$ ; Table 2, Fig. S2, Supplementary information), may be an indication of sulfide-S oxidation to  $\text{SO}_4$  from As-bearing (FeAsS,  $\text{As}_2\text{S}_3$ ) mineral phases which could possibly lead to release As and  $\text{SO}_4$  in the aquifers (Herath et al., 2016; Kumar et al., 2020). Depending on pH, redox conditions, temperature,  $\text{SO}_4$  concentrations and microbial activity, As anions remain in solution or undergo multiple sorption/desorption processes during formation and subsequent conversion of secondary minerals (Migaszewski et al., 2018). However, a detailed blanket testing and groundwater examination for As and other chemical and biological water quality attributes is needed in study area along these floodplains.

Also, it is crucial to examine the mineralogical composition of underground sediments for revealing As release mechanisms and sinks in Pakistan. In shallow aquifers, As release may be related to the reductive dissolution of As bound to Fe oxides, which have high As retention capacity, and can lead to low As content in groundwater in shallow wells as observed in this study (Erbs et al., 2010; Barringer and Reilly, 2013). Hence, future research is warranted to unveil these intriguing research aspects to precisely depict differences in groundwater As concentration in deep and shallow aquifers. Moreover, the low As concentration in shallow waters could be due to the recharge of shallow (unconfined)

**Table 2**

Physicochemical parameters of groundwater samples collected from the five study areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) of Punjab, Pakistan.

Parameters	Statistics	All samples	Gujranwala	Jhelum	Hafizabad	Kallur Kot	Bhakar
Sample #	–	133	46	15	21	40	11
pH	Mean $\pm$ SD	8.2 $\pm$ 0.6	8.6 $\pm$ 0.6	8.1 $\pm$ 0.2	8.3 $\pm$ 0.4	7.7 $\pm$ 0.2	7.7 $\pm$ 0.3
	Range	6.7–9.7	7.8–9.7	7.8–8.5	7.9–9.1	6.7–8.1	7–7.9
	Median	8.1	8.5	8.15	8.2	7.7	7.74
EC ( $\text{mS cm}^{-1}$ )	Mean $\pm$ SD	0.9 $\pm$ 0.5	0.6 $\pm$ 0.3	0.7 $\pm$ 0.3	0.5 $\pm$ 0.2	1.4 $\pm$ 0.03	1.4 $\pm$ 0.03
	Range	0.1–1.7	0.1–1.7	0.1–1.3	0.2–0.8	1.3–1.5	1.4–1.5
	Median	0.85	0.6	0.65	0.55	1.45	1.45
TDS ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	591 $\pm$ 303.3	392 $\pm$ 223.6	419 $\pm$ 221.2	351 $\pm$ 105.2	919 $\pm$ 21.4	921 $\pm$ 20.3
	Range	63.7–1071	63.7–1071.4	68.9–845.4	123–543.4	845–946.6	891–943.4
	Median	543	406	414	352	928	930
Na ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	110 $\pm$ 60.3	126 $\pm$ 61.9	118 $\pm$ 38	123 $\pm$ 44.5	89 $\pm$ 62.2	79.7 $\pm$ 72.4
	Range	3.7–256.7	25.7–256.7	47.7–179.7	36.7–179.7	3.7–229.2	9.2–179.7
	Median	108	108	119	141.2	99.9	36.7
K ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	2.6 $\pm$ 1.6	1.8 $\pm$ 1.2	2.7 $\pm$ 1.8	2.7 $\pm$ 1.7	3.2 $\pm$ 1.6	2.8 $\pm$ 1.5
	Range	0.3–5.5	0.3–5.5	0.5–5.4	0.5–5.4	0.6–5.4	0.6–5.4
	Median	2.6	1.5	2.6	2.6	2.6	2.6
Ca ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	120 $\pm$ 92.6	180 $\pm$ 95.6	46.4 $\pm$ 26	48.7 $\pm$ 16.7	112 $\pm$ 76.8	132 $\pm$ 108.9
	Range	2.4–519.2	37.6–519.2	6.4–106.4	23.2–95.2	2.4–309.6	3.2–350.4
	Median	95	164	43	47.2	111	108
Mg ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	93.2 $\pm$ 59.2	129 $\pm$ 69.3	40.8 $\pm$ 19	40.6 $\pm$ 10.8	98.1 $\pm$ 36.4	99.7 $\pm$ 53.5
	Range	7–355.7	17.8–355.7	7–78.2	24–68.2	42.2–185.8	34.1–210.2
	Median	82	117	40	38.4	94	95.04
Fe ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.02
	Range	0–0.6	0–0.6	0.1–0.3	0.1–0.3	0.1–0.6	0.1–0.2
	Median	0.15	0.1	0.21	0.15	0.18	0.14
$\text{CO}_3$ ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	53.5 $\pm$ 51.8	63.7 $\pm$ 68.4	54.9 $\pm$ 65.3	28.4 $\pm$ 12	54.1 $\pm$ 28.7	55.2 $\pm$ 55.2
	Range	2–402	2–402	2.4–229	9.6–55.2	3–102	4–186.0
	Median	43	56	31	27	58	34
$\text{HCO}_3$ ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	163.7 $\pm$ 115.9	255 $\pm$ 118.7	76.7 $\pm$ 38.9	74.2 $\pm$ 25.4	141.6 $\pm$ 88.5	151.9 $\pm$ 106.1
	Range	3.7–610	34–610	9.8–162.3	35.4–145.2	3.7–346.5	4.9–339.2
	Median	132	244	65.8	71.98	133	164.7
Cl ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	139.2 $\pm$ 88.1	194 $\pm$ 101.6	59.7 $\pm$ 29.5	60 $\pm$ 15.9	145.2 $\pm$ 53.9	147.5 $\pm$ 79.2
	Range	0–526.1	26.3–526.1	0–115.7	35.5–100.8	62.5–274.8	50.4–311.0
	Median	123	179.3	59.6	56.8	139.2	140.6
$\text{SO}_4$ ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	390.2 $\pm$ 378.2	486 $\pm$ 444.5	353 $\pm$ 299.3	407.4 $\pm$ 412.6	320.7 $\pm$ 315.5	259.6 $\pm$ 247.9
	Range	0.8–1656	18.9–1655.6	34.4–921.1	0.8–1353.2	13.5–1277.8	24.6–657.9
	Median	286	337.2	300	272.2	214.3	91.3
DO ( $\text{mg L}^{-1}$ )	Mean $\pm$ SD	6.8 $\pm$ 1.2	6.7 $\pm$ 1.2	6.8 $\pm$ 1.2	7.1 $\pm$ 1.4	6.7 $\pm$ 1.1	7.1 $\pm$ 1.4
	Range	4–8.3	4–8.3	4–8.3	4–8.3	4–8.3	4–8.3
	Median	7.2	6.9	7.2	7.5	6.85	7.5

