



Arsenic and heavy metal contaminations in the tube well water of Punjab, Pakistan and risk assessment: A case study



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ABSTRACT

The present study for the first time highlighted the arsenic and heavy metals (HM) concentrations as well as their source of contamination in tube-well water and associated potential health risk to local residents of Tehsil Mailsi (Punjab), Pakistan. 44 samples were collected from Jala Jeem and Dunia Pur. Results revealed average concentrations of anion and heavy metals such as Iron (Fe), (Cadmium) Cd, (Lead) Pb, (Sodium) Na⁺, (Bicarbonate) HCO₃⁻, (Sulfate) SO₄²⁻ and Arsenic (As) exceeded the WHO limits in the tube well water. The calculated target hazard quotient (THQ) of metals from local tube well water above 1 was observed for As (36.5) and Cd (6.2), which employed highly potential health risk to local residents. The suitability of water for irrigation is evaluated based on residual sodium carbonate (RSC), sodium adsorption ratio (SAR), Kelly's index (KI), Sodium percent (%Na) and Magnesium absorption ratio (MAR). Dominant ions in the study area are HCO₃⁻, Ca²⁺ and Mg²⁺ and water chemistry of the area is Ca²⁺-Mg²⁺-HCO₃⁻ type. However, different statistical tools, including principal component analysis (PCA), hierarchical cluster analysis (CA) and correlation matrices revealed the contribution of both natural as well as anthropogenic activities towards the high level of arsenic and heavy metals contamination in the local tube well water. The results show that consumption of heavy metals contaminated groundwater poses an emerging health threat to the populations in the study area, and hence needs urgent remedial and management measures. Continued monitoring of heavy metals levels is recommended for future management strategies.

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Abbreviations: AAS, atomic absorption spectrophotometer; EDI, estimated daily intake; CR, cancer risk; HMs, heavy metals; THQ, target hazard quotients; PCA, principle components analyses; TDS, total dissolved solids; US EPA, US Environmental Protection Agency; SDNP, Sustainable Development National programmed; APHA, American public health association.

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1. Introduction

Health risk assessment from contamination of tube well water with As and HM is the prime focus of environmental scientists now a days. Human life is highly affected due to discharge of effluents in water bodies (Ravenscroft et al., 2009; Alkarkhi et al., 2008). Pakistan is basically an agricultural country but most of its agriculturally productive area falls in the arid and semi-arid climate. It is predictable that around one third of the World's population use groundwater for drinking, agricultural purpose and industrial sector (Mishra and Bhatt, 2008). Presence of the heavy metals (HMs) in drinking water up to toxic levels in aquatic environment is a matter of great concern due to their impacts on plants, animals and human life (Khan et al., 2015; Muhammad et al., 2013; Sultana et al., 2014).

Generally these metals are released from different natural (i.e., weathering, erosion of bed rocks, ore deposits and volcanic activities) and anthropogenic (i.e., mining, smelting, industrial influx and agricultural activities) sources (Shah et al., 2012).

HMs such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), iron (Fe), copper (Cu) chromium (Cr) and zinc (Zn) are required in a specific amount, and their deficiency may cause retarded biological processes and functions, while their high concentrations may cause toxicity (Fahad and Bano, 2012; Fahad et al., 2014a,b; Fahad et al., 2015a,b,c,d,e; Fahad et al., 2016; Shah et al., 2012; Khan et al., 2013a,b). However, other metals such as Cd, Hg, Ni, and Pb are toxic metals and causing numerous human health risks after ingestion (Muhammad et al., 2010, 2011). Toxic effects of these metals incorporate abdominal pain, headache, irritability, blood pressure; kidney damage, nerve damages, skeletal damage, cancer, and upsets intellectual functions (Khan et al., 2013a,b). Several studies found that trace elements such as Fe, Cd, Cr, Mn, Ni, Pb, Co, Cu and Zn were at unsafe levels for consumption purposes (Agusa et al., 2006; Buschmann et al., 2008; Winkel et al., 2008; Frisbie et al., 2009; Luu et al., 2009). Multivariate statistical analyses such as cluster analysis (CA), inter-metals correlation and principal component analysis (PCA) were used for the identification of contamination sources of metals in water (Wunderkind et al., 2001; Muhammad et al., 2011).

In addition to HMs contamination, arsenic contamination in groundwater has become a challenge for the world. This has been evidently reported that As consumption from water has affected about 150 million people worldwide (Ravenscroft et al., 2009). More than 700,000 people in the South and East Asian region have been affected by arsenicosis and As-related diseases, especially skin and internal (lung, bladder, kidney) cancers (Frisbie et al., 2002; World Bank Policy Report, 2005; Schmoll et al., 2006; Rahman et al., 2009). As affected nations of the world include Bangladesh, India, China, Hungary, Pakistan, Argentina, Chile, Mexico, Taiwan, Vietnam and many parts of USA (Smedley and Kinniburgh, 2002). Additionally, more than 25 nations of the world are facing problem of heavy metal pollution. These nations include China, India, Pakistan, Sri Lanka, Ghana, Ivory Coast, Senegal, Algeria, Kenya, Uganda, Tanzania, Ethiopia, Mexico and Argentina (Rafique et al., 2009; Rahman et al., 2009).

In Pakistan, As affected areas include Jamshoro, Sindh (Baig et al., 2009a,b), Manchar lake, Sindh (Arain et al., 2008, 2009), Lahore and Kasur, Punjab (Farooqi et al., 2007a,b,c), Muzaffargarh, Punjab (Nickson et al., 2005), DG Khan, Punjab (Malana and Khosa, 2013) and Tharparkar, Sindh (Brahman et al., 2013a,b). In 2004, more than 40 people died in Hyderabad city due to the usage of drinking water contaminated with high level of As and other toxic metals (Arain et al., 2008). Similarly, heavy metal pollution in water has been detected in many areas of Pakistan including Naranji (KPK) (Shah and Danishwar, 2003), Lahore and Kasur (Punjab) (Farooqi et al., 2007a,b,c), Nagar Parkar (Sindh) (Naseem et al., 2010), Muzaffargarh district (Nickson et al., 2005), Peshawar basin (Shah and Tariq, 2007), Manchar Lake Sindh (Kazi et al., 2009), Kohistan region (Muhammad et al., 2010, 2011) and Tharparkar (Sindh) (Brahman et al., 2013a,b). Moreover, Pakistan Council for Research in Water Resources (PCRWR) has declared six cities as the most affected areas of Punjab with respect to elevated toxic metal levels, which include Multan, Bahawalpur, Sheikhopura, Vehari, Gujranwala, Kasur and Lahore (PCRWR, 2005).

