

# Quality of tube well water intended for irrigation and human consumption with special emphasis on arsenic contamination at the area of Punjab, Pakistan

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Received: 10 December 2015 / Accepted: 12 July 2016 / Published online: 16 July 2016  
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**Abstract** In the present study, the tube well water quality and the associated health risks, emphasizing on arsenic contamination, were investigated in rural and urban samples from Tehsil Mailsi located in Punjab, Pakistan. Arsenic concentrations ( $\mu\text{g/L}$ ) were ranged from 12 to 448.5 and which exceeded the WHO recommended limit ( $10 \mu\text{g/L}$ ) in all cases. The calculated average daily dose ( $3.3 \times 10^{-0.4}$  to  $1.2 \times 10^{-0.2} \text{ mg/kg day}$ ) and hazard quotient (1.1–40) reflected the potential health risk to local population due to tube well water consumption as

drinking purpose. Sodium percent ( $\text{Na}\%$ ), sodium absorption ratio, residual sodium carbonate, Kelly's index and magnesium absorption ratio were also determined to assess the suitability of tube well water for irrigation purpose. The resulting piper plot revealed the  $\text{Na-Ca-HCO}_3$  type water chemistry of the area and generally alkaline environment. The spatial distribution of arsenic in the tube well waters pinpoints the significant contribution of anthropogenic activities to arsenic pollution. Nevertheless, different statistical tools, including principal component analysis, hierarchical cluster analysis and correlation matrices, revealed the contribution of both natural and anthropogenic activities and alkaline type of aquifers toward the high level of arsenic contamination.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10653-016-9855-8) contains supplementary material, which is available to authorized users.

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**Keywords** Arsenic · Tube well water · Irrigation · Source apportionment · Health risk · Pakistan

## Introduction

Arsenic (As) pollution in groundwater (GW) is a human health threat affecting millions of people worldwide (Katsoyiannis et al. 2015), particularly in Bangladesh, India, China, Argentina, Chile, Mexico and Pakistan (Bhowmik et al. 2015; Amini et al. 2008). The situation is much worse in semiarid and arid regions, where groundwater availability is critical for both drinking and irrigation purposes (Adhikary et al. 2010). In many semiarid and arid regions of Pakistan, groundwater accounts for more than 40 % of water used for irrigation (Briscoe and Qamar 2007), although arsenic contamination has already been demonstrated in the groundwater of Muzaffargarh (Nickson et al. 2005), Kalalanwala (Naseem et al. 2001; Farooqi et al. 2007), Jamshoro (Arain et al. 2009) and Khairpur (Fatmi et al. 2009). However, in the different areas of Indus plain, a large number (about one million) of tube wells are installed to fulfill the irrigation water demand of growing agricultural areas and have become important irrigation feature, which also has long-term effects on the quality and quantity of groundwater. Nevertheless, available data on arsenic contamination in tube well waters and its associated health risk effects in these areas are limited. For the assessment of suitability of the studied water for irrigation, SAR, RSC, %Na, KI and MAR are reported to be helpful proxies (Singh et al. 2012; Ramkumar et al. 2010). Base-exchange and meteoric genesis indices can also be used to evaluate sustainable water resources for irrigation. Possible sources influencing water systems were identified using different multivariate approaches, such as principal components analysis (PCA) and cluster analysis (CA). These approaches are reported as valuable tools for reliable management and rapid solutions of water resources and pollution problems, respectively (Reghunath et al. 2002; Zhang et al. 2011).

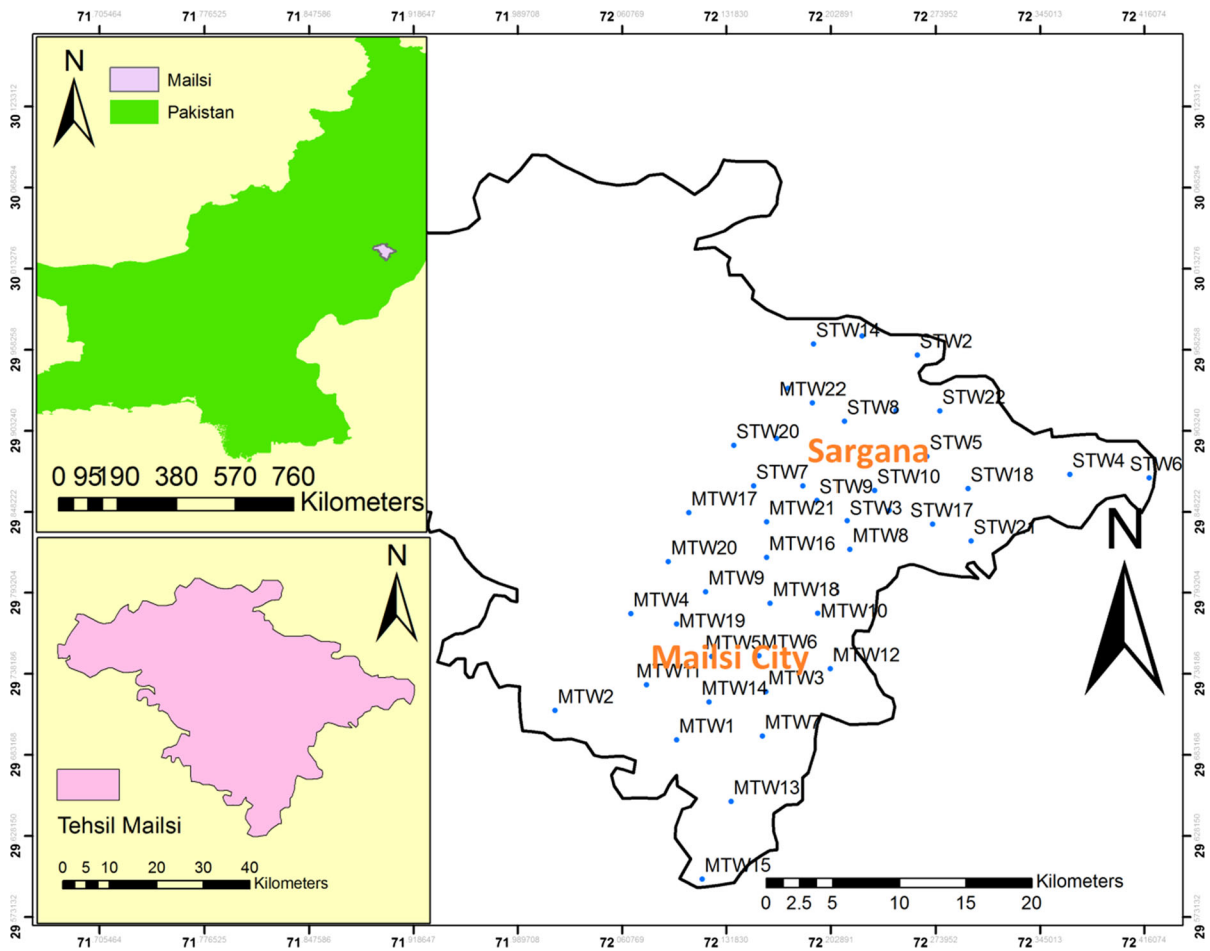
High arsenic concentrations have been reported from the surrounding areas of Sargana and Mailsi including Multan and Muzaffargarh (Nickson et al. 2005) and highlighted that arsenic concentrations are

spatially variable. Therefore, monitoring of arsenic contamination in the As-rich tube well groundwater is essential in order to estimate the extent of arsenic exposure to the exposed population of about 700 thousand people. The objectives of the current study were to study: (1) the groundwater irrigation quality and the extent of arsenic contamination in Tehsil Mailsi area, (2) the source identification of As contamination using multivariate analysis and other statistical tools and (3) evaluation of health risk to the local population due to As contamination. The findings of this study highlight for first time the exposure levels of the local population to arsenic in the groundwater (tube well) of Mailsi Tehsil area and underline the associated human health risks, contributing to achieving sustainable water resources management, which is fundamental for a better economic growth of the country.