aquifers with surface water (i.e., from river water, rainwater or irrigation water), which can dilute As levels in shallow groundwater (Neumann et al., 2010).

There was a consistent trend observed in As concentration from different pumping sources (Table 1). A slightly higher As content (mean:  $28.3 \mu\text{g L}^{-1}$ ; SD(+/-):  $32.7 \mu\text{g L}^{-1}$ ) was observed in tube well water possibly due to the deep well depth compared to those from electric pumps (mean As:  $13.8 \mu\text{g L}^{-1}$ ; SD(+/-):  $22.5 \mu\text{g L}^{-1}$ ; median:  $16.2 \mu\text{g L}^{-1}$ ) and handpumps (mean As:  $21.9 \mu\text{g L}^{-1}$ ; SD(+/-):  $8.4 \mu\text{g L}^{-1}$ ; median:  $12.7 \mu\text{g L}^{-1}$ ) along three floodplains in the five areas of Punjab (Table 1; Fig. S1B, Supplementary information). Interestingly, none of the groundwater samples collected from handpumps (27–52 m depth) had As content  $> 50$  and  $100 \mu\text{g L}^{-1}$ . Over  $\sim 94\%$  of the electric pumps (depth: 23–61 m) across the study area generally had As concentration above  $5 \mu\text{g L}^{-1}$ , 68% exceeded  $10 \mu\text{g L}^{-1}$ , 6% were above  $50 \mu\text{g L}^{-1}$  and 3% of the wells crossed the  $100 \mu\text{g L}^{-1}$  limit (Table S1, Supplementary information). Almost 76%, 55%, 23% and 5% of the tube well water samples (depth: 27–82 m) showed As concentration  $> 5$ , 10, 50 and  $100 \mu\text{g L}^{-1}$  (Table S1, Supplementary information). These data indicate that most of the tube wells have been installed at a deeper depth than that of handpumps and electric pumps, thus showing more As concentration in groundwater along the three floodplain of Punjab in Pakistan.