Tehsil Mailsi is situated in the active flood plains of Sutlej River, Southern Punjab, Pakistan. Geographically, Tehsil Mailsi is surrounded by metal polluted areas of Vehari, Multan and Bahawalpur, and has similar topography and geology. In the area focused in this study, no previous research has been conducted on heavy metal pollution in tube well water. As a result, little information is available on the sources of contamination in Tehsil Mailsi, and the roles

of geological processes (weathering, erosion of mafic and ultramafic rocks) and anthropogenic activities (agricultural activities, sewerage system, drainage system, solid waste management and land fill/dumping sites (Abbas et al., 2014; Hussain et al., 2014; Shah et al., 2010; Kavcar et al., 2009). Therefore, the present study is designed (1) to evaluate tube well water quality of the study area (2) to identify sources of As and HMs contamination using multivariate analysis and other statistical tools (3) to conduct health risk assessment in the study area. The findings of this study are beneficial to highlight exposure levels of HMs in local tube well water of Tehsil Mailsi and associated human health risks.

2. Materials and methods

2.1. 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 km², with an altitude of 126 m above sea level (Fig. 1). The estimated population of the selected area is 0.71 million. The study area has hot and semi-arid climate with average precipitation of 243 mm/year and a mean climate temperature of 26 °C (Rasool et al., 2015a,b). Cotton, wheat, rice, sugar cane, mangoes, citrus, guavas, dates, cauliflower, onion, tomato, carrot, turnip and ladyfinger are major crops, fruits and vegetables. It has the four distinct seasons including most extreme hot summer and cold winter. Mailsi is situated along river Sutlej; however, this river is dry in most part of the year that's why this area is facing shortage of good quality water. The main source for irrigation is Link Canal, Siphon Lake, and Sutlej River along with tube wells. The aquifer of the study area is under alluvial plains; with more than 340 m 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 (Farooqi et al., 2007a,b,c).

2.2. Water samplings and analysis

Two sites (Jallah Jeem and DurPur), potentially exposed to severe agricultural and anthropogenic activities, were selected for water sampling (Fig. 1). Site sampling was done in August 2013 following the standard procedures (Khan et al., 2012). Initially at both sites, questionnaire survey (interview) was conducted to collect the information about water use and water borne diseases. Groundwater is the source of water supply through tube wells and hand pumps in DurPur and Jallah Jeem town. Total 44 tube well water samples, 22 from DurPur and 22 from Jallah Jeem were collected (Fig. 1). For validation of results, duplicate sample was collected at every 10th site of sampling. All tube well water samples were from deep depths ranging from 75 to 80 m. All the water for geochemical analysis was filtered on site using Millipore Sterivex syringe capsules containing 0.45 μm cellulose acetate filters. Two filtered sub-samples were sealed in pre-cleaned 60 mL of Nalgene bottles, of which one sample was used for anion and the other for cation analysis (preserved using 10% ultrapure HNO_3^- , to acidify the sample pH to 2.0 or lower). A field duplicate was collected at every 10th sampling site for laboratory analysis precision cross check.

The temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) in groundwater samples were measured in the field. The latitudes and longitudes were recorded via global positioning system (GPS) receiver at the time of sample collection. All the samples either in the field or in the laboratory were preserved at 4 °C before analysis. Standard procedures were followed for

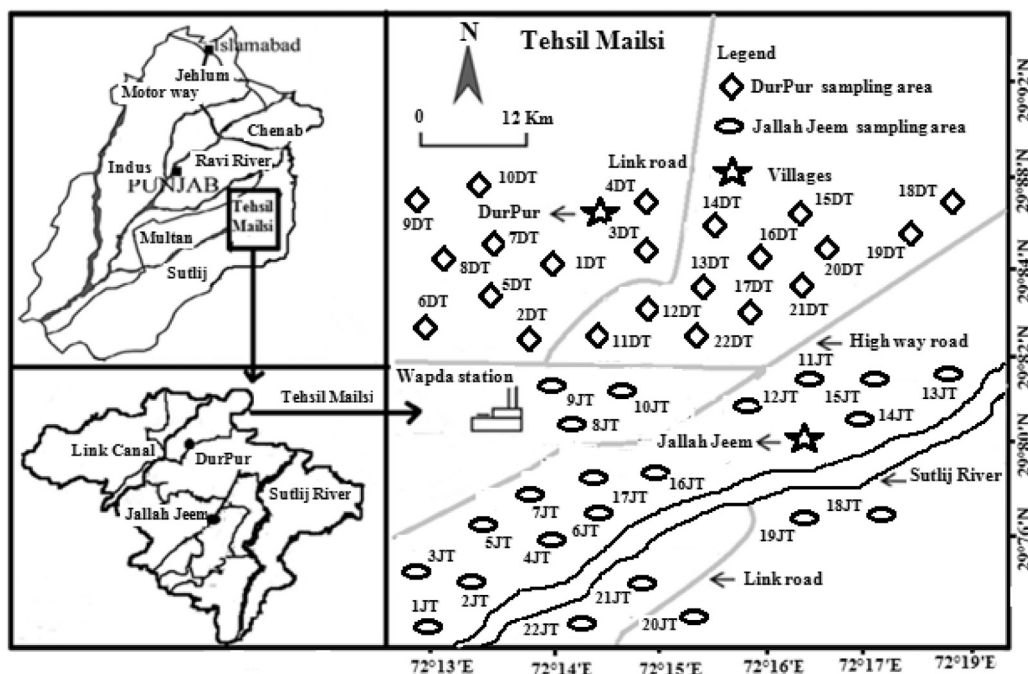


Fig. 1. Location maps showing the sampling points of tube well water from Durpur and Jallah Jeem study area.