## Materials and methods

### Description of the study area

Tehsil Mailsi is located in southern Punjab, Pakistan ( $72^{\circ}17'–72^{\circ}19'E$ ,  $29^{\circ}78'–29^{\circ}92'N$ ), covering an area of 14.88 km<sup>2</sup>, with an altitude of 126 m above sea level (Fig. 1). The southern Punjab, Pakistan, is located within an alluvial plain of the south-flowing Indus River and its major tributaries. The local population is 704,878 people according to census of Pakistan (2010). Farming is the basic occupation of population with major cash crops including cotton, wheat, sugarcane and rice. The groundwater obtained from tube wells serves as the main water supply for irrigation in these areas. From late June to August, the monsoon season starts, with heavy rainfall throughout the country. The average annual precipitation is 243 mm, and the mean temperature is 26 °C (DCR 1998). Mailsi is situated along river Sutlej; however, this river is dry in most part of the year that is why this area is facing shortage of good quality drinking water. Groundwater is the most important source of drinking water in this area. Unluckily, due to unplanned urbanization for the past few decades, the resource degraded in quality. The factors that are affecting water quality of Mailsi are extensive use of fertilizers, pesticides, sewerage system, drainage system, solid waste management and land fill/dumping sites.



**Fig. 1** Location maps showing the sampling points of tube well water samples from Sargana and Mailsi

Among all these factors, inappropriate sewerage system and use of fertilizers are the main causes of water pollution where sewerage water is mixing with ground water and fertilizers are seeping down the groundwater (Abbas et al. 2014).

The study area is characterized by shallow aquifers, which is under alluvial plains, with thick layer of Holocene and Pleistocene sediments transported by the River Sutlej (Greenman et al. 1967), originating from the southern slopes of the holy mountain Kailash, near the lake of Mansarovar and flows parallel to the Himalayas. High percentage of silt, clay, fine sand and low organic matter is present in these sediments. The study area consists of a thickened sequence of unconsolidated flood plain fluvial deposits and eolian deposits of Pleistocene to present age. Calcium carbonate concretions of

irregular shape, but of regular size and distribution, are associated with these sediments (Farooqi et al. 2007). The study area is toward the southwestern part of Bari Doab (the area between the two rivers, Sutlej and Ravi), which covers moderately older alluvial deposits that tend to coincide with zones of highly mineralized groundwater (Greenman et al. 1967). The geologic features that influence permeability and transmissibility are lateral lithological changes, disparity in sand thickness and grain size distribution. The eolian deposits occur above the water table and have no hydrological significance except at few places where the zone of saturation may be within them. The sediments formed as channel infill, levees and overbank flood plain deposits, show lateral and vertical variation. This is due to cyclic shifting in the course of Indus river and its tributaries, which laid

down these sediments. The grain size decreases from northeast to southwest, which points to heterogeneous conditions of deposition and cause for variation in the permeability values of the layers. The absence of continuous clay layers, in general, is indicative of the presence of unconfined aquifers in the fluvial sediments (Farooqi et al. 2007). The sedimentary formations along the Indus River system are similar to those that include the As-contaminated aquifers in the sedimentary basins associated with the Ganga and Brahmaputra River system in Bangladesh and West Bengal, composed of Quaternary alluvial-deltaic sediments derived from Himalayan source rocks. However, the sedimentary basins along the Indus River system, located at the western edge of the Asian monsoon area, are in a more arid climate than other sediments. The older Quaternary (i.e., Pleistocene) deposits are more widely distributed in the western sedimentary basin, probably promoting more aerobic aquifer conditions in the study area than in the other locations (Mahmood et al. 1998; Tasneem 1999).

#### Sampling and analysis

Mailsi city and Sargana were selected as sampling sites in Tehsil Mailsi (Fig. 1). Mailsi is situated in active flood plain area, around 3 km away from Sutlej River. All the samples were collected in 2012 by following the standard procedures (Khan et al. 2012). The study area has a semiarid climate with long and extremely hot summers, and dry and warm winters, monsoons and dust storms. A total of 44 tube well water samples, 22 from Sargana and 22 from Mailsi, were collected on the basis of geographical distribution with depth of 80–95 m. At each site, survey among the residents was also conducted to collect information about water sources, economic status, health, age, sex and dietary habits. In the study area, 57 % of the participating population used hand and electric pumps for drawing water to surface for potable use, 18 % was supplied with water from water treatment plants, 5 % of the people used canal water (surface water) and 20 % of participating population used tube well water.

All groundwater samples were filtered immediately upon sampling on-site using 0.45- $\mu\text{m}$  cellulose acetate filters in Millipore Sterivex syringe capsules. Nalgene-1 bottles (60 mL) were used to take

filtered samples, for anion and cation determination, and at every 11th sampling point, a field duplicate was also collected. On-site field measurements (i.e., pH, temperature, dissolved oxygen (DO) and electrical conductivity, EC) were conducted during sample collection. The latitudes and longitudes were recorded via global positioning system (GPS) at the time of sample collection. The pH, EC, DO and TDS values in all water samples were determined by W2015 pH/EC meter and dissolved oxygen meter (Sino well Company, Shanghai, China). The sealed samples were stored at 4 °C in portable coolers and then transported to laboratory for further analysis.

Calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) of water samples were analyzed by volumetric titration with ethylene diamine tetra acetic acid (EDTA, 0.05 N). Alkalinity (quoted as  $\text{HCO}_3^-$ ) by 0.1 HCl (Sultana et al. 2014).  $\text{NO}_3^-$  was determined spectrophotometrically using UV/VIS spectrophotometer (Shimadzu model UV 1601) at a wavelength of 220 nm. Measurement of UV absorption at 220 nm enables rapid determination of  $\text{NO}_3^-$ . To overcome interferences by dissolved organic matter, which also absorbs at 220 nm, measurements for  $\text{NO}_3^-$  at 275 nm, where DOC does not absorb, were conducted and  $\text{NO}_3^-$  values were accordingly corrected.  $\text{SO}_4^{2-}$  values were determined by gravimetric method as  $\text{BaSO}_4$ . Chloride ( $\text{Cl}^-$ ) was determined by titration method (APHA 1998).  $\text{Na}^+$  and  $\text{K}^+$  were determined using graphite furnace atomic absorption spectrometer (GFAAS AAS-700 PerkinElmer, USA). For total As analysis, 2 mL of 12 M HCl was added to 15 mL of sample water together with 0.25 mL of a solution containing 10 % KI and 10 % ascorbic acid. Graphite furnace atomic absorption spectrometer (GFAAS AAS-700 PerkinElmer, USA) was employed to measure the total As. The quality control of measurements was performed by using standard reference solutions of analytical grade chemicals with 99.9 % spectroscopic purity (Merck Darmstadt, Germany). Twice distilled water was used throughout the analysis, blank and duplicate samples. Reproducibility of the analytical data was within 5 %, and the analytical error estimated to be <10 %, based on the analytical results of standard stock solutions independently prepared from the commercially distributed standard solution using a standard calibration line.

