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Comparison of two alluvial aquifers shows the probable role of river sediments on the release of arsenic in the groundwater of district Vehari, Punjab, Pakistan

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Abstract

The study was done to assess the effect of the river Sutlej on arsenic (As) contamination. Sampling was done from the alluvial plain with increasing distance from the river Sutlej in district Vehari and compared with the study done in the proximity of River Sutlej. Sixty (60) groundwater samples mostly from shallow depths were collected and analyzed for As concentrations. Multivariate statistical tools (PCA and CA), saturation index, piper plots and Gibbs diagrams were used to detect evidence about the interrelationship and sources of As and other water quality variables responsible for groundwater contamination. Results revealed that As concentration ranged from below detection limit to 156 µg/L indicating that 50% samples exceeding the WHO guidelines (10 µg/L) and 17% exceeding the Pakistan National Environmental Quality Standards (NEQS) limits (50 µg/L) Sutlej. The piper plot revealed that water chemistry of the study area was $Ca–HCO_3^-$, Ca–Mg–Cl, type. Correlations between As and HCO_3^- ($r^2 = 0.433$) was positive, while negative correlations were observed between As–Mn^{2+} and As–Fe^{2+} ($r^2 = -0.102$), ($r^2 = 0.107$) respectively. Geochemical signatures of the groundwater in the study area showed that the As could be released by oxidative dissolution to some extent and elevated evaporation in the arid environment of the study area under the stimulus of alkaline water and high pH (range 7.1–8.4). Although the concentrations are exceeding the WHO limit in 50% of the water samples but, are less than the previous study done in Mailsi near River Sutlej. Further, the concentrations decreased as the distance from the River increased which shows the probable role of sediments deposited by the River Sutlej.

Keywords Arsenic · Alluvial deposits · Statistical analysis · Ground water · Punjab (Pakistan)

Introduction

In the last few decades, an event of high contamination of arsenic (As) in drinking water has been perceived as a notable general health concern in all around the world (Arain

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et al. 2009a, b). Worldwide 150 million people are suffering from arsenic contamination of drinking water (Ravenscroft et al. 2009). During the 1990s, naturally occurring As was found to be widespread in groundwater in the USA, Argentina, Taiwan, China, Hungary, Vietnam, and the Ganges Plain (Smedley and Kinniburgh 2002). There have been many documented incidents of arsenic contamination in ground water around the world (Galbacs and Galbacs 1995; Das et al. 2008; Zheng et al. 2004; Ahamed et al. 2006; Boyle et al. 1998; Wang and Mulligan 2006; Kundu and Gupta 2007; Sengupta et al. 2003; Rahman et al. 2005; Nickson et al. 2007).

There are different natural mechanisms with generalized geological and environmental conditions which are responsible for the release of As in ground water of aquifers all around the world including reductive dissolution, alkali desorption, sulfide oxidation, geothermal and evaporative

concentration are responsible for the release of arsenic in groundwater (Smith et al. 2003).

Generally As concentration is high near river in floodplain areas mainly composed of alluvial deposits, e.g. Bengal delta, Meghna flood plains in Bangladesh Ganges–Brahmaputra river system, old Brahmaputra floodplain of Bangladesh, area near Fairbanks, Alaska, and Western Snake River Plain of Idaho, USA, Ghazipur District in the middle Gangetic Plain India, Hetao Basin, located in the Great Bend of Yellow River in Inner Mongolia and Datong Basin area China, Kandal Province of Cambodia (Smedley et al. 2003; Ahmed et al. 2004, 2010; Berg et al. 2007; Verplanck et al. 2008; Busbee et al. 2009; Luu et al. 2009; Guo et al. 2010; Kumar et al. 2010; Li et al. 2012). Multan, Bahawalpur, Rahim Yar Khan in Punjab Province, and Khairpur, and Dadu in Sindh Province Pakistan are lying in alluvial deposits along the Indus River (Ahmad et al. 2004).

Like other countries Pakistan is also experiencing the elevated As concentration in groundwater (Shah and Danishwar 2003; Ahmad et al. 2004; Nickson et al. 2005; Tirmizi et al. 2005; Farooqi et al. 2007a, b, 2009; Haque et al. 2008; Arain et al. 2009a, b; Baig et al. 2009, 2011; Malik et al. 2009; Rafique et al. 2009, 2015; Ullah et al. 2009; Muhammad et al. 2010; Naseem et al. 2010; Malana and Khosa 2011; Ali et al. 2013; Brahman et al. 2013a, b, 2014; Jabeen et al. 2014; Bibi et al. 2015).

Arsenic in groundwater has developed as a general major concern in Pakistan. In the premise of drinking water quality observing system, UNICEF and Pakistan Council of Research in Water Resources (PCRWR) reported that As containing aquifers (10–200 μg/L) were observed in a few territories of Punjab area where more than 20% of the population is exposed to arsenic higher than WHO limit (10 μg/L) in drinking water while almost 3% of the population is exposed to > (50 μg/L).

This study was designed to evaluate the probable effect of alluvial sediments deposited by the River Sutlej by comparing the groundwater concentrations and geochemistry of the present study area located away from the River Sutlej with the previous study done near the River Sutlej. Moreover, the area has the arid environment. In arid environments, the evaporative concentration of salts has the potential to rise As concentrations in groundwater as well. The objective of this study **is**; to compare the As concentrations of two alluvial aquifers and establish a role of alluvial deposits of river Sutlej in presence and degree of concentration of As; to understand the geochemical processes and role of evaporative concentrations in controlling the As concentrations in groundwater Vehari, Punjab.

Materials and methods

Study area description

The study area is located between 29°36′N–30°22′N and 71°44′E–72°53′E, latitude and longitude respectively. The total area of the district is 4364 square kilometers. The population of the district Vehari is approximately 2,613,020 (Government of Punjab, 2007). It is located about 16 km from the southern-most of the five rivers (Sutlej) in Punjab.

Geology, hydrology, and climate of the area

The Punjab province of Pakistan is located at latitude 24 37°N and longitude 62 75°E within an alluvial plain of the south Indus River and its five major tributaries comprising >350-m-thick Holocene and Pleistocene sediments brought by the Ravi and Sutlej rivers (Fig. 1). The sediments are made mostly of sand, containing a high percentage of fine-to-very fine sand and silt with low organic matter content. Vehari is to the north of the Sutlej River. It comes to the alluvial aquifer region of Sutlej River which is made of unconsolidated surficial deposits of silt, sand, and gravel. Ground water is found in interbedded deposits of alluvial sand and silt which are present almost everywhere to depths of 304.8 m or more in the Punjab region. These deposits have been forming since late Tertiary times by the Indus River and its tributaries in a vast alluvial plain that extend from the foothills of the Himalaya to the Arabian Sea (Swarzenski 1968). People of this area rely on the groundwater and surface water for drinking, livestock and agriculture purposes. The Vehari District has an extreme climate; temperatures can range from approximately 48.7 °C in summer to 1 °C in winter. The average rainfall is about 127 mm per year.