the determination of As, heavy metals, and all the other groundwater quality parameters (APHA, 1998). The pH, EC and TDS in water samples were determined by pH/EC meter (W2015, Sino well Company, Shanghai, China). The DO meter was also used for determination of DO in all water samples. Analytical grade chemicals with 99.9% spectroscopic purity (Merck Darmstadt, Germany) were used for sample preparation and analysis. Double distilled water was used throughout the analysis. Standard solutions of all seven elements were prepared by diluting 1000 mg/L certified standard solutions (Fluka Kamica, Buchs, Switzerland) of corresponding metal ions. The concentrations of selected heavy metals (Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , Cd, As, Cr, Cu, Mn, Ni, Pb and Zn) in water samples were analyzed using graphite furnace atomic absorption spectrometer (GFAAS AAS-700 Perkin Elmer, USA) under standard operating conditions and anions including SO_4^{2-} , NO_3^- were determined spectrophotometrically using UV/VIS-Spectrophotometer (Shimadzu model UV 1601, Shanghai, China) at a wavelength of 220 nm. The standard titration method was followed for the determination of anions including Cl^- and HCO_3^- (APHA, 1998). The integration and delay time of AAS was 5 s. The instrumental detection limits of Cd, Cr, Cu, Mn, Ni, Pb and Zn were 0.0008, 0.0030, 0.0015, 0.0015, 0.0060, 0.0150 and 0.0015 mg/L, respectively. Twice distilled water was used throughout the analysis, blank and duplicate samples, and reproducibility of the analytical data was within 5% and the analytical error was estimated to <10%.

2.3. Health risk assessment

Health risk assessment (HRA) of the study area, the estimated daily intake (EDI) of metals through tube well water consumption is calculated according to the equation adopted from the US Environmental Protection Agency (US-EPA, 2011) and Shah et al. (2012).

$$\text{EDI} = C \times \text{IR} \times \text{ED} \times \frac{\text{EF}}{\text{BW}} \times \text{AT} \quad (1)$$

where C, IR, ED, EF, BW, AT represents the concentration of metals in water ($\mu\text{g/L}$), water intake rate (2 L/day), ED is exposure duration (assumed 67 years), exposure frequency (365 days/year), body

weight (72 kg) and AT average life time (24,455 days), respectively (Rasool et al., 2015a,b; US-EPA, 2010).

The THQs was calculated by following equation:

$$\text{THQs} = \frac{\text{EDI}}{\text{Rfd}} \quad (2)$$

where THQ is target hazard quotients and Rfd ($\mu\text{g/kg-day}$) represents reference dose of a particular metal e.g. $3.00\text{E}+02$, $1.40\text{E}+02$, $3.70\text{E}+01$, $3.60\text{E}+01$, $3.00\text{E}+02$, $2.00\text{E}+01$, $1.50\text{E}+03$, $5.00\text{E}-01$, $3.00\text{E}-01$ $\mu\text{g/kg-day}$ for the Fe, Mn, Cu, Pb, Zn, Ni, Cr, Cd and As $\mu\text{g/kg-day}$ Rasool et al. (2015a,b) and Muhammad et al. (2011).

Cancer risk was calculated by following equation:

$$\text{CR} = \text{EDI} \times \text{CSF} \quad (3)$$

Here CSF ($\mu\text{g/kg-day}$) represents cancer slope factor. The CSF value of As is $1.5\text{E}+03$ $\mu\text{g/kg-day}$ as adopted from (US-EPA, 2005) and Muhammad et al. (2010).

2.4. Tube well water quality parameters

In this study, the discussion of water quality for irrigation is mainly based on the following factors:

Sodium adsorption ratio (SAR) was calculated by following equation (Patterson, 1994);

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

where, all ionic concentrations are expressed in milli equivalents per liter (meq/L).

The sodium in tube well water is usually denoted as percent sodium and can be determined using the following equation;

$$\% \text{Na} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \times 100 \quad (5)$$

Where, the quantities of Ca^{2+} , Mg^{2+} , Na^+ and K^+ are expressed in (meq/L).

Residual sodium carbonate (RSC) was calculated using the following equation;

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (6)$$

Where, all ionic concentrations are expressed in (meq/L).

Kelly's index (KI) was calculated by using the following equation (Kelly, 1940);

$$\text{Kelly's index (KI)} = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad (7)$$

where, all the ions are expressed in meq/L.

Magnesium absorption ratio (MAR) was calculated by the following equation (Szabolcs and Darab, 1964);

$$\text{Magnesium absorption ratio (MAR)} = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100 \quad (8)$$

where, all the ions are expressed in meq/L.

2.5. Statistical analyses

All calculations were conducted using Microsoft Excel, version 2010. Multivariate and univariate statistical analyses (e.g., cluster analysis (CA), correlation matrix (CM) and principle component analysis (PCA) were carried out using Statistical Package for the Social Sciences (SPSS), version 17. Arc-GIS version 9 was used to make study area map. Hydro-chemical facies was determined by the Piper diagram (Piper, 1994). The major ion composition of groundwater samples were determined by Stiff diagram (Stiff, 1951).