### 3.3. Distribution of other groundwater attributes

The summary statistics of various groundwater attributes in the five studied areas is shown in Table 2A. All of the groundwater quality parameters are compared with WHO drinking water standard limits (WHO, 2011) (Table 3). Groundwater pH was alkaline and ranged between 7.2 and 9.7 (mean 8.2; SD(+/-): 0.6) with 20% samples exceeding the threshold limit of pH 6.5–8.5. The groundwater of the study areas contained variable salt concentration, with EC values spanning 0.1–1.7 mS/cm and TDS ranging from 64 to  $1071 \text{ mg L}^{-1}$ . None of the groundwater samples showed EC greater than 2 mS/cm, while only 1% of the total samples have TDS value  $> 1000 \text{ mg L}^{-1}$ . Both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were considered as major cations having maximum values of 519 and  $356 \text{ mg L}^{-1}$  and about 50% and 15% samples possessed  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration higher than the WHO limits, respectively (Table 3). Among the five different study areas, groundwater from Gujranwala along the Chenab River floodplain, was found to have a high concentration of cations and anions, with many water samples not meeting the WHO guideline values of water quality standards (Table 3).

The average concentration of  $\text{Na}^+$  and Fe in groundwater samples was  $110 \text{ mg L}^{-1}$  (Table 2) and  $0.2 \text{ mg L}^{-1}$  (Fig. 2B), respectively, with 5% and 13% of groundwater samples beyond the WHO safe limits of 200 ( $\text{Na}^+$ ) and  $0.3 \text{ mg L}^{-1}$  (Fe). The concentration of Fe, if higher than the safe limit value in water, may also cause adverse health effects when

ingested by the residents (Saleh et al., 2019). As discussed above,  $\text{SO}_4^{2-}$  was the dominant anion in groundwater (mean:  $390 \text{ mg L}^{-1}$ , SD(+/-):  $378.2 \text{ mg L}^{-1}$ ; range:  $0.8\text{--}1656 \text{ mg L}^{-1}$ ) (Fig. 2C) followed by  $\text{Cl}^-$  (mean:  $139 \text{ mg L}^{-1}$ ; range:  $0\text{--}526 \text{ mg L}^{-1}$ ) (Table 2). The concentration of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  spanned 2–402 and  $3.7\text{--}610 \text{ mg L}^{-1}$ , respectively. The DO concentration of groundwater in the three floodplains ranged from 4 to  $8.3 \text{ mg L}^{-1}$ , which may show the oxic environment of groundwater and oxidized situation of underneath sediments interacting with groundwater in the region investigated here. The depth profiles of the physicochemical variables of groundwater of five regions are given in Fig. S2, Supplementary information.

A pie chart of average concentrations of major ions was developed, which indicated that groundwater samples ( $n = 133$ ) mainly contained  $\text{SO}_4^{2-}$  (31%), Fe (14%),  $\text{HCO}_3^-$  (13%),  $\text{Cl}^-$  (11%),  $\text{Ca}^{2+}$  (9%),  $\text{Na}^+$  (9%),  $\text{Mg}^{2+}$  (7%) and  $\text{CO}_3^{2-}$  (4%) (Fig. S3B, Supplementary information). The low Fe concentration in most of the groundwater samples may indicate that Fe can be precipitated as Fe oxides under the prevailing oxidized and high pH conditions, and as such can play an important role in sorption/release of As into groundwater (Shakoor et al., 2018).

The high concentration of DO may also suggest the predominance of oxidizing aquifer environments in these areas of Punjab along the three river floodplains, which can trigger the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  mineral phase (see Section 2.7 Geochemical modeling below for further discussion). Another important factor for the release of As into aquifers is groundwater pH. The release of As in water systems from As-rich mineral sediments, such as Fe oxides, is highly pH-dependent process. Under oxidizing conditions, As is mobilized at alkaline pH ( $> 7.5$ ) (Jacks, 2017) and at groundwater pH  $> 8$ , the desorption of As from the sediments release high As into the groundwater (Welch et al., 2000).

### 3.4. Multivariate analysis

#### 3.4.1. Hydrogeochemical behavior of groundwater using the piper plot

Hydrogeochemical characterization showed that groundwater in the study area was dominated by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations, while  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were the predominant anions (Table 2). Groundwater chemistry was assessed using the Piper plot which demonstrated the dominance of Mg– $\text{HCO}_3/\text{SO}_4$ , Na– $\text{SO}_4$  and Na–Cl type mixed (saline) waters (Fig. S3A, Supplementary information). Also, the Piper plots for the hydrogeochemical characterization of each individual study area is given in Fig. S4, Supplementary information. The concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were higher than that of  $\text{Na}^+$  in all the study areas. Piper plot revealed that the dissolution/precipitation reactions of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  bearing mineral phases might have controlled the salinity of aquifers along the three floodplains of Punjab in Pakistan (Talib et al., 2019; Shah et al., 2020).