Sampling and methodology

Sampling was done from the urban and rural distribution of tehsil Vehari and distance from river Sutlej. Ten villages and one city of Vehari were selected for sampling at a different depth. Five samples from each village and ten samples from the city were collected according to the population density and distance from the river of the area. The study areas with their respective sampling points are shown in Fig. 1.

Sixty, 500-ml samples were collected during June 2015 in pre-washed duplicate bottles made of polyethylene; the bottles were previously soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. 49 samples were collected from shallow hand-pumped wells at 23–31 m depth, 4 samples from shallow electric motor-pumped wells at 25–50 m depth, and 7 samples from deep tube wells at depth of 61–153 m, used for community supply and irrigation of land.

Fig. 1 Study area showing locations of sampling points
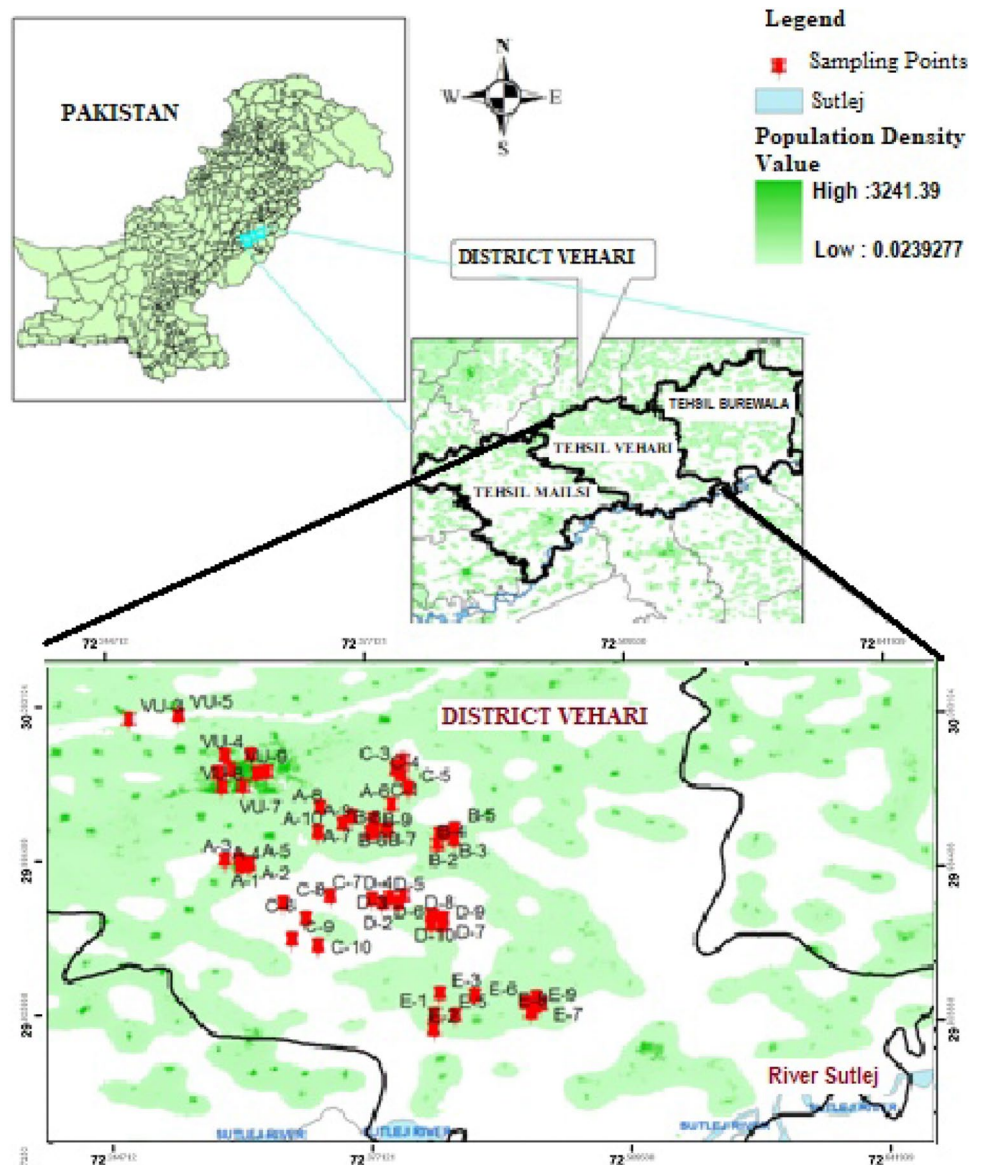
Duplicate water samples were collected and preserved either acidified for cations, or non-acidified samples that were used for anion analysis. At the sampling sites, these bottles were rinsed again with the groundwater to be sampled, completely filled, and tightened with sealed caps. For NO_3 analysis the samples were separately collected in pre-washed polyethylene bottles and preserved in ice-box and transported to Geochemistry Laboratory, Islamabad, for laboratory analysis. The samples were stored immediately in a refrigerator at 4 °C.

Analytical procedures

Different water quality parameters, their units, abbreviations and methods of analysis applied are summarized in Table 1.

In the field, pH, temperature (°C) and EC (µS/cm) of water samples were measured using a pH 25+ portable pH meter (CRISON instruments, S.A.) and digital conductivity meter (PCSIR laboratories complex Karachi model), respectively. Total alkalinity was determined using acid titration, with methyl-orange as an indicator (2320, Standard method, 1992).

Chloride was determined by potentiometric titration with a standard 0.0141 N silver nitrate solution and potassium chromate indicator (ISO 9297, 1989). Sulfate ions are precipitated as barium sulfate in an acidic medium with barium chloride. The absorption of light by this precipitated suspension was measured by spectrophotometer at 420 nm (APHA 2004). Phosphates were determined by using ammonium molybdate and stannous chloride reagent photo-metrically at 690 nm (APHA 2004). Nitrates were determined by using

Table 1 The variables with their respective abbreviation, units and analytical methods/equipments

Variables	Abbreviations	Units	Holding time	Preservative	Analytical methods
Temperature	T	°C	In situ	None	Thermometer
pH	pH	pH unit	In situ	None	CRISON instruments, S.A.
Electric conductivity	EC	mS/cm	In situ	None	EC meter
Total dissolve solids	TDS	mg/L	15 days	3–5 °C	Conductivity meter
Alkalinity	–	mg/L	4 days	3–5 °C	Titrimetric method APHA Standard Method 2320
Total hardness	TH	mg/L	3 days	3–5 °C	Titrimetric method APHA Standard Method 3500-Ca_D
Chloride	Cl^-	mg/L	3 days	3–5 °C	Titrimetric method APHA Standard Method 4500_Cl^-_B
Sulfates	SO_4^{2-}	mg/L	5 days	3–5 °C	Spectrophotometer (DR 2800)
Nitrates	NO_3^-	mg/L	6 days	3–5 °C	Spectrophotometer (DR 2800)
Phosphate	PO_4^-	mg/L	2 months	3–5 °C	Spectrophotometer (DR 2800)
Arsenic	As	µg/L	3 months	HNO_3, pH < 3	Graphite technique and hydride generation GTA110 Varian
Sodium	Na^+	mg/L	4 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)
Potassium	K^+	mg/L	5 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)
Calcium	Ca^{2+}	mg/L	5 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)
Magnesium	Mg^{2+}	mg/L	5 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)
Iron	Fe	mg/L	5 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)
Manganese	Mn^{2+}	mg/L	5 months	HNO_3, pH < 4	FAAS (Varian Spectra AA-240)

phenol disulphonic acid and sodium hydroxide or concentrated ammonium hydroxide. The absorbance was read at 410 nm using a spectrophotometer after the development of color (APHA 2004).