3. Results and discussion

3.1. Physico-chemical characteristics

Results of physico-chemical parameters in tube wells water of the Tehsil Mailsi summarized in Table 1. Average values of pH, DO, EC and TDS were found according to drinking water guidelines set by (PakEPA, 2008; US-EPA, 2011; WHO, 2011) in Jallah Jeem and DurPur respectively. Only 4% of Jallah Jeem and 9% of the DurPur site were found with higher values of EC, while 14% of the Jallah Jeem and 4% of the DurPur sampling sites surpass having the safe limit of TDS. The tube well water of the study area was slightly acidic. Among water quality parameters, pH is one of the important indicators of contamination level in an aquatic system and affects water quality (Jonnalagadda and Mhere, 2001). This suggests that study area groundwater has a great potential to dissolve salts and minerals. Average concentrations of all anions were found higher the drinking water guidelines suggested by WHO 2011, except for Cl^- . The concentration of SO_4^{2-} and NO_3^- differed significantly throughout the area and ranged between 205.8–873 and 169–748.9 ppm and 12.3–58.5 and 16.5–47.6 ppm in Jallah Jeem and DurPur, respectively. The higher concentration of NO_3^- and SO_4^{2-} in tube well water are attributed to sulphide mineralization and fertilizer based agriculture practices in Tehsil Mailsi. The predominant anion was HCO_3^- ranged from 25.3 to 988 and 87.8–965 ppm, in DurPur and Jallah Jeem, respectively. This indicates that dissolution of carbonate minerals could be the cause of elevated concentration of HCO_3^- in tube well water samples of the study area.

Among the trace metals, the average concentrations of Mg^{2+} , Ca^{2+} and K^+ were generally found within the range of drinking water guidelines set by (PakEPA, 2008; US-EPA, 2005; WHO, 2011) except for Na^+ (Table 1). The range of Na^+ concentrations varied from 222 to 452 and 184–453 ppm in Jallah Jeem and DurPur, respectively. The entire water sample in Jallah Jeem exceeded WHO

permissible limit, while 91% of DurPur water sample exceeded safe limit of WHO. Higher concentrations of Na^+ can be attributed to weathering of clay minerals, saline and water logged soil conditions of the study area (Gul, 2012; Khan et al., 2011). 63% tube well water samples of both areas were found with higher concentrations of Ca^{2+} in comparison with drinking water guidelines of (WHO, 2011). These high Ca^{2+} concentrations are consistent with the HCO_3^- which is suggesting the contribution from leaching of carbonate phases of limestone deposits (SDNP, 2003).

Among the trace metals, average concentrations of Mn, Co, Cu, Zn, Cr and Ni were generally found within the drinking water guidelines set by (WHO, 2011) except Fe, Pb, Cd, As (Table 1). Concentrations of Fe ranged from 74 to 1806 ppb with average concentration (568.7 ppb) in Jallah Jeem tube well water samples, while in DurPur tube well water samples it ranged from 173 to 2013 ppb with average content (719.3 ppb). 59% of Jallah Jeem and 73% of DurPur areas water samples were observed with relatively high Fe content (300 ppb) in comparison with (WHO, 2011). The concentrations of Pb in tube well groundwater samples ranged from 20 to 160 ppb with average value (68.9 ppb) in Jallah Jeem, while in DurPur tube well groundwater samples Pb ranged from 23 to 100 ppb with average content (70 ppb). All the tube well groundwater samples of both areas exceeded guidelines value of Pb (10 ppb) by (WHO, 2011), respectively. Cadmium concentration ranged from 28 to 111 ppb with average value (67.68 ppb) in Jallah Jeem tube well water, while in DurPur tube well water Cd ranged from 28 to 107 ppb with average content (67.4 ppb). All samples surpass safe limit of water of Cd content (3 ppb) adjusted by (PakEPA, 2008; US-EPA, 2011; WHO, 2011). The higher concentrations of Pb and Cd in tube well water were due to untreated industrial, sewage and domestic waste, plumbing and extensive agriculture practices in the study area. Consequently, Pb and Cd concentrations of the study area were observed highest than those reported by Muhammad et al. (2011) in drinking water from the Kohistan region, Pakistan. Arsenic concentration ranged from 15 to 395 ppb with average value (139.4 ppb) and 13–293 ppb with average content (130.2 ppb) in Jallah Jeem and DurPur study areas, respectively. Likewise, the As concentrations of all tube well groundwater samples exceeded WHO guidelines limit 10 ppb. Among tube well water As is one of the hazardous metalloids that originated from both natural and anthropogenic sources (Baig et al., 2009a,b; Muhammad et al., 2010).

3.2. Water quality assessment

A piper plot of major elements allowed for the approval of the chemical types of tube well water (Fig. 2). Groundwater quality showed the dominance of HCO_3^- among anions, while Ca^{2+} among cations. Further, it employed Ca^{2+} - Mg^{2+} - HCO_3^- type of water chemistry in study area with elevated sulfate, calcium and chloride concentrations (Fig. 2). Anions in tube well water showed following trend; $<SO_4^{2-} < HCO_3^- < Cl^- < NO_3^-$ while the cations followed the pattern like $Na^+ < Ca^{2+} < Mg^{2+} < K^+$. Stiff diagram represents the graphical demonstration of the different water ions in the study area (Fig. 3). The results signified the dominance of Ca^{2+} - HCO_3^- , Na^+ - Cl^- and Mg^{2+} - SO_4^{2-} . A polygonal shape was drawn from the four parallel horizontal axes extending to the sides of a vertical zero axes. Stiff patterns are valuable in making a rapid visual assessment between water samples from different sources.

Irrigation water quality compared on the basis of; (a) total salt concentrations as measured by electrical conductivity (EC) (b) relative proportion of sodium to other principal cations as expressed by SAR (c) RSC and (d) %Na (Wicox, 1995). The classification of tube well water of two sites; Jallah Jeem and DurPur with respect to sodium absorption ratio (SAR) is given in Table 2. The SAR of the tube well water ranged from 6.99 to 8.7 and 5.8–7.69 in Jallah Jeem

Table 1
Concentrations of heavy metals and physicochemical parameters of tube wells water in the study area.