Changes in groundwater properties (such as EC and pH) can affect the dissolution/precipitation of carbonate ( $\text{CO}_3$ )-rich minerals, altering

**Table 3**

Percentage of groundwater samples collected from the five study areas from five study regions along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) in Punjab, Pakistan, having physicochemical values higher than threshold values recommended by WHO.

Parameters	WHO limits	All samples	Gujranwala	Jhelum	Hafizabad	Kallur Kot	Bhakar
Sample #	–	133	46	15	21	40	11
pH	6.5–8.5	20	50	0	19	0	0
EC ( $\text{mS cm}^{-1}$ )	2	0	0	0	0	0	0
TDS ( $\text{mg L}^{-1}$ )	1000	1	2	0	0	0	0
$\text{Na}^+$ ( $\text{mg L}^{-1}$ )	200	5	11	0	0	3	0
$\text{K}^+$ ( $\text{mg L}^{-1}$ )	200	0	0	0	0	0	0
$\text{Ca}^{2+}$ ( $\text{mg L}^{-1}$ )	100	50	80	7	0	55	55
$\text{Mg}^{2+}$ ( $\text{mg L}^{-1}$ )	150	15	33	0	0	8	18
Fe ( $\text{mg L}^{-1}$ )	0.3	13	13	13	5	20	0
$\text{CO}_3^{2-}$ ( $\text{mg L}^{-1}$ )	500	0	0	0	0	0	0
$\text{HCO}_3^-$ ( $\text{mg L}^{-1}$ )	500	1	2	0	0	0	0
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	250	12	28	0	0	5	9
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	500	27	37	33	24	18	18
DO ( $\text{mg L}^{-1}$ )	14	0	0	0	0	0	0

mineral composition for As release/retention (Meng et al., 2016). Arsenic associated with  $\text{CO}_3$  minerals can be susceptible to changes in wetting and drying patterns and changes in water quality components such as pH and salinity (Jensen, 2020; LeMonte et al., 2017). Moreover, the  $\text{CO}_3$  anion present in groundwater may form complexes on the surface sites of Fe oxides and substitute As from the surface of minerals/sediments resulting in release of As into groundwater (Anawar et al., 2004). The dissolved  $\text{Ca}^{2+}$  content in groundwater may be a result of dissolution of  $\text{CaCO}_3$  mineral phase and/or, at least partially, by the silicate mineral weathering. Hence,  $\text{CO}_3$  mineral phases may also be partly responsible for As retention/release in the aquifers (Rasool et al., 2016).

### 3.4.2. Pearson correlation matrix and principal component analysis (PCA)

Pearson correlation matrix indicated some of the strongly correlating variables in the groundwater system of the three river floodplains. A strong and positive correlation was found between Ca–Mg ( $R^2 = 0.92$ ), Ca–Cl ( $R^2 = 0.93$ ), Ca– $\text{HCO}_3^-$  ( $R^2 = 0.82$ ), Mg– $\text{HCO}_3^-$  ( $R^2 = 0.75$ ) and  $\text{HCO}_3^-$ –Cl ( $R^2 = 0.77$ ) (Table 4). However, the distribution of As and the other groundwater quality parameters did not show any relationship (Table 4), indicating that As association with other parameters of aquifers may not be predicted by Pearson correlation. Hence, the groundwater data were subjected to a principal component analysis (PCA) to determine if there is any relationship among potential contributors for As release/sequestration (Fig. 3; Fig. S5, Supplementary information). The PCA is a multivariate tool that has been successfully applied in hydrogeochemical investigations to identify major water groups, redox states and factors affecting groundwater quality (Shah et al., 2020; Murtaza et al., 2019).

Seven major principal components (F1, F2, F3, F4, F5, F6 and F7) affecting the quality of groundwater were identified, showing 81% variance of the original data structure (Table 5). In Table 5, values in bold correspond to each variable which may control hydrogeochemistry of the study area. In F1 (variance: 26%),  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  were the major contributors (Table 5). These ions in groundwater could be due to the dissolution of  $\text{CO}_3$  minerals as discussed above, which might have significantly affected the composition of groundwater (Blowes et al., 2014). The pH, EC and TDS were the major contributors in F2 (18% variance), which could possibly be ascribed to the high dissolved ions in groundwater.