For cations and heavy metals, the analysis was done by using flame atomic absorption spectrophotometer (FAAS) method 7000B US EPA (Kopp and McKee 1979). To determine the arsenic concentration, use of an instrumental atomic absorption spectrophotometer (graphite technique) was applied at Geo-science advanced research lab (Geological Survey of Pakistan). Samples were left unfiltered in order to provide accurate values. This is consistent with the assumption that those populations consuming the water were also not filtering the water.

To assess the quality assurance and quality control of data field blanks, calibration blanks, spiked samples and replicates were used. In order to validate the data, reagent blanks were regularly analyzed within each series of analysis. During the experimental process all reagents used were certified and all glassware was soaked in 10% HNO_3 for at least 48 h before use.

Statistical analysis

All mathematical and statistical computations were made using Statistica v5.5, XLSTAT-Pro v7.5.2 software. The application of different multivariate statistical techniques, such as cluster analysis (CA) and principal component analysis (PCA) helped in the interpretation of complicated data matrices. To better understand the temporal and spatial variances of water quality MVSP (Version 3.21) was used. For mapping of sampling locations and distribution of arsenic Arc GIS (Version 9.3) was being used.

Results and discussion

Groundwater chemistry

The WHO limits, no. of observations, minimum, maximum (range), mean and standard deviation values of each parameter are shown in Table 2. Groundwater samples were categorized into three groups for convenience according to the well depth: shallow (20–37 m), middle (46–76 m) and deep (122–153 m). The results revealed that most of the variables for groundwater of tehsil Vehari significantly deviate from WHO limits and Pakistan National Environmental Quality Standards (NEQS).

The pH ranged between 7.03 and 8.4 in groundwater samples, which were within the WHO regulated values for drinking water. The pH of the groundwater is slightly alkaline. Although pH of drinking water has no direct effects

Table 2 Descriptive statistics of physiochemical parameters classified by well depth

Variables	Units	WHO limits	Pakistan NSDWQ	Shallow ($n = 51$)			Middle ($n = 5$)			Deep ($n = 4$)		
				Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
T	$^\circ$C	–	–	25.5	29.9	27.6	26.8	28.4	27.9	27.9	27.1	27.6
pH		6.5–8.5	6.5–8.6	7	7.9	22.9	7.3	8.7	7.7	7.7	7.4	7.5
EC	µS/cm	0.25	0.25	0.2	3	1.3	0.6	2.1	1	1	0.26	1.8
TDS	mg/L	1000	1000	147.2	1907	8.4	403	1324	6.9	6.9	166	1.1
HCO_3^-	mg/L	500	–	30	900	3.7	50	600	3.9	3.9	60	1.4
TH	mg/L	500	500	494	1103	9.4	403	1452	6.4	6.3	779	3.7
As	µg/L	10	50	BDL	100	20.3	BDL	155	59.9	59.9	BDL	BDL
Cl^-	mg/L	250	250	142	1278	4.9	319	994	4.8	4.8	248	9
F^-	mg/L	1.5	1.5	0	0.9	0.6	0.3	0.8	0.5	0.5	0.2	0.7
NO_3^-	mg/L	50	50	3	190	29	5	87	29	29	6	10
PO_4^{3-}	mg/L	0.1	–	2	46	13	4	27	11	11	8	18.7
SO_4^{2-}	mg/L	250	–	49	906	3.1	110	882	6	5.9	41	3.4
Fe	mg/L	0.3	–	BDL	0	BDL	BDL	BDL	BDL	BDL	BDL	0.1
Ca^{2+}	mg/L	100	–	96.5	176	2.1	104	309	1.9	1.9	44	97
Mg^{2+}	mg/L	50	–	33.4	69.5	1	64	176	1	1	26	52
Na^+	mg/L	200	–	51.3	255	2.3	147	583	2.1	2.1	127	3.8
K^+	mg/L	12	–	3.2	38	13	6.1	15	10	10	7.2	11.3
Pb	mg/L	0.01	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu^{2+}	mg/L	2	2	BDL	0.5	BDL	BDL	0.5	0.1	0.1	BDL	BDL
Cr^{3+}	mg/L	0.05	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cd	mg/L	0.1	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Mn	mg/L	0.5	0.5	BDL	47	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Detection limits Fe = 0.02 mg/L, for Pb = 0.05, Cu = 0.1, Cr = 0.05, Cd = 0.01, Mn = 0.4 mg/L F^- = 0.5 mg/L and arsenic = 0.01 µg/L

BDL below detection limits

on human health, it can control adsorption and desorption processes of As and can change other water quality parameters, thus playing an indirect role (Farooqi et al. 2009). TDS and EC in all groundwater samples were in the range of 147–2054 mg/L and 0.23–3.21 µS/cm, respectively. High EC represents water with high electrolyte concentration, may be due to high rate of evaporation. The high values of EC were attributed to the high salinity and soluble electrolytes in underground water samples and lower water table (Baig et al. 2009; Kazi et al. 2009).

Chemical analysis of groundwater exposed variations in most of the anions, some are within the limits and some deviating from the WHO and Pakistan NEQS. Chemical quality parameters revealed that the concentration of chlorides in 80% water samples was exceeding the permissible limits set by WHO (250 mg/L) and Pakistan NEQS with the range of 142–1810 mg/L. The average values of chlorides in all sampling sites was 522 mg/L. Chloride is naturally present in groundwater, particularly in deep bedrock aquifers (Aichele 2004). High rainwater runoff, sewage discharge, evaporation of the salt solution in the aquifer and industrial effluent are major sources for increasing the concentration of chloride in groundwater (Malana and Khosa 2011).

Bicarbonates (HCO_3^-) are relatively higher with concentrations ranging from 30 to 900 mg/L. This concentration of bicarbonates, indeed, is rather undesirable in terms of the chemical composition of water. According to the WHO guidelines, the permissible limits of sulfates in water is 250 mg/L and in this study about 60% of water samples exceeded the limits ranging from 41 to 906 mg/L with e mean value of 340 mg/L. The tremendously high concentration of sulfate is mainly due to the poor drainage system of domestic effluents and sludge disposal, in addition, fertilizers being used for the agricultural purpose in the study area. Similarly, nitrates were also high in 10% of the samples with a range of 3–190 mg/L. The elevated nitrate affected sites mainly reveal direct impact from agricultural activities. Moreover, sewage and industrial effluent including septic tanks discharged to unsaturated aquifers, rain fall and animal excreta could also be sources for an elevated concentration of nitrates in nitrate-rich samples (Singh et al. 2005).