Parameters	Statistics	DurPur	Jallah Jeem
pH	Range (Average)	4.9–8.2(7.07)	5.8–8.3(7.3)
DO (ppm)	Range (Average)	6.8–8.1(7.63)	6.7–8.2(7.59)
EC (mS/cm)	Range (Average)	0.22–1.87(0.885)	0.29–1.93(0.79)
TDS (ppm)	Range (Average)	167–1285(520.64)	223–1312(652.45)
Ca ²⁺ (ppm)	Range (Average)	24–174.72(90.77)	34–126.72(84.53)
Mg ²⁺ (ppm)	Range (Average)	26–54.24(39.45)	25–45.97(36.91)
HCO ₃ ⁻ (ppm)	Range (Average)	25.30–988(549.82)	87.84–965(456.49)
Cl ⁻ (ppm)	Range (Average)	33–150.2(80.67)	56–355.39(169.29)
SO ₄ ²⁻ (ppm)	Range (Average)	169–748.9(420.9)	205.8–873(468.87)
NO ₃ ⁻ (ppm)	Range (Average)	16.5–47.6(32.26)	12.3–58.5(31.38)
Na ⁺ (ppm)	Range (Average)	184–453(333.13)	222–452(379.17)
K ⁺ (ppm)	Range (Average)	2.4–4.78(3.68)	2.2–26(4.65)
Cr (ppb)	Range (Average)	12–58(32.77)	12–61(32.82)
Co (ppb)	Range (Average)	0.1–0.80(0.39)	0.00–1.00(0.38)
Mn (ppb)	Range (Average)	1.8–14.9(6.94)	1.4–42.1(8.66)
Fe (ppb)	Range (Average)	173–2013(719.32)	74–1806(568.73)
Pb (ppb)	Range (Average)	23–100(70)	20–160(68.91)
Zn (ppb)	Range (Average)	52–4291(1034.23)	16.1–4392(844.82)
Ni (ppb)	Range (Average)	12–81(32.36)	11–67(35.27)
Cd (ppb)	Range (Average)	28–107(67.4)	28–111(67.68)
As (ppb)	Range (Average)	13–293(130.18)	15–395(139.36)
Cu (ppb)	Range (Average)	1.6–138(48)	4.4–121(49.32)

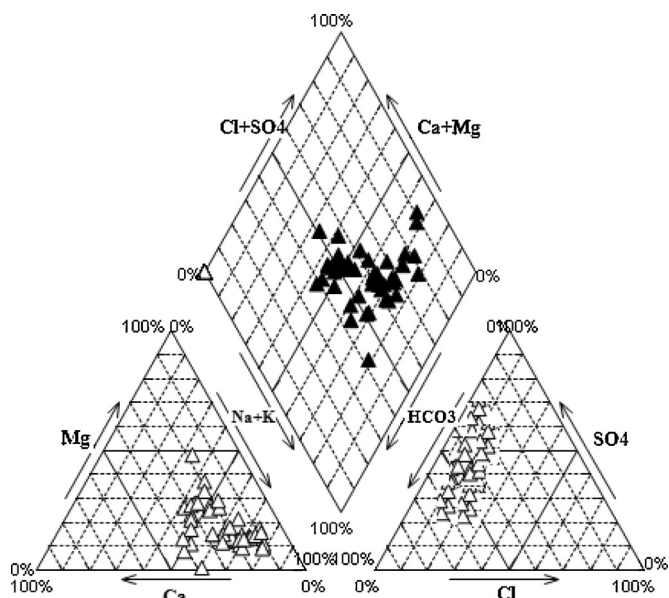


Fig. 2. Piper plot showing the major water types of tube well water samples.

and DurPur, respectively. Relative frequency distribution of SAR was less than 10 (Table 2) that indicated the tube well water is fit for irrigation (Malik et al., 1984; Muhammad et al., 1996; Richards, 1954). The classification of tube well water samples with respect to percent sodium is shown in (Table 2). The average value of sodium percentage 69.3% in Jallah Jeem tube well water samples while in DurPur average value of sodium percentage is 65.23% in tube well water samples. Considering relative frequency distribution regarding percentage sodium (Table 2), in both study areas all samples were unfit for irrigation (Malik et al., 1984; Richards, 1954). The classification of tube well water of two sites; Jallah Jeem and DurPur with respect to residual sodium carbonate (RSC) is given in Table 2. The average value of RSC of tube well water from 0.47 and 1.24 in Jallah Jeem and DurPur, respectively. Relative frequency distribution of RSC was <1.25 (Table 2) that indicated the tube well water is fit for irrigation (Malik et al., 1984; Muhammad et al., 1996; Richards, 1954).

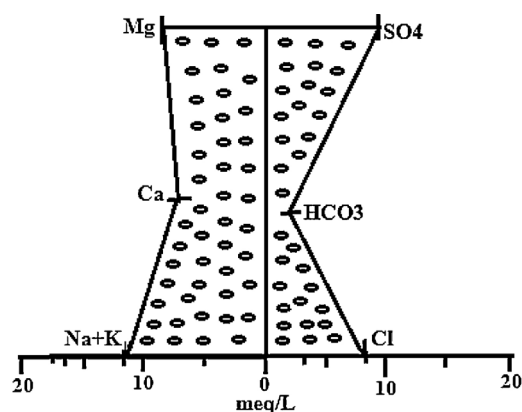


Fig. 3. Spatial variations in tube well water samples of the study area by stiff diagram.

Kelly's index (KI), calculated by using Eq. (7), whereas tube well water is suitable with $KI < 1$, while those > 1 considered unsuitable (Sundaray et al., 2009). In study area from Jallah Jeem to DurPur, KI average values varied 2.27 and 1.89, respectively (Table 2). According to this KI classification, all tube well water of both area are unsuitable for irrigation purpose ($KI > 1$). Magnesium absorption ratio (MAR) are important parameters in determining the water quality for agricultural purposes (Nagaraju et al., 2006). The MAR average value 42% in both study area tube well water, respectively (Table 2). All samples in both area within the ranged of acceptable magnesium ratio limit of 50%, so water is suitable for irrigation (Ayers and Westcot, 1985).