Interestingly,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  were grouped together in each PCA plot (Fig. S5, Supplementary information). Thus, these variables showed co-variance suggesting that an inter-correlation and may vary together in the groundwater of studied areas (Fig. 3). From the PCA

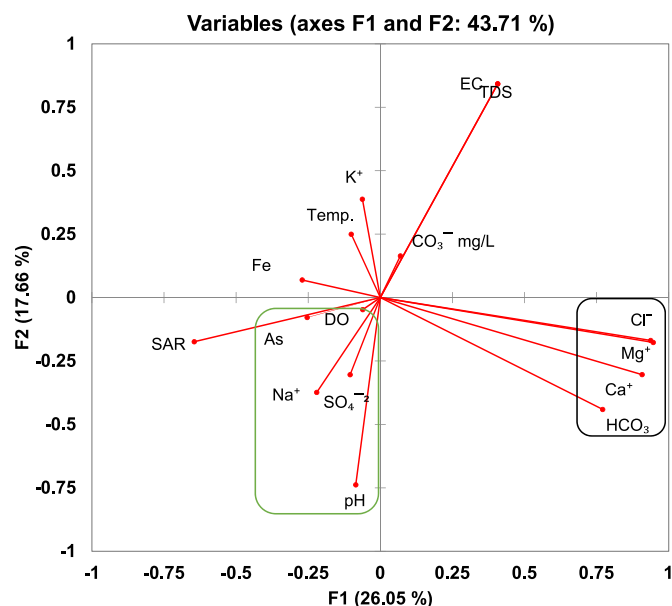


Fig. 3. Principal component analysis (PCA) of arsenic (As) contents and other physico-chemical groundwater parameters ( $n = 133$ ) from five study regions along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

plot of Jhelum groundwater (Jhelum floodplain), Fe, As, DO were grouped together, indicating their covariance (Fig. S5, Supplementary information) and supporting the release/sorption of As into the aquifers due to reductive dissolution of As-bearing Fe oxide phases in oxic sediments, which is in agreement with high DO concentration and low aqueous Fe content. However, the PCA of River Chenab floodplain (Hafizabad and Gujranwala) groundwater grouped As, pH and  $\text{SO}_4^{2-}$  together indicating the pH and  $\text{SO}_4^{2-}$  dependent release of As, which may be attributed to oxidation of As-rich sulfide phases (e.g.,  $\text{FeAsS}$ ,  $\text{As}_2\text{S}_3$ ) as mentioned above (Flora, 2015; Shaheen et al., 2016).

Some previous studies also showed that weathering of rocks due to water-rock interaction could influence the major ions in the geological systems (Jiang et al., 2015; Mahmud et al., 2007; Halim et al., 2010). Similar to our findings, other researchers have reported the geogenic release of As due to weathering of As-containing minerals in oxidizing conditions (Shakoor et al., 2018; Bibi et al., 2015). In the current study, we observed comparable levels of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$ ,  $\text{HCO}_3^-$

Table 4

Pearson correlation matrix for different variables of groundwater samples of five study areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

Variables	As	EC	TDS	Temp.	pH	Na	K	Ca	Mg	$\text{CO}_3$	$\text{HCO}_3$	Cl	$\text{SO}_4$	SAR	DO
EC	-0.15														
TDS	-0.15	1.00													
Temp.	-0.06	0.08	0.08												
pH	-0.02	-0.62	-0.62	-0.15											
$\text{Na}^+$	0.01	-0.22	-0.22	-0.01	0.08										
$\text{K}^+$	0.00	0.21	0.21	0.15	-0.15	-0.13									
$\text{Ca}^{2+}$	-0.18	0.10	0.10	-0.09	0.09	-0.02	-0.12								
$\text{Mg}^{2+}$	-0.18	0.25	0.25	-0.08	0.02	-0.01	-0.10	<b>0.92</b>							
$\text{CO}_3^{2-}$	-0.07	0.13	0.13	0.14	-0.05	-0.04	-0.10	-0.03	0.10						
$\text{HCO}_3^-$	-0.11	-0.05	-0.05	-0.14	0.17	0.08	-0.14	<b>0.82</b>	<b>0.75</b>	-0.07					
$\text{Cl}^-$	-0.19	0.25	0.25	-0.08	0.02	-0.01	-0.11	<b>0.93</b>	0.98	0.10	<b>0.77</b>				
$\text{SO}_4^{2-}$	0.02	-0.22	-0.22	-0.07	0.18	0.08	-0.01	-0.03	-0.07	-0.06	0.07	-0.08			
SAR	0.16	-0.27	-0.27	0.12	0.01	<b>0.80</b>	-0.09	-0.46	-0.45	0.00	-0.38	-0.45	0.03		
DO	0.07	-0.09	-0.09	0.10	-0.03	0.07	-0.08	0.02	-0.01	0.09	-0.08	-0.02	-0.11	0.06	
Fe	-0.11	-0.09	-0.09	0.02	0.00	0.03	0.16	-0.22	-0.18	0.05	-0.20	-0.21	-0.01	0.12	0.02

As: Arsenic, EC: electric conductivity, TDS: total dissolved solids, Temp: temperature, Na: sodium, K: potassium, Ca: calcium, Mg: magnesium,  $\text{CO}_3$ : carbonate,  $\text{HCO}_3^-$ : bicarbonates, Cl: chlorides,  $\text{SO}_4$ : sulfate, SAR: sodium absorption ratio, DO: dissolved oxygen, Fe: iron.