Phosphate is the major constituent and essential anion in the soil for the growth of plants, but its excess amount penetrates groundwater. In study area, elevated phosphate has been observed in many samples exceeding the WHO limits with the range of 0.02–6 mg/L. It is primarily due to the

excessive use of phosphate fertilizers such as DAP (diammonium phosphate) and their run-off from the agricultural field as well as human and animal waste, detergents, leaking septic tanks and disturbed land areas (Agusa et al. 2004).

The hardness of the water body is determined largely by the level of calcium (Ca^{2+}) and magnesium (Mg^{2+}) salts such as calcite and dolomite (Singh et al. 2005). Apparently, in the study area, the concentration of Ca^{2+} in all sampling locations varied widely. The increasing trend of Ca^{2+} was observed with increase of the depth of aquifers, shallow, middle and deep aquifers showed the maximum concentration of calcium as 196 mg/L, 336 mg/L, and 440 mg/L, respectively (Table 2). The varied concentration of Ca^{2+} due to the weathering of carbonates and plagioclase feldspar minerals, which are abundant in flood plain regions (Kumar et al. 2010). In the case of magnesium, the same trend was observed with 69, 176, and 258 mg/L in shallow, middle and deep aquifers, respectively (Table 2). The groundwater of tehsil Vehari is hard which increases with the increase of depth of aquifers.

The concentration of Na^+ in about 50% water samples were higher than the maximum permitted concentration of WHO (200 mg/L). The concentration of Na^+ revealed that it was increasing with the increase of the depth of the wells. The maximum concentration in shallow wells was 255 mg/L, in middle 583 mg/L and in deep wells were 618 mg/L (Table 2). The major source of Na^+ in water is mineral deposits, sewage, fertilizers and agricultural wastes (Sayyed and Bhosle 2011). For potassium concentration 49% groundwater samples showed higher concentration than the WHO permissible limit (10 mg/L). The concentration of potassium at different depths showed that it decreases with the increase of depth of aquifers, so the main reason of increasing potassium into groundwater seems to be due to agricultural activities (Sayyed and Bhosle 2011).

Pearson's correlation was done to find out the relationship of different physiochemical parameters of water to estimate the water quality and water chemistry of ground water of tehsil Vehari. A number of significant positive and negative correlations are observed as presented in Table 3. Results from the table revealed that some parameters show slight positive correlation like HCO_3–EC, HCO_3–TDS, HCO_3–pH, TH–pH, TH–HCO_3, Cl–TH, NO_3–TDS, NO_3–TH, PO_4–Cl, SO_4–TDS, SO_4–HCO_3, while significant correlation was shown in many parameters including TDS–EC, As–HCO_3 (0.433), As–SO_4 (0.511), Cl–EC (0.569), Cl–TDS (0.569), Ca–TH (0.84), Mg–TH (0.87), Mg–Ca (0.693).

Major water type and mechanism controlling groundwater chemistry

Water quality characterization of the study area was done through the use of piper plot at different depth of aquifers.

These water types show hydro-chemical diversity among the groundwater samples. The results revealed that water displayed Ca–HCO_3, Ca–Mg–Cl, $CaCl_2$, types of water. About 55% had Ca–Mg–Cl-dominant types of water chemistry, while 33% samples had the Ca–HCO_3-dominant type of water chemistry, about 11% samples showed $CaCl_2$ type of water and only one shallow water sample had Na-Ca-HCO_3^- type water chemistry (Fig. 2).

There are many factors which control the groundwater chemistry including the physical condition of the well, mineralogy of bedrocks and climatic condition. Gibbs (1970) suggested the TDS against $Na^+/Na^+ + K + Ca^{2+}$ for cations and TDS against $Cl^- + HCO_3^-$ for anions to demonstrate the natural controlling factors of groundwater chemistry, including the rainfall dominance, rock weathering dominance, and evaporation and precipitation dominance. According to the Gibbs diagram, 60–70% samples including shallow, medium and deep depth may have been influenced by rock weathering reaction (Fig. 3a, b). Around 30–40% of shallow depth, ground water samples were controlled by the evaporation–precipitation dominance field (Fig. 3a, b). It seems that the ion chemistry of groundwater generally related to carbonate and silicate weathering process. However, evaporation was the secondary factor that mostly controls the groundwater chemistry.

Spatial variation of arsenic and its comparison with previous study to understand the probable contribution of alluvial deposits of Sutlej River

The recommended value of arsenic (As) in drinking water by WHO is 10 µg/L and is 50 µg/L for Pakistan National Environmental Quality Standards (NEQS). In the study area, most of the water samples displayed variation among sampling points. The mean, minimum and maximum of all locations classified on the basis of the depth of the wells are summarized in Table 1. The highest concentration of As was found in the middle depth of aquifers, i.e. 156 µg/L while in deep aquifers all samples were BDL (below detection limit) or less than zero. About 50% samples were exceeding to WHO limits and about 20% samples were exceeding the Pakistan NEQS. In the study area, the concentration of arsenic (As) in groundwater was lower than those reported in tehsil Mailsi of same district Vehari (Rasool et al. 2015) (Fig. 4) which is located near River Sutlej.

Arsenic concentrations decrease as the distance between river increases as shown in Fig. 4 for the district Vehari. Also, high arsenic concentrations were observed in the rural area (10–155.6 µg/L) as compared to an urban area far away from the alluvial plain (0–30 µg/L). To compare the present study of tehsil Vehari with tehsil Mailsi (Rasool et al. 2015), we have plotted the results of a previous study by Rasool et al., with the arsenic concentrations for the present

Table 3 The correlation coefficient matrix of the physio-chemical parameter with arsenic and fluoride ($n = 60$)

Variables	T	pH	EC	TDS	HCO3	TH	As	Cl	F	NO$_3$	PO$_4$
T	**1**										
pH	−0.09	**1**									
EC	−0.01	−0.128	**1**								
TDS	−0.01	−0.128	**1.000**	**1**							
HCO$_3$	−0.13	0.097	0.017	0.017	**1**						
TH	−0.08	0.002	−0.032	−0.032	0.112	**1**					
As	−0.14	0.289	−0.240	−0.240	**0.433**	0.033	**1**				
Cl	0.143	−0.14	**0.569**	0.569	−0.16	**0.340**	−0.020	**1**			
F⁻	0.084	0.141	−0.21	−0.210	−0.06	**−0.352**	−0.081	−0.06	**1**		
NO$_3$⁻	0.012	−0.062	0.020	0.020	−0.07	0.151	−0.109	−0.010	−0.08	**1**	
PO$_4$	−0.010	−0.125	−0.07	−0.07	−0.04	−0.882	0.091	0.031	0.298	−0.22	**1**
SO$_4$	−0.191	0.155	0.094	0.094	0.342	0.062	**0.511**	−0.058	−0.212	−0.057	−0.07
Fe^{2+}	0.055	0.152	0.147	0.147	−0.108	−0.040	−0.107	0.116	0.344	−0.139	0.176
Ca^{2+}	−0.093	−0.145	−0.085	−0.085	0.110	**0.84**	−0.034	0.05	−0.302	0097	−0.607
Mg^{2+}	−0.055	0.168	0.324	0.324	0.196	**0.875**	−0.107	**0.316**	−0.345	0.192	−0.125
Na$^+$	0.070	−0.123	**0.303**	0.303	−0.094	−0.038	−0.042	**0.424**	0.095	0.012	0.067
K$^+$	0.192	0.020	0.155	0.155	−0.286	0.138	−0.204	**0.376**	−0.027	0.014	0.291
Pb	−0.172	−0.139	0.242	0.242	−0.177	0.012	−0.070	0.144	0.164	−0.128	0.232
Cu	−0.075	−0.062	−0.018	−0.018	0.304	0.108	0.113	0.059	0.032	0.083	0.058
Cr	0.003	−0.031	−0.058	−0.058	0.218	−0.107	0.126	−0.223	−0.070	−0.046	−0.047
Mn	−0.064	−0.023	−0.088	−0.088	−0.115	−0.106	−0.102	−0.065	**0.695**	−0.104	**0.477**
Cd	−0.200	0.016	0.173	0.173	0.086	0.065	−0.069	0.113	0.120	−0.064	0.189