3.3. Health risk assessment

In study area, HRA was carried out from tube well water samples that were used for drinking, domestic and agricultural purposes. For this purpose basic information about drinking water sources were collected in field.

3.3.1. Chronic risk assessment

Health risk assessment data of tube wells water are presented in Table 3. The average estimated daily intake (EDI) values for HMs concentrations in tube well water of Jallah Jeem study area were

Table 2
Range of irrigation quality parameters of tube well water of the study area Jallah Jeem and DurPur.

Parameters	Statistics	DurPur	Jallah Jeem
		Tube well water n=22	Tube well water n=22
SAR	Range (Average)	5.8–7.69(7.4)	6.99–8.7(8.6)
RSC	Range (Average)	0.05–2.99(1.24)	0.64–5.64(0.47)
%Na	Range (Average)	59.55–70.1(65.23)	64.4–71.48(69.3)
KI	Range (Average)	1.49–2.38(1.89)	0.95–1.93(2.27)
MAR	Range (Average)	0.64–0.34(0.42)	0.55–0.37(0.42)

found as follows: Cr (0.91), Mn (0.24), Fe (15.79), Pb (1.9), Zn (23.46), Ni (0.97), Cd (1.88), Cu (1.37) and As (3.87) $\mu\text{g}/\text{kg}\cdot\text{day}$ (Table 3). Average EDI values for HMs concentrations in tube well water of DurPur area were found as follows: Cr (0.91), Mn (0.19), Fe (19.98), Pb (2.36), Zn (28.72), Ni (0.89), Cd (1.87), Cu (1.33) and As (3.6) $\mu\text{g}/\text{kg}\cdot\text{day}$ (Table 3). The highest EDI values of As and Cd are due to its high contamination level in tube well water of the study area. The higher EDI of As and Cd may be attributed to provide contamination from industrial and wastewater sewage. The EDI values of the study area were observed higher than those reported by Shah et al. (2012) for drinking water from the Mohammad Agency, Pakistan.

The target hazard quotient (THQ) values for all the HMs of the tube well water samples are summarized in Table 3. The EDI values of metals were evaluated for the risk assessment through the THQ. Highest THQ was observed for Cd (0.62E+01) and As (3.65E+01) in tube well water of the Jallah Jeem area, whereas lowest (1.12E-03) for Cr (Table 3). The highest THQ values for Cd (0.59E+01) and As (2.7E+01) were noted in tube well water samples of DurPur study area and the lowest (1.06E-03) for Cr (Table 3). Carcinogenic and chronic toxicity risk of HMs in the drinking water depends on type, consumption rate, toxicity and concentrations (Kapaj et al., 2006). The highest THQ values for Cd and As in the study were due to its RfD values and higher concentration than other toxic metals. Therefore, people of the study area at chronic health risk due to consumption of contaminated tube well water with HMs. The THQ values for the study area were observed to be higher than the reported by Muhammad et al. (2011) for drinking water from the Kohistan region, Pakistan.

Table 3
Health risk assessment through tube well water consumption in the Tehsil Mailsi study area (n=44).

Parameters	Statistics	DurPur	Jallah Jeem
		Tube well water n=22	Tube well water n=22
EDI			
Cr	Range (Average)	0.33–1.6(0.91)	0.33–1.69(0.91)
Mn	Range (Average)	0.05–0.41(0.19)	0.038–1.17(0.24)
Fe	Range (Average)	4.8–55.9(19.98)	2.1–50.16(15.79)
Pb	Range (Average)	0.63–2.77(2.36)	0.55–4.44(1.9)
Zn	Range (Average)	1.4–119.19(28.720)	0.45–122(23.46)
Ni	Range (Average)	0.33–2.25(0.89)	0.305–1.86(0.97)
Cd	Range (Average)	0.77–2.97(1.87)	0.77–3.1(1.88)
As	Range (Average)	0.36–8.1(3.6)	0.41–10.97(3.87)
Cu	Range (Average)	0.044–3.8(1.33)	0.12–3.36(1.37)
THQ			
Cr	Range (Average)	0.22E-03–1.06E-03(0.606E-03)	0.22E-03–1.12E-03(0.61E-03)
Mn	Range (Average)	0.035E-02–292E-02(0.13E-02)	0.027E-02–0.84E-02(0.17E-02)
Fe	Range (Average)	1.6E-02–18.6E-02(6.66E-02)	0.7E-02–16.72E-02(5.26E-02)
Pb	Range (Average)	0.175E-01–0.77E-01(0.65E-01)	0.15E-01–1.23E-01(0.52E-01)
Zn	Range (Average)	0.466E-02–39.73E-02(9.57E-02)	0.15E-02–40.66E-02(7.82E-02)
Ni	Range (Average)	0.165E-01–1.125E-01(32.36E-01)	0.152E-01–0.93E-01(0.49E-01)
Cd	Range (Average)	0.154E+01–0.594E+01(0.374E+01)	0.154E+01–0.62E+01(0.376E+01)
As	Range (Average)	0.12E+01–2.7E+01(1.2E+01)	0.14E+01–3.65E+01(1.29E+01)
Cu	Range (Average)	0.011E-01–1.02E-01(0.359E-01)	0.032E-01–0.91E-01(0.37E-01)
CR			
As	Range (Average)	0.54E+03–12.15E+03(5.4E+03)	0.615E+03–16.45+03(5.8E+03)

3.3.2. Cancer risk

The cancer slope risk factor is only available for arsenic, therefore cancer risk (CR) was calculated for As concentrations in tube well water of the study area (Table 3). The CR value ranged from 0.165E+03 to 16.45E+03 with average value of 5.8E+03 in tube well water of Jallah Jeem area (Table 3) indicating high risk. Similarly in DurPur study area tube well water samples CR values ranged from 0.54E+03 to 12.15E+03 with average value of 5.4E+03 (Table 3). According to USEPA, CR values higher than one in a million (10^{-6}) are consider to be significant. Result revealed that tube well water may pose a high risk, when compare with the USEPA, (2010) approach. Consequently, cancer risk assessment of the study area suggests that there is high health risk due to the arsenic contamination.