Human health risk assessment

*Average daily dose (ADD)*

A health risk assessment model derived from US-EPA (2011) was applied to assess health risk in individuals exposed to As. The average daily dose (ADD) of arsenic through water consumption was calculated using the following equation:

$$ADD = (C \times IR \times ED \times EF)/(BW \times AT) \quad (1)$$

where *C* = concentration of As (µg/L) in water, *IR* = the daily average intake of water rate (L/d, assumed to be 2 L/d for adult) (US-EPA 2011), *ED* = the exposure duration (assumed 67 years), *EF* = the exposure frequency (365 days/year), *BW* = the body average weights (kg, assumed to be 72 kg for adult), and *AT* = the average life time (24,455 days), respectively (Khan et al. 2012; Muhammad et al. 2011).

*Non-carcinogenic and carcinogenic risk*

The ratio of ADD and the highest reference dose without any adverse effect risk is called hazard quotient (HQ) and is used to express the risk of non-carcinogenic effects (US-EPA 2011). Oral reference dose (*R<sub>o</sub>/D*) of arsenic could be used to assess HQs through water exposure. Non-carcinogenic health risks in the study area, because of tube well water consumption, were assessed by hazard quotient (HQ) under standard assumptions (US-EPA 2011). When HQ value >1 represents potential health risk concern, while the value less than one is considered safe for consumers (Khan et al. 2008) and RefD equal to 0.0003 mg/kg day can be toxic (US-EPA 2011; Muhammad et al. 2010; Shah et al. 2012). THQ was calculated by using the following relationship:

$$HQ = ADD/R_o/D \quad (2)$$

We characterized the risk by estimating the risk of cancer using the Cancer Slope Factor index and lifetime average daily dose with a probabilistic approach. Carcinogenic risks (CRs) were estimated by ADD and exposure life time to arsenic (US-EPA 2011). The CSF is also called a “potency factor” and is used to calculate the Incremental Lifetime Cancer Risk by multiplying the CSF by the chronic daily

intake (ADD). The ADD is the dose over a lifetime and is expressed in mg/kg-day (Chen et al. 1985). The Cancer Slope Factor is used to derive the risk-specific dose (RSD) (mg/kg-day) for direct acting carcinogenic agents. The RSD is often calculated based on a one-in-a-million extra risk (10<sup>-6</sup> risk) or a one-in-a-hundred-thousand risk (10<sup>-4</sup> risk) for other than highly exposed individuals (Chen et al. 1985). The range of risk levels for carcinogens is from 10<sup>-4</sup> to 10<sup>-6</sup> over a human lifetime. CR was calculated by the following equation:

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

$$CSF = CR/ADD \quad (4)$$

where CSF = 1.5 mg/kg day is the cancer slope factor for arsenic (US-EPA 2011).

Tube well water quality parameters

In the current study, the discussion of water quality for irrigation is mainly based on the following factors: Sodium absorption ratio (SAR) was calculated using the following formula (Patterson 1994);

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (5)$$

where all ionic concentrations are in meq/L. The sodium in tube well water is denoted as percentage of sodium (%Na) and calculated by the following formula:

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

The quantities of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> are expressed as meq/L. Residual sodium carbonate (RSC) was determined by the following formula:

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (7)$$

Ion concentrations were taken in meq/L.

Base-exchange index was calculated by the following equation (Soltan 1998):

$$\text{Base exchange index}(r_1) = Na^+ - \frac{Cl^-}{SO_4^{2-}} \quad (8)$$

Equation (8) was used for estimating the meteoric genesis index (Singh et al. 2012):

$$\text{Meteoric genesis index } (r_2) = (K^+ + Na^+) - \frac{Cl^-}{SO_4^{2-}} \quad (9)$$

The concentrations of  $Na^+$ ,  $K^+$ ,  $Cl^-$  and  $SO_4^{2-}$  were taken in meq/L. Kelly's index (KI) was calculated as follows (Kelly 1940):

$$\text{Kelly's index (KI)} = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad (10)$$

MAR was calculated using Eq. (10) (Szabolcs and Darab 1964):

$$\begin{aligned} \text{Magnesium absorption ration (MAR)} \\ = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \end{aligned} \quad (11)$$

Ion concentrations were expressed in meq/L.

#### Multivariate statistical analysis and maps

Hierarchical cluster analysis (HCA), principle component analysis (PCA) and correlation matrix (CM) were conducted using SPSS statistic software. The distribution maps of arsenic were made using Arc-GIS and Surfer software. Piper diagram (1994), Chadha (1999) and Stiff diagram (1951) were used to determine hydro-chemical facies and major ion composition, respectively.

## Results and discussion

### Major ion composition

Table 1 summarizes the analytical determinations of major cations and anions in tube well water samples from Mailsi and Sargana. The results were compared with the corresponding permissible limits recommended by the World Health Organization (WHO). Ground waters generally showed a weak alkaline behavior with a pH range of 6.5–8.3 and 6.4–8.4 in Sargana and Mailsi, respectively (Table 1). The pH of tube well water indicated that the dissolved carbonates in groundwater were predominantly in the bicarbonate form (Lopez et al. 2010; Baig et al. 2009b). Total dissolved solids (TDS), pH, dissolved oxygen (DO) and EC values were within permissible limits (WHO 2008) except for one sample of Mailsi area. The samples contained high value of EC and TDS most

likely due to domestic waste with high dissolved solids (Pradeep 1998; Shyamala et al. 2008). Concentration of  $SO_4^{2-}$  ranged from 132 to 943.6 mg/L (Table 1). Higher concentrations of  $SO_4^{2-}$  were observed in Mailsi area, and 59 % tube well water samples were exceeding the permissible limit of 250 mg/L (WHO 2008) in both Sargana and Mailsi. From both sites, 77 % of samples exceeded the  $NO_3^-$  permissible concentration limit of 50 mg/L (WHO 2008). The higher concentration of  $NO_3^-$  and  $SO_4^{2-}$  in tube well water may be attributed to rock minerals, sewage discharges, animal manure, detergents and fertilizer-based agriculture practices in Tehsil Mailsi and its surrounding agricultural areas (Kahlowan et al. 2006). The  $Cl^-$  concentration in most samples was below the permissible limit of 250 mg/L (WHO 2008). Some water samples had higher  $Cl^-$  concentrations possibly due to local inputs from fertilizers at orchards and/or domestic wastes disposals in these areas. In 59 % of the samples, the concentration of  $HCO_3^-$  exceeded the standard value (500 mg/L, WHO 2008). Increased concentrations of  $HCO_3^-$  salts are due to weathering of carbonate rocks (Ahmed et al. 2004).

In current studied area, the concentrations of  $K^+$ ,  $Fe^{2+}$  and  $Mn^{2+}$  were lower than the recommended limits (WHO 2008). However, relatively higher values of  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  concentration were measured in collected water samples. The major sources of  $K^+$  are the weathering of mafic and ultramafic rocks (Singh et al. 2004) as well as sewage and industrial effluents. Lower concentrations of  $K^+$  in all water samples can be justified due to the low disintegration rate on fixed clay minerals (Geleijnse et al. 2003). The higher values of  $Na^+$  (119.2–587 mg/L) in our study might be related to the precipitation and/or coating on the minerals and also due to extensive use of detergents, discharged municipal waste and effluent percolation into water pathways (Manzoor et al. 2006). Weathering of silicate minerals is the main cause for higher concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  in tube well water in both areas (Ramkumar et al. 2010).