Variables	SO$_4$	Fe	Ca	Mg	Na	K	Pb	Cu	Cr	Mn	Cd
T											
pH											
EC											
TDS											
HCO$_3$											
TH											
As											
Cl											
F⁻											
NO$_3$⁻											
PO$_4$											
SO$_4$	**1**										
Fe^{2+}	0.001	**1**									
Ca^{2+}	−0.306	−0.075	**1**								
Mg^{2+}	0.008	−0.806	**0.693**	**1**							
Na$^+$	0.049	0.316	0.091	−0.186	**1**						
K$^+$	−0.091	0.158	0.233	0.108	**0.316**	**1**					
Pb	−0.134	**0.318**	−0.040	−0.091	**0.435**	0.200	**1**				
Cu	0.155	−0.201	0.141	0.309	−0.207	−0.088	−0.089	**1**			
Cr	0.098	−0.207	−0.107	−0.089	−0.024	−0.036	−0.124	−0.003	**1**		
Mn	−0.082	**0.410**	−0.019	−0.084	0.221	0.125	**0.407**	0.017	−0.187	**1**	
Cd	−0.022	0.283	0.138	0.008	0.116	0.104	**0.531**	0.064	**−0.295**	**0.53**	**1**

Bold values indicate significant correaltion

Table 4 Represents the composition of sampling site classes obtained from cluster analysis

Groups	Sampling sites
Group 1	VU-1, VU-2, VU-3, VU-5, VU-7
Group 2	VU-4, VU-6, VU-8, VU-9, VU-10, A-1, A-3, A-4, A-5, A-7, A-8, A-9, A-10, B-1, B-4, C-2, C-4, D-6, E-1, E-3, E-10
Group 3	A-2, A-6, B-2, B-3, B-5, B-6, B-7, B-8, C-1, C-3, C-7, C-10, D-1, D-2, D-4, D-5, D-7, D-8, D-9, E-2, E-4, E-5, E-6, E-7, E-8, E-9
Group 4	B-9, B-10, C-5, C-6, C-8, C-9, D-3, D-10

Fig. 2 Classification of ground-water of the study area according to Piper's scheme
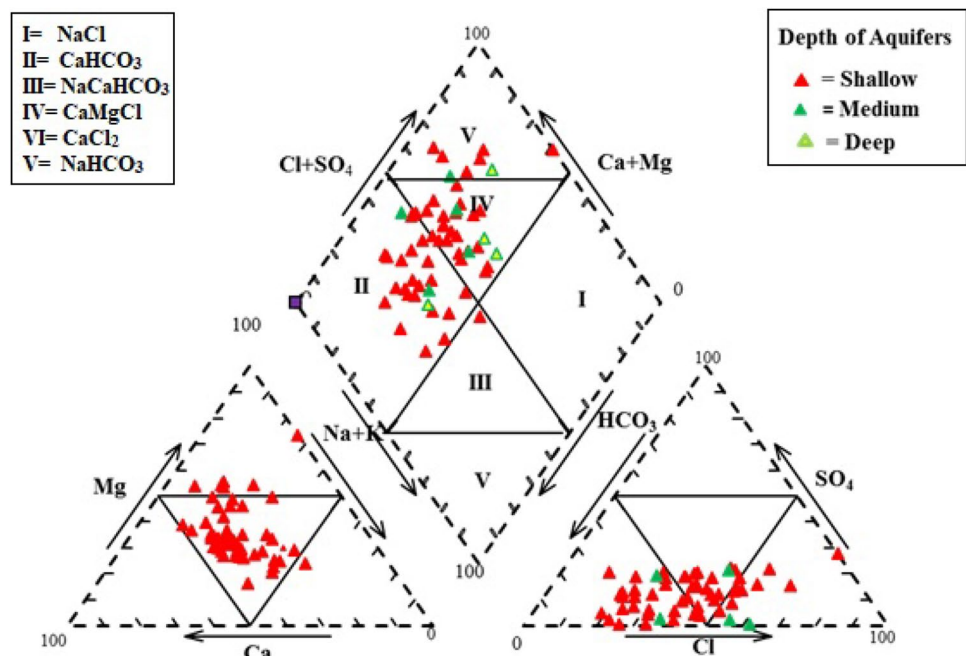
study (Fig. 4). Interestingly, within a given district, areas lying closer to the river Sutlej were found to have relatively higher As concentration than those away from the river system irrespective of the depth of aquifers. This showed that the concentrations of As were much higher in tehsil Mailsi (11–823 µg/L) closer to the river and in the present study tehsil Vehari the concentrations of As are less (BDL- 156 µg/L) get lower because of the more distance from the River.

Generally, the As concentration is observed higher in alluvial bedrocks worldwide which shows the contribution of river sediments for higher As in groundwater (Arain et al. 2009a, b; Malana and Khosa 2011). Higher arsenic concentration is observed near river in floodplain areas which is mainly composed of alluvial deposits, e.g. Bengal delta, Meghna flood plains in Bangladesh Ganges–Brahmaputra river system, old Brahmaputra floodplain of Bangladesh (Ahmed et al. 2004, 2010; Berg et al. 2007; Busbee et al. 2009), area near Fairbanks, Alaska, and Western Snake River Plain of Idaho, USA (Verplanck et al. 2008; Busbee et al. 2009), Kandal Province of Cambodia (Luu et al. 2009),