The bold values indicate the strong correlation among the variable.

**Table 5**

Values of squared cosines for groundwater samples of five study areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

Variables	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15
As	0.06	0.01	0.00	0.04	<b>0.38</b>	0.08	0.02	0.21	0.16	0.03	0.01	0.00	0.00	0.00	0.00
EC	0.17	<b>0.71</b>	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.05	0.01	0.00	0.00	0.00
TDS	0.17	<b>0.71</b>	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.05	0.01	0.00	0.00	0.00
Temp.	0.01	0.06	0.06	0.15	0.03	0.15	<b>0.31</b>	0.11	0.01	0.09	0.01	0.00	0.00	0.00	0.00
pH	0.01	<b>0.54</b>	0.08	0.03	0.02	0.00	0.00	0.02	0.02	0.07	0.22	0.01	0.00	0.00	0.00
Na	0.05	0.14	<b>0.66</b>	0.08	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.01	0.00
K	0.00	0.15	0.04	0.02	0.16	<b>0.33</b>	0.01	0.02	0.03	0.22	0.01	0.00	0.00	0.00	0.00
Ca	<b>0.82</b>	0.09	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.00
Mg	<b>0.88</b>	0.03	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.01	0.01	0.01
CO <sub>3</sub>	0.00	0.03	0.06	<b>0.34</b>	0.00	0.24	0.07	0.09	0.09	0.06	0.02	0.00	0.00	0.00	0.00
HCO <sub>3</sub>	<b>0.59</b>	0.19	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.03	0.14	0.00	0.00	0.00
Cl <sup>-</sup>	<b>0.90</b>	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01
SO <sub>4</sub>	0.01	0.09	0.03	0.08	0.05	0.03	<b>0.35</b>	0.16	0.19	0.00	0.00	0.00	0.00	0.00	0.00
SAR	0.42	0.03	<b>0.47</b>	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00
DO	0.00	0.00	0.06	<b>0.31</b>	0.11	0.13	0.03	0.05	0.27	0.03	0.00	0.00	0.00	0.00	0.00
Fe	0.07	0.00	0.00	0.06	<b>0.38</b>	0.00	0.17	0.17	0.01	0.13	0.01	0.00	0.00	0.00	0.00
Eigenvalue	4.2	2.8	1.6	1.2	<b>1.2</b>	1.0	1.0	0.8	0.8	0.6	0.4	0.2	0.1	0.0	0.0
Variability (%)	26.0	17.7	9.9	7.6	<b>7.4</b>	6.4	6.0	5.3	5.0	4.0	2.5	1.4	0.5	0.3	0.1
Cumulative %	26.0	43.7	53.6	61.2	<b>68.6</b>	75.0	81.0	86.2	91.2	95.2	97.7	99.1	99.6	99.9	100.0

Values in **bold** correspond for each variable to the factor for which the squared cosine is the largest.

and pH in groundwater of three floodplains in Punjab, Pakistan, thereby indicating that As release is mainly associated with these attributes in the aquifers.

### 3.5. Saturation indices for estimating possible mineral-phases, using geochemical data

Table 6 presents the saturation index values from geochemical speciation modeling for groundwater samples in the study areas. The geochemical modeling data showed that the aquifer conditions were mostly unsaturated for CO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup>-containing minerals, such as dolomite [(CaMg(CO<sub>3</sub>)<sub>2</sub>) (-6.06)], calcite [(CaCO<sub>3</sub>) (-2.92)], siderite [(FeCO<sub>3</sub>) (-8.89)], gypsum [(CaSO<sub>4</sub>·2H<sub>2</sub>O) (-6.78)] and Jarosite-K [(KFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>) (-11.87)]. This indicates that there may be no potential role of these mineral phases in sorption/desorption of As in groundwater due to their negative SI values (Bibi et al., 2011). However, the positive SI values observed for Fe oxy(hydro)oxides mineral phases, including goethite (3.12), hematite (9.31), magnetite (8.69) and ferrihydrite (Fe(OH)<sub>3</sub>) (0.54) (Migaszewski et al., 2018). This may depict that Fe oxides could possibly be the main scavengers of As in aquifers of the study area, releasing As due to water-rock interface reactions (Shakoor et al., 2018; Zhang et al., 2017).