### Evaluation of tube well water quality

Tube well water samples were classified on the basis of major groundwater ion chemistry (Piper 1994). Approximately 83 % of tube well water samples showed distribution of mixed type cations, 16 % were of ( $Na^+ + K^+$ ) type, whereas one sample was of  $Mg^{2+}$

**Table 1** Concentrations of major ions and field parameters of tube well water in the Tehsil Mailsi area ( $n = 44$ )

Parameters	Sargana		Mailsi	
	Irrigation water ( $n = 22$ )		Irrigation water ( $n = 22$ )	
	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
pH	6.5–8.3	7.4 $\pm$ .52	6.4–8.4	7.6 $\pm$ 0.56
EC	430–1370	910 $\pm$ 0.24	440–1930	890 $\pm$ 0.31
TDS	292–941	622 $\pm$ 161	299–1312	608 $\pm$ 206
DO	6.6–8.2	7.4 $\pm$ 0.462	6.7–8.2	7.6 $\pm$ 0.46
Ca <sup>2+</sup>	45.5–174	107.4 $\pm$ 31.2	69.7–126	102 $\pm$ 17.1
Mg <sup>2+</sup>	13.2–54.2	31.1 $\pm$ 12.38	17–51	34.8 $\pm$ 9.6
HCO <sub>3</sub> <sup>-</sup>	270–880	591.3 $\pm$ 181.5	411–1054	565 $\pm$ 161.2
Cl <sup>-</sup>	53.5–195	120.7 $\pm$ 34.4	95.85–319	179.8 $\pm$ 61.2
SO <sub>4</sub> <sup>2-</sup>	132–748.9	402 $\pm$ 219	98.5–943	341 $\pm$ 214
NO <sub>3</sub> <sup>-</sup>	2.3–47.6	22.6 $\pm$ 12.6	1.5–58.5	18.7 $\pm$ 13.1
Na <sup>+</sup>	137–587	323 $\pm$ 107	119.2–439	278 $\pm$ 112
K <sup>+</sup>	2.3–8.4	4.4 $\pm$ 1.56	2.2–9.5	5.56 $\pm$ 2.58
Mn	0.0019–.096	0.012 $\pm$ 0.019	0.001–.042	0.008 $\pm$ .0108
Fe	0.001–0.298	0.117 $\pm$ 0.105	0.003–0.29	0.123 $\pm$ .115

All the values are expressed in mg/L except EC in ( $\mu$ S/cm)

type, as shown in Piper diagram (Fig. S-1). Among the major anions, 64 % of samples fall within mixed type area and 25 % turned out to be of Cl<sup>-</sup> type. Na<sup>+</sup>–HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup>–HCO<sub>3</sub><sup>-</sup> were two major types of water, identified by Piper diagram (Fig. S-1). This indicates that the dominant anion is HCO<sub>3</sub><sup>-</sup> while the dominant cations are Na<sup>+</sup> and Ca<sup>2+</sup>. High Na<sup>+</sup>, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations also make the water improper for irrigation purposes. This suggested that concentrations of major ions Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> increase due to water–rock interactions. The water–rock interactions generally include chemical weathering of rock-forming minerals, dissolution precipitation of secondary carbonates, and ion exchange between water and clay minerals (Moghaddam and Fijani 2008).

Chada (1999) proposes a hydro-geochemical scheme for drinking water purpose by plotting the difference between (CO<sub>3</sub><sup>2-</sup> + HCO<sub>3</sub><sup>-</sup>) and Cl<sup>-</sup> + SO<sub>4</sub><sup>2-</sup> concentrations in meq/L expressed as percent versus (Ca<sup>2+</sup> + Mg<sup>2+</sup>) and (Na<sup>+</sup> + K<sup>+</sup>) concentrations in meq/L as percent, based on Piper diagram (1994). The resulting diagram has four fields representing four types of hydro-geochemical processes (Fig. S-2). It can be seen by Figure S-2 that 16 % ( $N = 7$ ) of the samples collected in the study area

were of Na–Cl type, which showed the dominance of evaporation, while 84 % of the samples fall in the category of Ca–Mg–Cl, Na–HCO<sub>3</sub> and Ca–HCO<sub>3</sub> type. Similarly, Figure S-3 shows that 9 % ( $N = 4$ ) were of Ca–Mg–Cl type, 50 % ( $N = 22$ ) as Na–HCO<sub>3</sub> type and only 25 % as Ca–HCO<sub>3</sub> ( $N = 11$ ). However, these samples showed the water quality of recharge and least affected by the evaporation. Water quality of Na–HCO<sub>3</sub> type is produced because of the base ion exchange, and Ca–Mg–Cl type water quality represents the reverse ion exchange (Chae et al. 2006; Guo et al. 2007). Moreover, the average ionic composition analysis by stiff diagram has also shown in Fig. S-3, which represents the dominance of Na<sup>+</sup>–Cl<sup>-</sup>, Mg<sup>2+</sup>–SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup>–HCO<sub>3</sub><sup>-</sup>.

The suitability of GW for irrigation depends on their mineral composition. Criteria to determine tube well water quality include: EC, SAR, RSC, KI, MAR and %Na. Table 2 shows the classification of tube well water samples from Sargana and Mailsi. SAR values ranged from 2.6 to 13.56 and 3.3 to 8.3 in Sargana and Mailsi cities, respectively. Considering relative frequency distribution regarding SAR (Table 6), in Sargana, 7 samples of tube well water (32 %) were fit for irrigation, while in Mailsi, 11 samples (50 %) were suitable for irrigation (Richard 1954). However,

**Table 2** Range of irrigation quality parameters of tube well water, Tehsil Mailsi

	Parameters	Sargana		Mailsi	
		Irrigation water <i>n</i> = 22		Irrigation water <i>n</i> = 22	
		Range	Mean ± SD	Range	Mean ± SD
	SAR	2.6–13.56	1.945 ± 0.935	3.3–8.3	1.9 ± 0.89
	r <sub>1</sub>	0.55–10	2.55 ± 2.68	0.37–3.10	1.543 ± 0.83
Residual sodium carbonates (RSC), sodium absorption ratio (SAR), percentage of sodium (%Na)	r <sub>2</sub>	0.56–10.56	2.57 ± 2.69	0.38–3.12	1.56 ± 0.82
	KI	0.88–3.74	1.90 ± 0.78	0.65–2.26	1.51 ± 0.53
	MAR	32–52	31 ± 8.7	22–48	35 ± 5.9
Base-exchange index (r <sub>1</sub> ) and Meteoric genesis index (r <sub>2</sub> )	RSC	6.6–8.21	7.4 ± 0.52	6.7–8.24	7.5 ± 0.566
	%Na	38.8–78.5	43 ± 1.37	51.5–62.5	38 ± 1.78