Ghazipur District in the middle Gangetic Plain, India (Kumar et al. 2010), Huhhot Basin, Hetao Plain located in the Great Bend of Yellow River in Inner Mongolia and Datong Basin area China (Smedley et al. 2003; Guo et al. 2010; Li et al. 2012) (Appendix 1). Arsenic released from these sediments has caused the most widespread contamination in the world. The province of Punjab is in an alluvial plain, comprising more than 350-m-thick Holocene and Pleistocene deposit carried by two rivers Ravi and Sutlej (Swarzenski 1968). The comparison of the present study with the previous study (Rasool et al. 2015) showed the aquifers near the active flood plain have higher arsenic concentrations as compared to the district Vehari (present study). Although the sediments were not analyzed in the current study, the evidence shows that the alluvial sediments of the active flood plain of river Sutlej may be responsible for the presence of elevated arsenic in groundwater near the river, which further needs validation by collecting river sediments with distance and analyzing the arsenic concentrations.
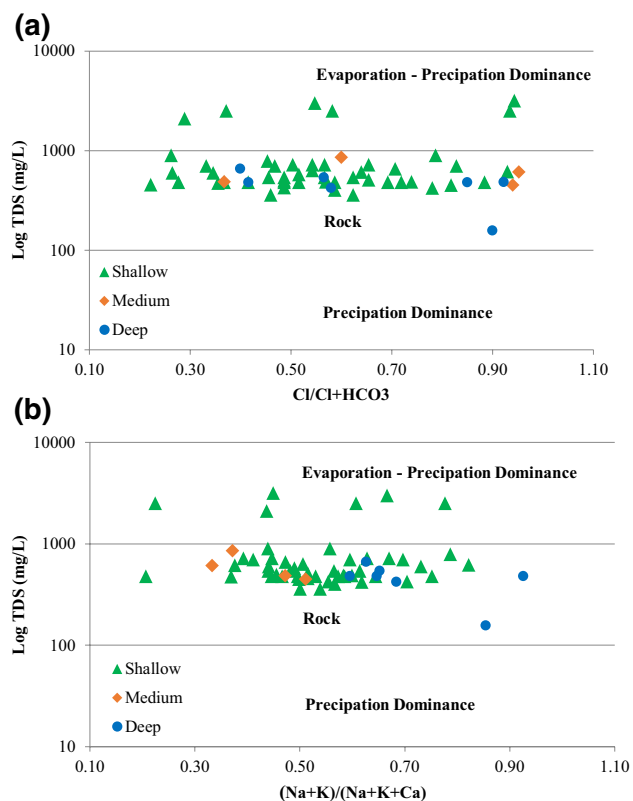
Fig. 3 Represents Gibbs plots that explain groundwater chemistry and geochemical process in the study area. **a** Gibbs plot of anions, **b** Gibbs plot cations

Geochemical control of arsenic mobilization in groundwater: role of evaporative concentration

There seem to be two distinct mechanisms that can lead to the abundant release of As into groundwater. The first mechanism is the increase of strongly reducing conditions at near-neutral pH values, leading to the desorption of arsenic from mineral oxides and to the reductive dissolution of iron and manganese oxides, leading to arsenic release. Iron and arsenic are relatively abundant in these ground waters and sulfate concentrations are lower (typically 1 mg/L or less). Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of arsenic because of competition for adsorption sites (Smedley and Kinniburgh 2002).

Second mechanism is the development of high pH (> 8.5) conditions in semi-arid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads either to the desorption of adsorbed As and a range of other anion-forming elements (V, B, F, Mo, Se and U) from mineral oxides, or it prevents them from being adsorbed (Robertson 1989; Nicolli et al. 2010).

In oxidizing aquifers, arsenic (As) mobilization from sediments into groundwater is controlled by pH-dependent As desorption from and dissolution of mineral phases. If climate is dry, then the process of evaporative concentration contributes further to the total concentration of dissolved As (Nicolli et al. 2010).

In semi-arid and arid regions of different parts of the world including, Mexico and southwestern USA, northern Mexico, Atacama Desert, northern Chile and Argentina, Muzaffargarh and Tharparkar, Pakistan, reported that the evaporative concentration leading to high pH, high salinity in oxidizing aquatic environment is responsible for the release of arsenic into ground water (Nickson et al. 2005; Nicolli et al. 2010; Camacho et al. 2011; Brahman et al. 2013a, b).

In the present study, the correlation between As and some important parameters was drawn for investigating the mechanism of As release. The correlations are presented in scatter diagrams in Fig. 5. The results from present study area showed some trend of oxidative desorption with increase evaporative concentration mechanism concluded on the basis of alkaline pH (7.03–8.7), low iron (BDL-0.07 mg/L), high bicarbonates (HCO_3^-) with the range of (30–900), high sulfates with range of (142–1810), negative correlation of iron and manganese with arsenic ($-0.107\ r^2$), ($-0.102\ r^2$), respectively, and significant positive correlation between As–HCO_3^- (0.433) and As–SO_4^{2-} (0.511), and slight positive correlation with pH (0.3) in ground water of tehsil Vehari. The evaporative mechanism is also justified with the Gibbs diagram which showed that evaporation is also dominant natural phenomena in controlling water chemistry of the study area (Fig. 3).

Hierarchal cluster analysis

The multivariate treatment of environmental data is useful for validating temporal and spatial variations caused by natural and anthropogenic factors (Dixon and Chiswell 1996; Vega et al. 2001). The application of different multivariate statistical techniques, such as cluster analysis (CA) and principal component analysis (PCA) helps in the interpretation of complicated data matrices to better understand the temporal and spatial variances of water quality, to identify spatial similarity and dissimilarity for grouping of sampling origins. In cluster analysis, the objects are grouped such that the similar objects fall into the same class (Danielsson et al. 1999; Brahman et al. 2013b).

The dendrogram (Fig. 6) grouped all the 60 sampling sites into four statistically significant clusters. The dataset was treated (after data scaling by z-transformation) by the Ward's method of linkage with squared Euclidean distance as a measure of similarity. The sampling sites VU-1, VU-2, VU-3, VU-5, and VU-7 made one cluster