The Fe oxides mineral phases could likely to precipitate in underground sediments-aquifer system and potentially control As release in the aquifers of Punjab, Pakistan (Shakoor et al., 2018; Mukherjee et al., 2008). Kumar et al. (2017) also suggested that the possible formation of Fe oxide minerals and their role in As release under favorable (alkaline) situations, which is in agreement with the pH data of groundwater was

**Table 6**

The PHREEQC-based calculated saturation indices values of some important mineral-like phases using groundwater attributes of total 133 samples from five areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) floodplains of Punjab, Pakistan.

Mineral	Composition	Mean (n = 133)	SD (+/-)	Median	Minimum	Maximum
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-6.06	1.21	-5.99	-12.4	9.2
Calcite	CaCO <sub>3</sub>	-2.92	0.97	-2.70	-8.51	-2.02
Goethite	FeOOH	3.12	0.48	4.09	-0.05	5.1
Hematite	Fe <sub>2</sub> O <sub>3</sub>	9.31	1.02	9.02	2.31	10.29
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	8.69	2.98	8.98	-6.12	14.02
Ferrihydrite	Fe(OH) <sub>3</sub>	0.54	0.62	1.01	-0.87	1.90
Gibbsite	Al(OH) <sub>3</sub>	-3.89	0.89	-3.77	-7.42	-1.98
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-6.78	1.73	-6.59	-11.64	-4.86
Jarosite-K	KFe <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	-11.87	1.96	-11.66	-15.23	-3.98
Halite	NaCl	-11.77	0.98	-11.64	-15.67	-5.79
Siderite	FeCO <sub>3</sub>	-8.89	0.78	-8.78	-9.23	-4.98

found to be in alkaline range in most of the water samples in the current study. Contrary to our findings, Brahman et al. (2013) reported the high saturation of calcite (SI > 0) in the aquifers of Tharparkar, Sindh province of Pakistan, suggesting its precipitation and dissolution in As release process.

### 3.6. Exposure risk assessment

The probability of adverse non-carcinogenic and carcinogenic effects from exposure of As in five study areas is shown in Table 7. It is evident from the health risk data that groundwater of all the five areas can pose potential health concerns to the local inhabitants. For non-carcinogenic risk, the average HQ values remained > 1.00 in groundwater samples from the three river floodplains in the region (mean: 2.1; range: 0.01–11.3). If HQ ≥ 1.00, As concentration in groundwater may be associated with a potential non-carcinogenic risk (Dadar et al., 2017; Razzaghi et al., 2018; Shahab et al., 2019; Yousefi et al., 2018). The mean HQ value in groundwater from Hafizabad, Bhakkar, Jhelum, Kallur Kot and Gujranwala remained 3.8, 3, 2.9, 1.6 and 1.4, respectively. Recently, some studies in Pakistan have also highlighted the health risk associated with the ingestion of As-contaminated water in different areas (Iftikhar et al., 2020; Mushtaq et al., 2020; Ehsan et al., 2020).

Similar to HQ, the results showed that total CR from groundwater of all the areas was high (mean: 0.0009; range: 0.000004–0.01), which is significantly greater than the maximum acceptable CR value of US EPA (i.e.  $1 \times 10^{-4}$  or 0.0001) (USEPA, 2011; Qasemi et al., 2019). If CR is > 0.0001, the exposed population can be at considerable cancer risk



**Table 7**

Health risk assessment of arsenic (As) for groundwater samples from five study areas along the Jhelum River (Jhelum), Indus River (Kallur Kot, Bhakar) and Chenab River (Gujranwala, Hafizabad) in Punjab, Pakistan.

Parameter	Statistics	CDI	HQ	CR
All (n = 133)	Mean ± SD	0.0006 ± 0.0007	2.1 ± 2.4	0.0009 ± 0.001
	Range	0.00003–0.003	0.01–11.3	0.00004–0.01
	Median	0.0004	1.2	0.0005
Gujranwala (n = 46)	Mean ± SD	0.0004 ± 0.0006	1.4 ± 2.0	0.0006 ± 0.0009
	Range	0.00003–0.003	0.01–9.9	0.00004–0.004
	Median	0.0003	0.88	0.0004
Jhelum (n = 15)	Mean ± SD	0.0009 ± 0.001	2.9 ± 3.5	0.001 ± 0.002
	Range	0.00004–0.003	0.1–9.8	0.0001–0.004
	Median	0.0003	1.1	0.0005
Hafizabad (n = 21)	Mean ± SD	0.0011 ± 0.001	3.8 ± 3.2	0.002 ± 0.001
	Range	0.0001–0.003	0.2–11.3	0.0001–0.005
	Median	0.001	2.9	0.001
Kallur Kot (n = 40)	Mean ± SD	0.0005 ± 0.0004	1.6 ± 1.5	0.001 ± 0.0007
	Range	0.0001–0.003	0.2–9.5	0.0001–0.004
	Median	0.0004	1.3	0.0006
Bhakar (n = 11)	Mean ± SD	0.001 ± 0.0007	3 ± 2.2	0.0014 ± 0.001
	Range	0.0004–0.003	1.4–8.7	0.001–0.004
	Median	0.0007	2.3	0.0010