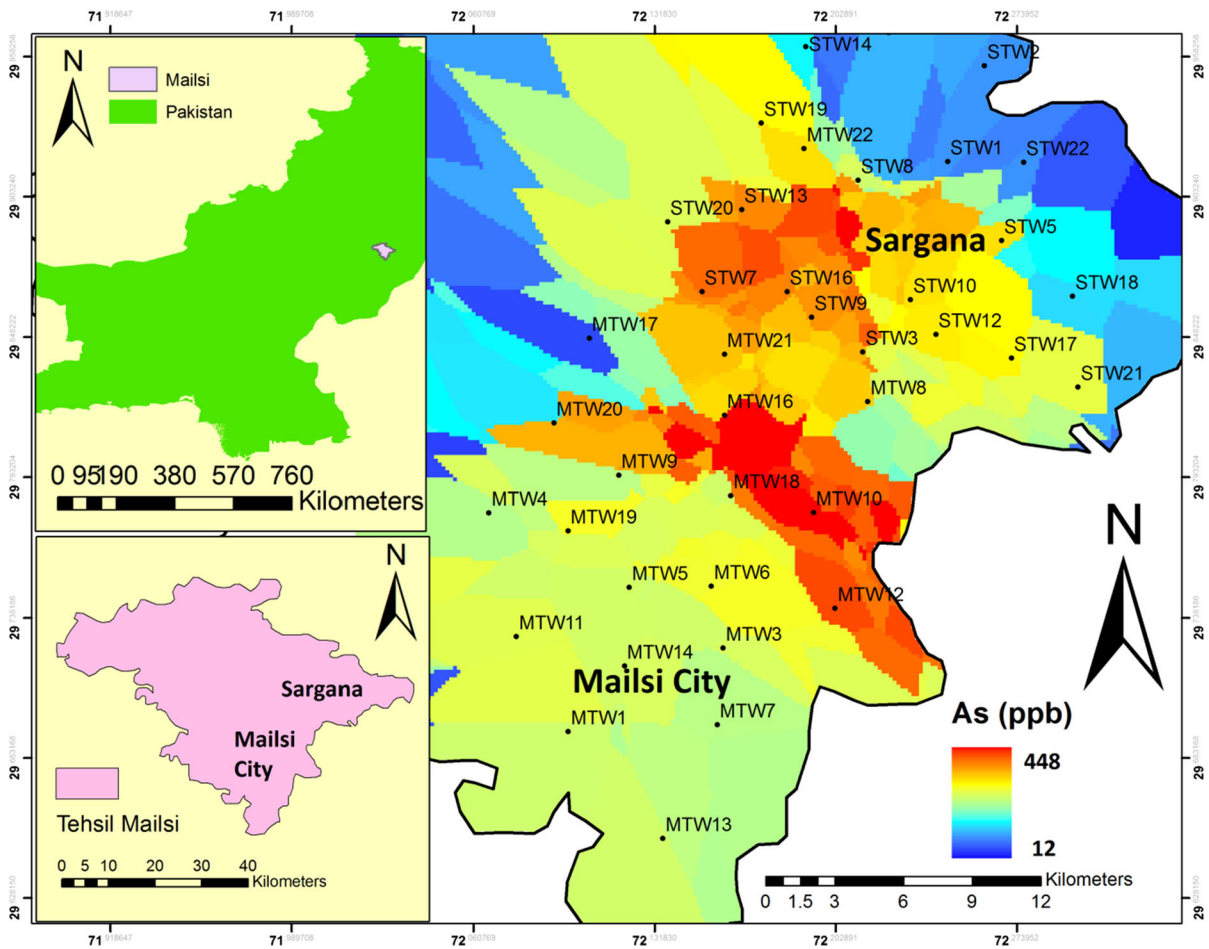
12 samples (54 %) were marginally appropriate in Sargana for irrigation purpose, while 11 samples (50 %) were marginally appropriate for irrigation purpose in Mailsi (Muhammad et al. 1996), and 3 samples (14 %) were found as improper in Sargana (Richard 1954). Increase in sodium absorption values was due to increase in Na<sup>+</sup> proportion as compared to Ca<sup>2+</sup> + Mg<sup>2+</sup> in water samples (Emerson and Bakker 1973). Ability of soil to transmit water is severely reduced by excessive sodicity in Sargana as compared to Mailsi. The classification of tube well water samples according to % Na is also given in Table 2. The range of sodium percentage was 38.8–78.5 and 51.5–62.5 % in Sargana and Mailsi, respectively (FAO 1992). Considering relative frequency distribution regarding percentage of sodium (Table 6), in both study areas, 10 samples (45 %) in Sargana and 10 samples (45 %) in Mailsi were marginally suitable for irrigation (Muhammad 1996). The range of RSC values in water samples was from 6.6 to 8.21 and 6.7 to 8.24 meq/L in the study area (Table 2). Considering relative frequency distribution regarding RSC (Table 6), in Sargana 7 samples (32 %) were fit, while in Mailsi 16 samples (73 %) were fit for irrigation (Richard 1954), and 3 samples (14 %) were marginally fit in Sargana, while 3 samples (14 %) were marginally fit in Mailsi (Muhammad 1996). Good quality water has RSC values below 1.25 meq/L, and water is considered as harmful if RSC values exceed 2.5 meq/L (Table 6). Similarly, Kelly's index (KI) and Meteoric genesis index (r<sub>2</sub>), calculated using Eq. (8) for each sample, are also given in Table 2 to further assess the water quality of studied areas.

### Spatially distributed arsenic in active flood plain

Arsenic concentrations in tube well waters ranged from 12 to 448.5 µg/L (Fig. 2) in the study area (Table 5). In both sites, all tube well water samples exceeded the WHO permissible limit of As (10 µg/L) in tube well water intended for human consumption. In the study area, As concentrations in tube well water were higher than those reported by Arain et al. (2009) in Manchar lake water (35–157 µg/L) and the nearby ground waters (23.3–96.3 µg/L), as well as in Jamshoro surface and groundwater (3–106 µg/L) (Baig et al. 2009a, b) but lower than the previous studies conducted in East Punjab (Farooqi et al. 2007) and Muzaffargarh (Nickson et al. 2005). Total arsenic concentration in unfiltered samples was higher near the Sutlej River areas than far ones (Fig. 2), and similar pattern was also recorded in the districts Multan and Muzaffargarh (Nickson et al. 2005). In south East Asia, As-affected areas include Red River Delta, Vietnam, Mekong basin, Cambodia (Berg et al. 2007), Ganga–Meghna–Brahmaputra plain, India (Chakraborti et al. 2002) Bengal delta, Bangladesh (Berg et al. 2001) and Western Snake River Plain, Idaho, USA (Busbee et al. 2009).