Fig. 4 Spatial variation of arsenic in tehsil Vehari in comparison to the spatial distribution of As in previously reported area tehsil Mailsi by Rasool et al. (2015). The trend in the present study shows that as the distance from the river increases the concentrations of As decrease. While, in the previous study which was closer to river higher concentrations of As were observed
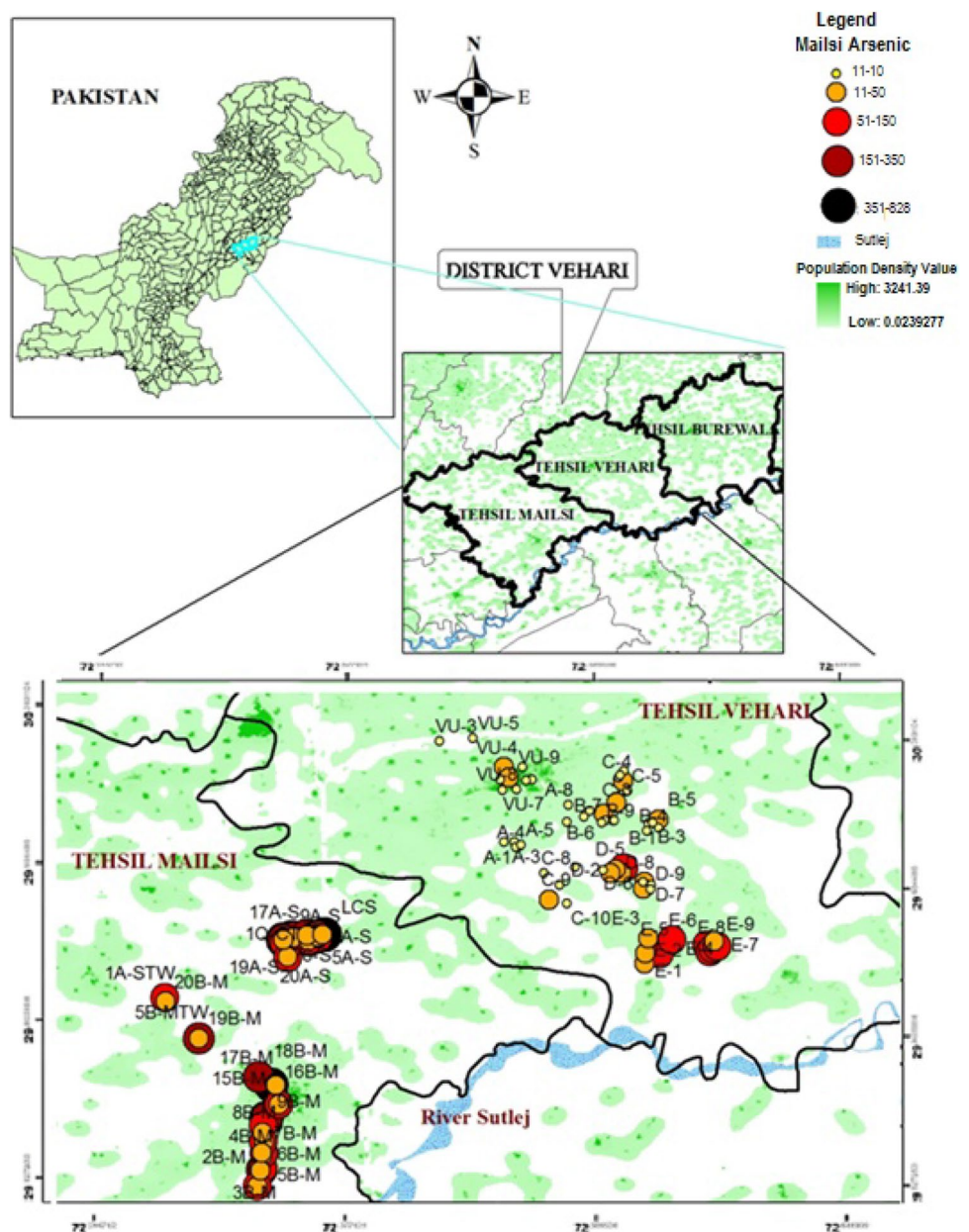
as Group 1, which corresponds to 8.3% of all the sample sites, the underground water samples of sites in this cluster are within WHO limit (10 µg/L). While due to mutual dissimilarity among other sampling origins of ground water made of Group 2, which corresponds to 35%, involving VU-4,VU-6, VU-8, VU-9, VU-10, A-1, A-3, A-4, A-5, A-7, A-8, A-9, A-10, B-1, B-4, C-2, C-4, D-6, E-1, E-3 and E-10 sites which shows As concentration in the range of 0-50 µg/L. Moreover, 63% of this group has As level below WHO limit while 36% content As below National Standard. Group 3, involving A-2, A-6, B-2, B-3, B-5, B-6, B-7, B-8, C-1, C-3, C-7, C-10, D-1, D-2, D-4, D-5, D-7, D-8, D-9, E-2, E-4, E-5, E-6, E-7, E-8, and E-9 sites

corresponds to 43% of total sampling sites, contains As in concentration range of 0–156 µg/L. This group showed highly spatial distribution of As; 43% of sample in this group are within WHO limit, 27% 10–50ug/L while 30% above 50 µg/L. Group 4 contained B-9, B-10, C-5, C-6, C-8, C-9, D-3 and D-10 sites corresponding to 16% of total sampling sites and more than 63% of sample are within WHO limit (10 µg/L) with the range of As 0–30 µg/L. The groundwater sample of 60 sites was grouped into clusters 1, 2, 3 and 4, classified as low, high and medium-polluted areas with As contamination listed in Table 4.
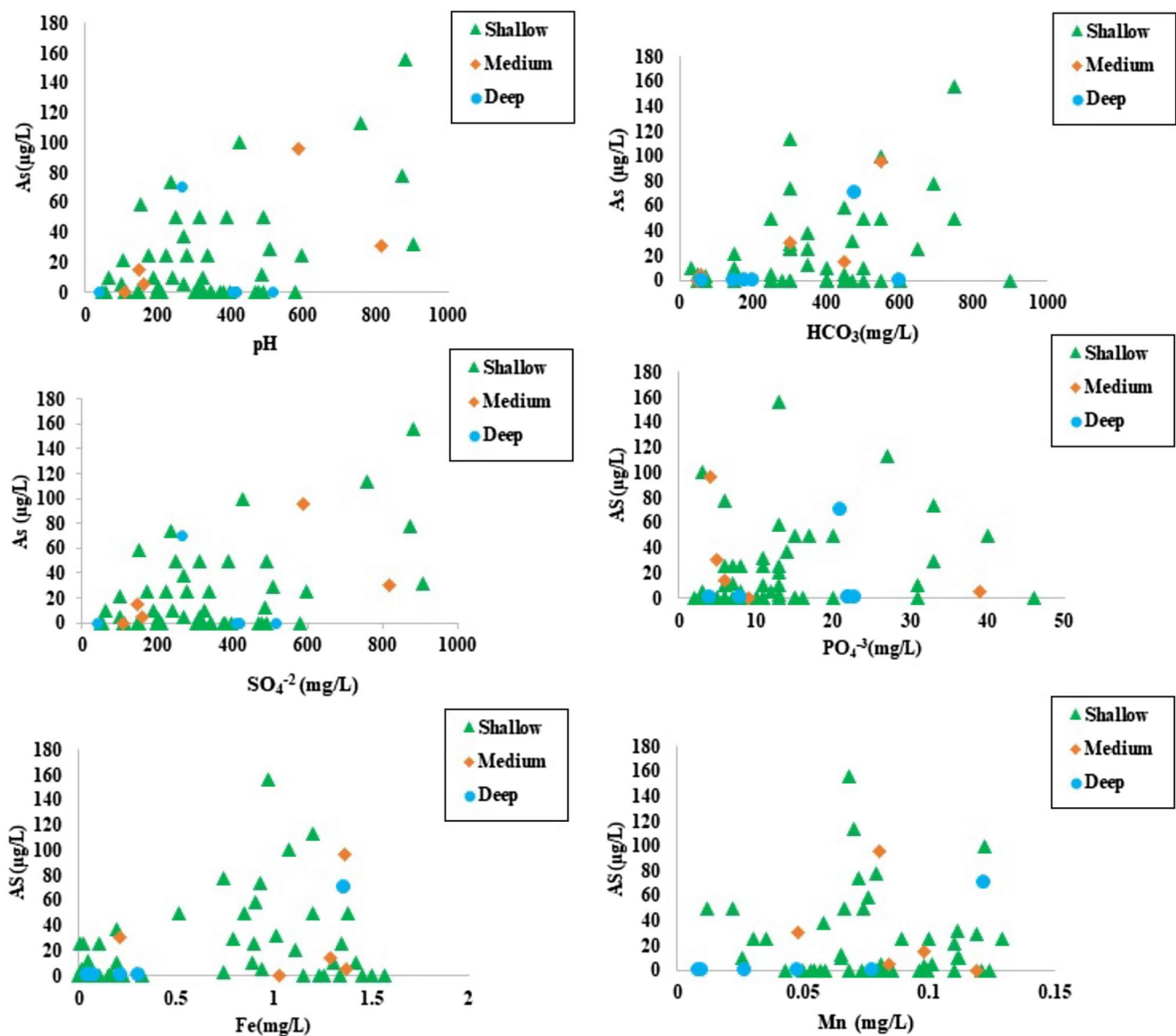
Fig. 5 Scatter diagram showing the correlation between arsenic and different variables in groundwater