CDI: chronic daily intake, HQ: hazard quotient, CR: cancer risk.

(Rahmani et al., 2018). The order of CR values estimated separately for groundwater of the five areas had the same trend as it was for HQ (Table 7). The average CR values from these areas remained higher than the respective threshold value of  $1 \times 10^{-4}$ . Moreover, it is evident that in terms of As concentration and associated health risk, the groundwater from Chenab River floodplain (Hafizabad) is more contaminated compared to the other areas and may provoke relatively great As induced risk to the population than that of other areas (Ehsan et al., 2020).

### 3.6.1. Risk assessment based on well depth and pumping sources

Table S2, Supplementary information shows the health risk assessment results in terms of the non-carcinogenic (HQ) and carcinogenic health risks (CR) associated with As in the groundwater sampled from different pumping sources and at various well depths irrespective of the areas. Both deep and shallow groundwater samples showed associated non-carcinogenic ( $HQ > 1.00$ ) and carcinogenic health risks ( $CR > 0.0001$ ), whereas the risk was more pronounced for deep groundwater owing to the high As concentration (Ali et al., 2019).

Groundwater collected from tube wells had high HQ and CR values due to high boring depths, while the groundwater from handpumps and electric pumps had low level of risk. As stated earlier, As concentration and associated health risk prevails with increasing well depth. Accordingly, the risk evaluated from the source of collection directly correlated with well depth and can be given as tube wells > electric pumps > handpumps. Overall, the samples collected from different sources with two depths (shallow: < 35 m; deep: > 35 m) showed the HQ and CR values in groundwater above the standard line.

## 4. Conclusions

The results presented herein revealed a high concentration of As present in the groundwater of five areas along three river floodplains (mean As:  $22.9 \mu\text{g L}^{-1}$ ) with 61% of the groundwater samples exceeding As content >  $10 \mu\text{g L}^{-1}$ . The highest As concentration was detected in Hafizabad (Chenab River floodplain) with the maximum As value of up to  $121.7 \mu\text{g L}^{-1}$ . Noticeably, As concentration was higher in deep wells (> 35 m) where mainly tube wells were installed for pumping. Besides As concentration, the other groundwater attributes including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , Fe, pH were higher than the WHO guideline values, which also restrict the water for human consumption, especially in the Hafizabad, Gujranwala (Chenab River floodplain) and Jhelum

(Jhelum River floodplain).

Owing to high As concentration in groundwater, the health risk indices (HQ and CR) also exceeded their respective thresholds. This depicts the severe risks of chronic As poisoning to the exposed population, especially for the groundwater from deep wells having tube wells as a major pumping source. Groundwater samples from the five areas in three floodplains were dominated by Mg– $\text{HCO}_3^-/\text{SO}_4^-$ , Na– $\text{SO}_4^-$  and Na–Cl type saline waters, with most of the waters showing alkaline pH (> 7.5). Geochemical modeling provided information on the role of Fe oxide minerals phases, mainly goethite, hematite and magnetite in the sorption/mobilization of As into groundwater systems.

The current research provides baseline information to launch detailed and blanket testing covering a widespread groundwater examination for As and other water quality parameters along the three floodplains around these areas in Punjab. The study may also help in adopting suitable As mitigation and remediation programs and it opens an opportunity for the governments and national/international environmental agencies to educate and train local drillers, which will help to target As-safe wells for drinking around these locations in Pakistan.

## CRedit authorship contribution statement

Natasha, Irshad Bibi, Muhammad Shahid and Nabeel Khan Niazi wrote and edited/finalized the paper. Fazila Younas collected samples. Salman Raza Naqvi, Sabry M. Shaheen, Hailong Wang, Khalid Mahmud Hussaini read and edited the paper. Muhammad Imran made figures and edited paper. Zhang Hua and Jörg Rinklebe edited and improved draft of paper.

## Declaration of Competing Interest

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.

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## Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:[10.1016/j.jhazmat.2020.124074](https://doi.org/10.1016/j.jhazmat.2020.124074).

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