Natural enrichment of tube well water by As can arise in numerous ways such as hydrothermal volcanism, agricultural activities, oxidation of arsenical sulfide minerals (Singh and Jangveer 2011; Schreiber et al. 2000), reduction of FeOOH and the release of its sorbed load in groundwater (Ravenscroft et al. 2009), desorption of As from mineral sorption sites in response to increase in pH (Robertson 1989), and





**Fig. 2** Spatial distribution of arsenic in tube well water of Sargana and Mailsi

finally evaporative enrichment (Nicolli et al. 1989). In order to understand the possible mechanism for groundwater As release in the study area, earlier studies can be followed where different mechanisms have been suggested (Nickson et al. 2005; Farooqi et al. 2007; Halim et al. 2009). A study by Katsoyianis et al. (2007) reported oxidative dissolution mechanism for the enrichment of As in groundwater on the basis of following indicators: high pH,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and As are present in the form of  $\text{As}^{\text{V}}$ . On the other hand, oxidative dissolution mechanism has been suggested when high concentrations of  $\text{HCO}_3^-$  (>500 mg/L) and  $\text{SO}_4^{2-}$  (>250 mg/L) and pH (>7.5) occurred in groundwater (Smedley and Kiniburgh 2002). In the present study, higher concentrations of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and high DO values along with alkaline pH (Table 1) are the indicative of

oxidative environment. Hence, our findings are well supported by oxidative dissolution and to some extent by evaporative enrichment. In arid environments, evaporative concentration of dissolved materials can produce elevated As in groundwater (Bhattacharya et al. 2006). In these systems, evaporation enhances the concentrations of all ions in residual waters, a process likely to be occurred in regions where water table is very close to the surface and affected by evaporation (Nickson et al. 2005). Additionally, human activities can promote evaporative enrichment of As by decreasing water table to the near surface or by groundwater pumping for irrigation (Nickson et al. 2005). The main anthropogenic activities that may release As into the environment include smelting, fossil fuel processing and combustion, wood preserving, pesticide production, agricultural activities,

disposal, incineration of municipal and industrial wastes (Popovic et al. 2001; Prosun et al. 2002). The use of arsenical pesticides presents a nonpoint anthropogenic source of arsenic. Arsenical pesticides include lead arsenate [ $\text{Pb}_3(\text{AsO}_4)_2$ ], calcium arsenate [ $\text{Ca}_3(\text{AsO}_4)_2$ ], magnesium arsenate [ $\text{Mg}_3(\text{AsO}_4)_2$ ], zinc arsenate [ $\text{Zn}_3(\text{AsO}_4)_2$ ], zinc arsenite [ $\text{Zn}(\text{AsO}_2)_2$ ] and Paris green [ $\text{Cu}(\text{CH}_3\text{CCOO})_2\text{Cu}(\text{AsO}_2)_2$ ], (Martin et al. 2000).

In the present study, high  $\text{Cl}^-$  in some samples and high  $\text{Na}^+$  concentrations are the indicators of high evaporation rates. This is consistent with dendrogram (Fig. S-4), as  $\text{Cl}^-$  and As are in the same group. The ground waters from the basins are greatly affected by evaporative concentrations, resulting in high TDS values (Fujii and Swain 1995). Likewise, high EC in some samples is also related to high As concentrations in the study area (Table 1). This could be inferred from our results that As is released by oxidative dissolution under the influence of high alkaline water and high pH and to some extent by high evaporation rates.

As(V) can be effectively adsorbed on Fe-oxyhydroxide/oxide in pH less of equal to 7. At pH values higher than 7.5, arsenic starts to get desorbed from iron oxides and released into the groundwater (Katsoyiannis and

Katsoyiannis 2006; Katsoyiannis and Zouboulis 2006). Natural evaporation over long periods can cause solute concentrations in shallow groundwater to increase (Welch et al. 2000), and effects of evaporative concentration under toxic conditions will be sorption of As to soils (Jones et al. 2009) and aquifer sediments (Nimick 1998).

#### Multivariate analysis for source apportionment

Table 3 shows correlation matrices (CM) for selected parameters, which were measured in tube well waters. The Pearson's correlation coefficients and their significance levels ( $p < 0.05$ ) were employed between all the variables presented (Table 3). The correlation matrix showed that various parameter pairs had significant positive correlations such as EC–TDS ( $r = 0.99$ ),  $\text{Ca}^{2+}$ – $\text{Mg}^{2+}$  ( $r = 0.47$ ),  $\text{Mg}^{2+}$ – $\text{SO}_4^{2-}$  ( $r = 0.42$ ),  $\text{Mg}^{2+}$ – $\text{HCO}_3^-$  ( $r = 0.43$ ),  $\text{SO}_4^{2-}$ – $\text{Na}^+$  ( $r = 0.46$ ),  $\text{SO}_4^{2-}$ –As ( $r = 0.39$ ),  $\text{NO}_3^-$ – $\text{HCO}_3^-$  ( $r = 0.45$ ),  $\text{Na}^+$ –As ( $r = 0.28$ ),  $\text{Mg}^{2+}$ –As ( $r = 0.38$ ),  $\text{HCO}_3^-$ –As ( $r = 0.49$ ),  $\text{Mn}^-$ –As ( $r = 0.31$ ). These relationships were supplementary supported by dendrogram of CA in tube well water (Fig. S-4) and highlighted both natural and anthropogenic source of arsenic in the study area (Bhowmik et al. 2015).

**Table 3** Correlation matrix of selected physicochemical parameters of tube well water in the study area ( $n = 44$ )

Pm	pH	EC	TDS	DO	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{HCO}_3^-$	$\text{Na}^+$	$\text{K}^+$	Mn	Fe	As
pH	1														
EC	-0.17	1													
TDS	-0.16	<b>0.99</b>	1												
DO	0.11	-0.01	-0.01	1											
$\text{Ca}^{2+}$	-0.1	0.26	0.24	0.16	1										
$\text{Mg}^{2+}$	-0.26	0.38	0.39	0.1	<b>0.47</b>	1									
$\text{Cl}^-$	0.02	0.17	0.16	-0.02	0.17	0.08	1								
$\text{SO}_4^{2-}$	-0.25	0.18	0.19	0.31	0.05	<b>0.42</b>	-0.17	1							
$\text{NO}_3^-$	-0.23	0.22	0.22	-0.31	0.18	<b>0.41</b>	0.12	0.17	1						
$\text{HCO}_3^-$	-0.22	0.23	0.23	-0.26	0.21	<b>0.43</b>	-0.02	0.08	<b>0.45</b>	1					
$\text{Na}^+$	-0.34	0.05	0.06	0.08	0.12	<b>0.36</b>	0.28	<b>0.46</b>	0.24	0.35	1				
$\text{K}^+$	0.15	-0.09	-0.1	-0.05	-0.09	-0.23	-0.13	-0.41	-0.07	-0.14	-0.45	1			
Mn	-0.21	0.09	0.09	0.18	0.09	0.25	-0.1	0.03	0.02	0.11	0.02	0.02	1		
Fe	-0.06	0.26	0.24	-0.03	0.09	0.01	0.13	0.09	-0.08	0.04	0.03	0.12	0.09	1	
As	-0.15	0.06	0.74	0.16	0.05	<b>0.38</b>	-0.01	<b>0.39</b>	0.14	0.49	<b>0.28</b>	-0.16	<b>0.31</b>	0.03	1

Bold correlation is significant at the 0.05 level

$n$  number of samples;  $Pm$  Parameters

For example, the use of arsenical pesticides in the study is already reported and may cause arsenic contamination in different ecological settings of Pakistan (Alamdar et al. 2016). Thus, As contamination is likely to occur due to the leaching process of pesticides and fertilizers from soils to groundwater (Sharma 2006). Exogenous introduction of As into the environment through the use of pesticides in the form of calcium arsenate, arsenic acid, lead arsenate and sodium arsenate (Alloway 1970; Woolson et al. 1971) is considered a major source of metal pollution in water. Water-soluble As in fertilizers (DAP) is estimated to be 5–10 mg/kg with an average value of 7.4 mg/kg (Farooqi et al. 2007b). Such a high concentration of As in fertilizers would be a pollutant source of soil surface and underlying groundwater associated with cultivation in the study area (Farooqi et al. 2007b). However, arsenical pesticides have infrequently been migrated with depth (Welch et al. 2000). Similarly, Hudak (2000) reported that groundwater pollution with As was associated with extensive use of arsenical agro-chemicals and other agricultural activities.