3.4. Statistical analysis

Table 4 showed the correlation analysis among heavy metals and physico-chemical parameters in the tube well groundwater sources, respectively. The inter-relationship of physico-chemical parameters provided interesting and valuable information about the sources and pathways of contamination (Manta et al., 2002; Mico et al., 2006; Muhammad et al., 2011). In tube well water some of the selected physico-chemical and heavy metal parameters showed positive correlation such as DO-Cr, pH-HCO₃⁻, EC-TDS, EC-Ca²⁺, EC-Mg²⁺, TDS-Mg²⁺, Ca²⁺-Mg²⁺, Ca²⁺-Na⁺, Ca²⁺-Fe, Ca²⁺-Pb, Ca²⁺-Cd, Mg²⁺-Pb, Mg²⁺-Cd, HCO₃⁻-As, HCO₃⁻-Cu, Cl⁻-Ni, SO₄²⁻-Na⁺, Na⁺-K⁺, K⁺-Co, Cr-As, Fe-Pb, Fe-Cd and As-Cu, while some of the pairs also showed negative correlation such as DO-Cl⁻, DO-Na⁺, EC-K⁺, TDS-NO₃⁻, Mg²⁺-Cl⁻, Mg²⁺-Cr, HCO₃⁻-Fe, SO₄²⁻-Co, NO₃⁻-Co, Cr-Mn, Co-Ni, Co-Cd, Fe-Cu, Pb-As, Ni-As and Cd-As as shown in (Table 4). These correlations showed that the major sources of contamination in tube well water in the study area anthropogenic in nature rather than geogenic. Results of this study are reliable with those reported by Khan et al. (2013a,b) and Shah et al. (2012) for groundwater. These results of correlation analysis were further supported by the PCA.

Table 5 summarizes the PCA results for heavy metals and physico-chemical parameters of tube well groundwater samples, having total variance of 75.24% for 9 factors of association. Factor-1 contributed 14.14% to the total variance with high loading on

Table 4
Pearson correlation coefficient matrix of selected heavy metals and physicochemical parameters in tube well water of the study area (n=44).

Parameters	DO	pH	EC	TDS	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	K ⁺	Cr	Co	Mn	Fe ²⁺	Pb	Zn	Ni	Cd	As	Cu	
DO	1																						
pH	-0.005	1																					
EC	-0.132	0.179	1																				
TDS	0.072	-0.058	0.43	1																			
Ca ²⁺	-0.128	0.068	0.353	0.238	1																		
Mg ²⁺	0.043	-0.016	0.316	0.296	0.421	1																	
HCO ₃ ⁻	-0.287	0.262	0.137	-0.146	-0.003	0.127	1																
Cl ⁻	-0.371	0.101	0.271	0.222	-0.055	-0.305	-0.196	1															
SO ₄ ²⁻	0.207	0.187	-0.021	0.01	0.206	0.205	0.075	-0.091	1														
NO ₃ ⁻	-0.046	-0.057	-0.058	-0.305	-0.122	-0.198	-0.094	0.137	0.23	1													
Na ⁺	-0.363	0.059	-0.15	-0.016	0.327	0.021	0.069	0.094	0.361	-0.095	1												
K ⁺	0.198	0.09	-0.233	0.125	-0.1	-0.264	-0.159	-0.003	0.001	-0.181	0.263	1											
CR	0.269	-0.003	-0.106	-0.082	-0.184	-0.355	-0.21	-0.052	0.088	0.16	0.128	0.197	1										
Co	0.012	0.004	-0.227	-0.015	-0.365	-0.037	0.045	-0.13	-0.304	-0.344	-0.033	0.29	-0.072	1									
Mn	-0.141	-0.131	0.059	0.006	0.252	0.109	-0.115	-0.043	0.183	-0.02	0.13	-0.091	-0.328	-0.011	1								
Fe ²⁺	0.032	0.005	0.114	-0.059	0.351	0.001	-0.216	-0.227	-0.139	0.002	0.042	-0.023	0.213	-0.213	-0.055	1							
Pb	-0.14	-0.063	0.193	-0.056	0.377	0.337	-0.018	-0.185	-0.163	-0.121	0.184	-0.118	-0.175	0.052	-0.006	0.3	1						
Zn	-0.048	0.038	-0.201	-0.167	-0.009	0.054	-0.95	-0.065	0.219	0.038	-0.018	0.131	-0.019	-0.144	-0.026	-0.307	-0.214	1					
Ni	-0.244	-0.123	0.245	0.02	0.26	-0.018	-0.46	0.266	-0.049	0.172	0.194	-0.001	-0.166	-0.303	0.149	-0.161	0.175	-0.179	1				
Cd	-0.045	0.148	0.224	0.208	0.438	0.217	-0.025	0.086	0.04	-0.163	0.152	-0.048	0.126	-0.359	0.155	0.245	0.064	-0.075	0.174	1			
As	0.045	0.085	0.075	0.239	-0.015	-0.106	0.261	0.031	0.129	-0.195	-0.04	-0.051	-0.128	0.287	-0.037	0.004	-0.272	-0.7	-0.392	-0.273	1		
Cu	-0.17	0.255	-0.026	0.001	-0.296	0.066	0.358	0.078	-0.084	-0.255	-0.084	-0.109	-0.151	0.195	-0.097	-0.281	-0.085	-0.16	-0.169	0.102	0.121	1	

Bold correlation is significant at the 0.05 level.

n = number of samples.

Table 5
Factor loading for selected heavy metals and physicochemical parameters in tube well water (n=44).