Principal component analysis

The principal component analysis (PCA) is a dominant tool used to determine the variance of a large dataset of inter-correlated variables with a smaller set of independent variables (Simeonov et al. 2003). PCA was performed on the dataset to associate the compositional patterns between the groundwater samples and to identify the factors which were responsible for the interaction between them. Four components of PCA analysis showed 64.991% of the variance on the resulted data of ground water samples as shown in Table of annexure 3. The first component (Factor 1) corresponds to over 21.96% of the total variance in the dataset of groundwater, have positive loading with alkalinity, arsenic,

nitrates, and sulfates show strong geochemical associations. The second component (Factor 2), explaining 17.87% of the total variance, has strong positive loadings with depth, pH, alkalinity, arsenic, phosphates, sulfates, iron and manganese the geogenic effects and anthropogenic sources. The third component (Factor 3) of PCA shows 13.4% of the total variation has relationship between depth, pH, arsenic, alkalinity, sulfates and chlorides describes the contribution from arid climate, weathering of minerals and is responsible for the significant relationship between those parameters (Kumar et al. 2010), while fourth component (Factor 4) of PCA shows only 11.1% of the total variation has positive loading with pH, alkalinity, chlorides, manganese, may due to

Fig. 6 Dendrogram showing clustering of different sites of groundwater according to the distribution of As species and other physicochemical parameters
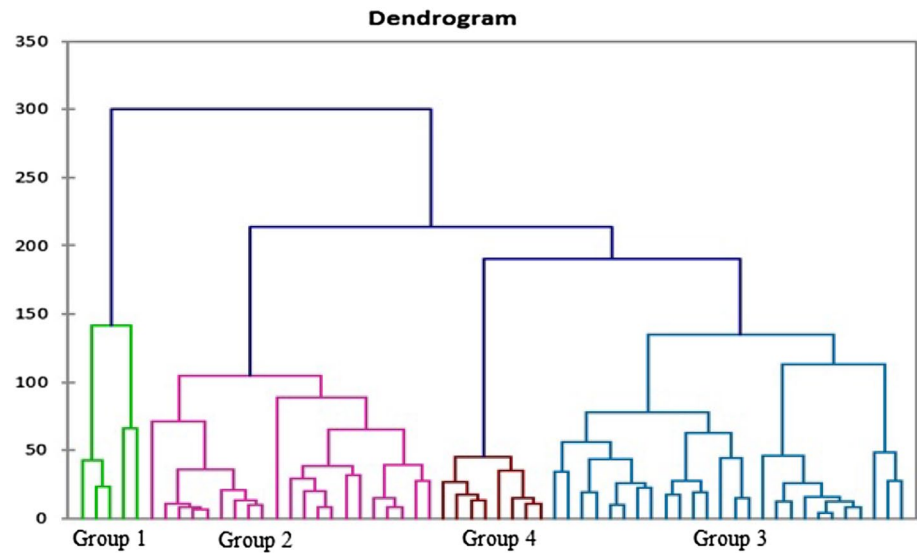
geological and environmental effect (Simeonov et al. 2003; Zhang et al. 2010).

The above observation is clearly shown in Fig. 7 which shows the characteristics of samples and helps to understand the factors responsible for the relationships among these parameters. It is evident that samples distributed in the upper-right quadrant are more enriched with arsenic, sulfates, and HCO_3^{-2} while those in the lower-right quadrant are enriched with nitrates. The samples distributed in the upper-left quadrant are enriched with calcium, magnesium, nitrates and HCO_3^{-2} while lower-left quadrant highly enriched with depth, pH, iron, manganese, and phosphates.
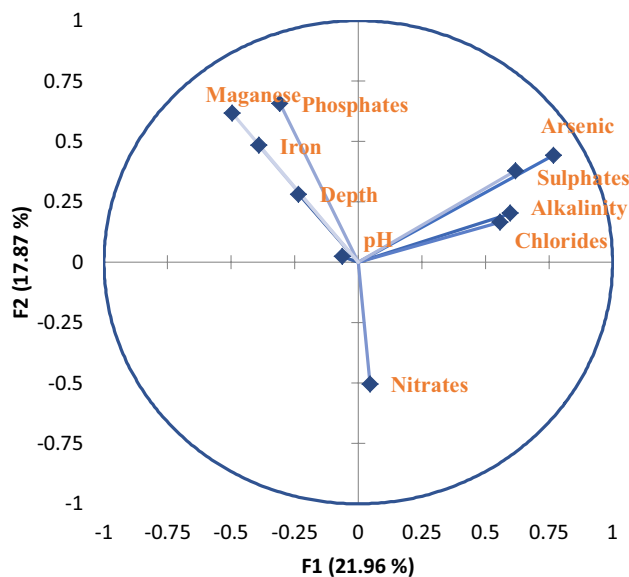

Fig. 7 PCA showing the distribution of As with other water quality parameters

The variables (axes F1 and F2) for the groundwater samples shows the high distribution of As species and other water quality parameters in groundwater samples of tehsil Vehari, which mostly appeared in the upper-right and left quadrants. The high level of As in groundwater samples introduced by, geo-hydrological and geochemical factors (Smedley and Kinnburgh 2002).

Conclusions

The study was conducted on water quality parameters and As of groundwater samples of tehsil Vehari of district Vehari and compared with tehsil Mailsi of district Vehari. Concentrations of As although high are relatively lower as compared to tehsil Mailsi. High arsenic concentrations (up to 156 μg/L) were detected in alluvial aquifers near Sutlej River, with 50% samples exceeding the WHO limit (10 μg/L) and 17% exceeding the Pakistan NSDWQ limits. This trend showed that areas near rivers are more prone to arsenic contamination. Sediments laid by rivers originating from the Himalaya have pronounced effect on arsenic concentrations which further need to be validated by analyzing the river sediments with increasing distance. As the results revealed that occurrence of high arsenic could be mainly due to some trend of oxidative desorption with increase in evaporative concentration mechanism with alkaline pH (7.03–8.7), low iron (BDL-0.07 mg/L), high bicarbonates (30 to 900), high sulfides (142–1810), it is an urgent need to evaluate the prevalence of arsenic in other nearby areas for taking any remedy or preventive action for the provision of safe drinking water to populaces of affected area.

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