According to cluster analysis, the first group of parameters, such as Fe, pH,  $K^+$ , EC, Mn, DO,  $Mg^{2+}$  and  $NO_3^-$  (Fig. S-4), suggested that all these parameters originate from agricultural activities, industrial activities and weathering of mafic and ultramafic rocks (Shah et al. 2010).

The second group of parameters, such as As,  $Ca^{2+}$  and  $Cl^-$  (Fig. S-4), possibly originated from parent rock material, agricultural and human activity. High As concentration in the region near to Sutlej River was compared to the area located far from it (Fig. 1) due to weathering and erosion of mafic and ultramafic rocks (Shah et al. 2010; Kavcar et al. 2009) and anthropogenic contribution of extensive use of fertilizers, pesticide, coal combustion, acid rain, sewerage system, drainage system, solid waste management, and landfills/dumping sites (Abbas et al. 2014; Khan et al. 2012; Shah et al. 2010; Nickson et al. 2005). This similar pattern was also observed in previous study of district Muzaffargarh and Multan (Nickson et al. 2005). The third group of parameters, consist of  $Na^+$ , TDS,  $HCO_3^-$  and  $SO_4^{2-}$  (Fig. S-4), were considered as the result of agricultural waste: sewage waste and weathering of parent rock material. High  $SO_4^{2-}$  concentrations were from household waste, fertilizer leaching and animals dung (Kahlowan et al. 2006).

$HCO_3^-$  salts are added to water sources from weathering of carbonaceous rocks (Ahmed et al. 2004). High  $Na^+$  concentrations may be derived from leaching of chemical fertilizer, household waste and animals manure (Kahlowan et al. 2006).

Factor analyses (FA) that include principal component analysis (PCA) are used to further explain the source of arsenic and other studied variables (Table 4). Factor-1 contributed 24 % with moderately strong positive loading on EC ( $r = 0.613$ ), TDS ( $r = 0.622$ ),  $Mg^{2+}$  ( $r = 0.789$ ),  $NO_3^-$  ( $r = 0.532$ ),  $SO_4^{2-}$  ( $r = 0.576$ ),  $HCO_3^-$  ( $r = 0.587$ ),  $Na^+$  ( $r = 0.582$ ). The sources of EC, TDS,  $NO_3^-$ ,  $Mg^{2+}$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  and  $Na^+$  could be anthropogenic due to domestic waste water, agriculture activities and geogenic due to weathering minerals and Calc-silicate rocks (Farooqi et al. 2007a, b). The total variance is contributed by 14 % by factor-2 and 11 % by factor-3 with high value of  $Cl^-$  ( $r = 0.484$ ),  $K^+$  ( $r = 0.425$ ) and DO ( $r = 0.775$ ), Fe ( $r = 0.257$ ), which is due to the local geochemical conditions, influenced by mafic and ultramafic rocks weathering (Shah et al. 2000). Factor-4 contributing 8.1 % shows high concentration of Mn ( $r = 0.751$ ), demonstrating adulteration from both natural and anthropogenic sources. Factor-5 has contributed by 7.2 % to the total variance with high loading of As ( $r = 0.331$ ), which indicates the involvement of both geogenic and anthropogenic sources (Khan et al. 2012). Factor-6 has contributed by 6.8 % to the total variance with a high loading on pH ( $r = 0.458$ ), due to same reason as for factor-2 and factor-3 (Shah et al. 2000). The overlapped plotting on rotated space diagram (Fig. S-5) between  $Ca^{2+}$  and  $Mn^{2+}$ , and between  $K^+$  and  $Fe^{3+}$  is very important elements for the evaluation of their relation with groundwater (Jones et al. 2009). Some parameters like  $Na^+$  and  $SO_4^{2-}$  appeared in left component, while other parameters were present in right component, which shows small variations of physiochemical parameters in both areas, presumably due to climatic and agricultural effect.

Human health risk due to high arsenic in tube well water

Toxic risk index is higher in Mailsi than Sargana (Table 5). Average daily doze (ADD) calculations of As are summarized in Table 5. The results suggest that in Mailsi and Sargana areas, where people are

**Table 4** Factor loading for selected physicochemical parameters in tube well water ( $n = 44$ )

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
pH	-0.48	0.1	0.106	-0.149	-0.21	<b>0.458</b>
EC	<b>0.613</b>	0.65	0.252	-0.23	-0.104	0.027
TDS	<b>0.622</b>	0.64	0.259	-0.232	-0.106	0.036
DO	0.023	-0.302	<b>0.775</b>	0.093	-0.098	0.216
Ca	0.442	0.169	-0.252	0.151	-0.592	0.123
Mg	<b>0.789</b>	0.006	0.035	0.18	-0.004	0.329
Cl	-0.086	<b>0.484</b>	0.233	-0.009	0.654	0.174
SO <sub>4</sub>	<b>0.576</b>	-0.423	0.373	-0.222	0.03	-0.071
NO <sub>3</sub>	<b>0.532</b>	0.043	-0.538	0.008	0.129	0.13
HCO <sub>3</sub>	<b>0.587</b>	0.047	-0.447	0.139	0.259	0.041
Na	<b>0.582</b>	-0.521	-0.072	-0.192	0.029	-0.245
K	-0.424	<b>0.425</b>	-0.066	0.479	0.044	-0.01
Mn	0.254	-0.038	0.221	<b>0.751</b>	-0.168	-0.058
Fe	0.142	0.339	<b>0.257</b>	0.131	0.002	-0.695
As	0.473	-0.318	0.199	0.32	<b>0.331</b>	0.175
Eigen values	3.605	2.048	1.65	1.21	1.078	1.01
Variability (%)	24.033	13.65	11.02	8.08	7.18	6.75
Cumulative (%)	24.033	37.68	58.7	56.79	63.97	70.7

Values of dominant element in each factor are reported in bold  
 $n$  number of samples

consuming groundwater contaminated with As, the ADD values ranged from  $3.3\text{E}-04$  to  $9.4\text{E}-03$  and  $3.4\text{E}-04$  to  $1.2\text{E}-02$  mg/kg day, respectively. In our study area, the ADD values of As were lower than those reported (Karim 2000) for Bangladeshi groundwater ( $5.00\text{E}-02$ – $5.00\text{E}-01$  mg/kg day) and Vietnam groundwater ( $5.00\text{E}-03$ – $4.9\text{E}-01$  mg/kg day) (Nguyen et al. 2009). However, they are higher than reported values in Turkey ( $2.3\text{E}-05$ – $5.21\text{E}-03$  mg/kg day) in groundwater (Caylak and Halifeoglu 2010) and were much higher than ( $0.00$ – $5.56\text{E}-07$  mg/kg day) for other areas in Pakistan (Muhammad et al. 2010). Hazard quotient values (HQs) in tube well water ranged from 1.1 to 31.1 and 1.13 to 40 in Sargana and Mailsi areas, respectively (Table 5). The results showed that residents of both areas have a higher toxic risk index in Mailsi than in Sargana. Notably, 100 % of tube well water samples are exceeding the typical toxic risk index of 1.00. The highest HQ value was found in Mailsi (Max HQ = 40). In this area, the groundwater is used for irrigation and domestic purposes, and therefore, people (60 %) of both areas are under risk as arsenic in this water is more than permissible limit given by USEPA (USEPA 2011). In Sargana and Mailsi sites, the potential cancer risk (CR) value ranged from

$4.9\text{E}-04$  to  $1.4\text{E}-02$  and  $5.1\text{E}-04$  to  $1.8\text{E}-02$  in tube well water samples (Table 5). Cancer risk values lower than  $10^{-6}$  are considered to be negligible, but CR values higher than  $10^{-4}$  are considered deplorable (USEPA 2010), and risk values lying between  $10^{-6}$  and  $10^{-4}$  are generally considered as acceptable (Islam et al. 2014). In the study area, the CR values in all tube well water samples were greater than one in a million ( $10^{-6}$ ), considered significant by the USEPA (2010). Arsenic concentrations in all groundwater sampled, as well as all other relevant values (ADD, HQ and CR), were elevated, due to anthropogenic activity such as agricultural activities, industrial activities, climatic bustle and household waste. This constitutes an urgent situation, which requires immediate remedial action for protecting the health of local population. These results designate that study area has an elevated contamination level of arsenic, which is not safe for agricultural and other domestic uses (Table 6).

### Concluding annotations and recommendations

The present study investigated the geochemistry of tube well waters with  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$

**Table 5** Arsenic concentrations in tube well water samples along with ADD, HQs and CR values of study area

Samples	As ( $\mu\text{g/L}$ )	ADD ( $\text{mg/kg/d}$ )	HQs	CR
STW1	91	2.50E-03	8.3	3.80E-03
STW2	65	1.80E-03	6	2.70E-03
STW3	285	7.90E-03	26.3	1.19E-02
STW4	14	3.90E-02	1.3	5.90E-02
STW5	123	3.40E-03	11.3	5.10E-03
STW6	21	5.80E-02	1.9	8.70E-02
STW7	274	7.60E-03	25.3	1.14E-02
STW8	59	1.60E-03	5.3	2.40E-03
STW9	340	9.40E-03	31.3	1.41E-02
STW10	106.1	2.90E-03	9.7	4.40E-03
STW11	87.3	2.40E-03	8	3.60E-03
STW12	12	3.30E-02	1.1	5.70E-02
STW13	33.2	9.20E-02	3.1	1.40E-03
STW14	14.2	3.90E-02	1.3	5.90E-02
STW15	37.4	1.04E-03	3.5	1.60E-03
STW16	73.2	2.03E-03	6.8	3.10E-03
STW17	65.4	1.80E-03	6	2.70E-03
STW18	61.7	1.70E-03	5.7	2.60E-03
STW19	89.4	2.50E-03	8.3	3.80E-03
STW20	34.2	9.50E-03	3.2	1.40E-03
STW21	36.2	1.00E-03	3.3	1.50E-03
STW22	47.2	1.30E-03	4.3	1.95E-03
MTW1	22	6.10E-02	2.03	9.20E-02
MTW2	62	1.70E-03	5.7	2.60E-03
MTW3	122	3.40E-03	11.3	5.10E-03
MTW4	12.5	3.50E-02	1.2	5.30E-02
MTW5	284	7.90E-03	26.3	1.19E-02
MTW6	448.5	1.25E-02	41.7	1.88E-02
MTW7	63	1.80E-03	6	2.70E-03
MTW8	23	6.40E-02	2.1	9.60E-02
MTW9	65	1.80E-03	6	2.70E-03
MTW10	12.3	3.40E-02	1.1	5.10E-02
MTW11	13.4	3.70E-02	1.2	5.60E-02
MTW12	19.5	5.40E-02	1.8	8.10E-02
MTW13	21.5	5.90E-02	1.96	8.90E-02
MTW14	45	1.30E-03	4.3	1.95E-03
MTW15	24.9	6.90E-02	2.3	3.50E-03
MTW16	85.3	2.40E-03	8	3.60E-03
MTW17	71.5	1.98E-03	6.6	2.97E-03
MTW18	34.2	9.50E-02	3.2	1.40E-03
MTW19	31.2	8.70E-02	2.9	1.30E-03
MTW20	19.5	5.40E-02	1.8	8.10E-02
MTW21	13.5	3.80E-02	1.3	5.70E-02
MTW22	91.3	2.50E-03	8.3	3.80E-03

**Table 6** Relative frequency distribution of tube well waters for different irrigation quality characteristics from both studied sites

Parameters	Status	Richards (1954)	Muhammad (1996)	Sargana		Mailsi	
				Tube well water <i>n</i> = 22		Tube well water <i>n</i> = 22	
				No. of sample	(%)	No. of sample	(%)
EC ( $\mu\text{S}/\text{cm}$ )	Fit	750	<1500	5	22	6	27
	Marginal	751–2250	1500–2700	15	68	15	68
	Unfit	>2250	>2700	2	9.1	1	5
SAR	Fit	<10	<7.5	7	32	11	50
	Marginal	>10<18	7.5–15	12	54	11	50
	Unfit	>18	>15	3	14	0	0
RSC (meq/L)	Fit	<1.25	<2.0	7	32	16	73
	Marginal	1.25–2.50	2.0–4.0	3	14	3	14
	Unfit	>2.5	>4.0	12	54	3	14
%Na	Fit	<40	<60	0	0	0	0
	Marginal	40–60	60–80	10	45	10	45
	Unfit	>60	>80	12	55	12	55

and  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$  inclination. The predominating water type in the study area is of  $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ , reflecting the geology and climate of the area. Indexes such as SAR and MAR revealed good quality of tube well water for irrigation purposes, whereas RSC, %Na and KI values showed that this water is not suitable for agriculture and domestic use. The maximum concentration of As was 12–448.5  $\mu\text{g}/\text{L}$  with mean value 80.87  $\mu\text{g}/\text{L}$ . Phosphatic fertilizers are extensively used in the area. In many studies, elevated arsenic concentrations in groundwater have been found due to application of phosphatic fertilizers containing high concentrations of sodium (Campos 2002; Davenport and Peryea 1991). Therefore, positive relationship between As and  $\text{Na}^+$  ( $r = 0.283$ ,  $p < 0.05$ ) in the study area indicates that the source of As is application of phosphatic fertilizers and industrial waste and weathering of sodium arsenite and sodium arsenate. However, the possibility for arsenic release due to phosphate competition is possible, although it usually takes place in anoxic environments and reductive dissolution of ferric oxides. The statistical approaches PCA and HCA traced out the possible sources of contamination of As and other physicochemical parameters in tube well waters, which included local geochemistry, weathering of rocks and agricultural activity in the study area. Toxic risk index of As is in

the order of Mailsi > Sargana, with all samples exceeding the typical toxic risk index 1.00, indicating that residents are under threat. Environmental isotopes technique is suggested to trace the sources of high arsenic and nitrate concentration in groundwater. Precise and high efficiency irrigation systems and practices must be adopted to reduce the use of contaminated water for growing crops.

**Acknowledgments** We are highly thankful to Geological Survey of Pakistan and Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, for technical support and research facilities, respectively. We are also thankful to Dr. Sajid Masood, Department of Plant Sciences, Quaid-I-Azam University, for technical review of the manuscript. We wish to thank people of Tehsil Mailsi visited, for their cooperation at the time of sampling.

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