Parameters	F1	F2	F3	F4	F5	F6	F7	F8	F9
Ca ²⁺	0.821	-0.071	0.243	0.14	0.005	0.117	-0.03	0.189	-0.044
EC	0.586	0.278	-0.059	-0.068	0.354	-0.368	0.045	0.128	0.105
Cd	0.573	-0.087	0.079	0.111	0.294	0.042	0.292	-0.375	-0.241
Mg ²⁺	0.542	0.314	0.411	0.087	-0.276	-0.153	-0.15	-0.272	0.043
Co	-0.497	0.459	0.217	-0.261	-0.021	0.402	-0.135	0.058	0.086
Pb	0.48	0.041	0.235	-0.448	-0.305	0.242	0.22	0.075	0.169
Cu	-0.178	0.639	-0.172	0.103	0.001	0	0.326	-0.349	-0.098
HCO ₃ ⁻	0.036	0.561	0.171	0.303	-0.317	-0.008	0.366	0.076	0.226
Cr	-0.274	-0.529	0.14	0.092	0.372	0.029	0.403	-0.008	0.189
NO ₃ ⁻	-0.054	-0.522	-0.436	0.103	-0.216	-0.373	0.028	0.176	0.213
Cl ⁻	0.098	0.042	-0.676	0.026	0.544	0.004	-0.11	0.11	-0.171
DO	-0.291	-0.255	0.589	0.075	0.164	-0.324	-0.123	-0.3	0.33
Ni	0.485	-0.168	-0.534	-0.202	-0.003	0.144	-0.107	-0.193	0.311
Fe	0.277	-0.343	0.451	-0.202	0.064	-0.017	0.394	0.428	-0.255
SO ₄ ²⁻	0.155	-0.193	0.078	0.823	-0.117	-0.045	-0.176	0.001	0.284
TDS	0.312	0.296	0.209	-0.003	0.65	-0.086	-0.368	-0.045	0.077
Na ⁺	0.296	-0.129	-0.101	0.347	-0.008	0.751	0.063	0.174	0.163
K ⁺	-0.284	-0.179	0.168	0.094	0.372	0.612	-0.106	-0.169	0.074
Mn	0.328	0.015	-0.063	0.079	-0.229	0.146	-0.518	0.006	-0.138
Ph	0.028	0.243	-0.031	0.466	0.172	0.013	0.481	-0.062	-0.068
As	-0.248	0.48	0.189	0.295	0.203	-0.11	-0.158	0.624	0.041
Zn	-0.133	-0.253	0.055	0.402	-0.212	0.006	-0.179	-0.092	-0.618
Eigen value	3.112	2.415	2.033	1.801	1.737	1.642	1.515	1.22	1.077
Variance%	14.14	10.97	9.24	8.18	7.89	7.46	6.88	5.54	4.89
Cumulative%	14.14	25.123	34.36	42.55	50.44	57.91	64.8	70.34	75.24

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.
Values of dominant parameters in each factor are reported in bold.

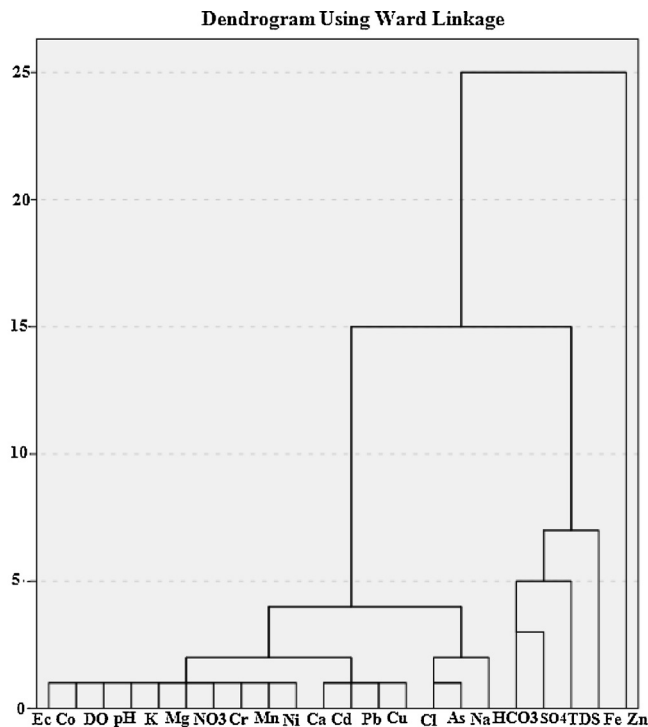


Fig. 4. Cluster analyses of heavy metals and physicochemical parameters in tube well water samples of study area.

Ca²⁺ (r=0.821), EC (r=0.586), Cd (r=0.573), Mg²⁺ (r=0.542), Pb (r=0.480) and Mn (r=0.382). The relationship of these parameters may be attributed to the presence of mafic rocks and agricultural activities present in the study area suggesting anthropogenic and geogenic sources (Harvey et al., 2002). Factor-2 contributed 10.97% to total variance with high loading observed on Co (r=0.459), Cu (r=0.639) and HCO₃⁻ (r=0.561). The sources of these parameters could be attributed carbonaceous rocks, industrial and also

the use of agrochemical (Hasan et al., 2007). Factor-3 contributed 9.24% with high loading on DO (r=0.589) and Fe (r=0.451) suggesting the contribution from mafic and carbonate rocks, hence indicating geogenic source (Zhang et al., 2011). Factor-4 has contributed 8.18%, with high loading on SO₄²⁻ (r=0.823), pH (r=0.466) and Zn (r=0.402). The sources of SO₄²⁻, pH and Zn may be due to mafic rocks, industrial and agricultural activities in the study area. This indicates the involvement of both geogenic and anthropogenic sources. Factor-5 contributed 7.98% with high loading on Cl⁻ (r=0.544) and TDS (r=0.650) which could be due to the mafic rocks (Mico et al., 2006; Hasan et al., 2007). Factor-6 contributed 7.46% to the total variance with high loading on Na⁺ (r=0.751) and K⁺ (r=0.612), this could be attributed to the geogenic source (Villalobos et al., 2001). Factor-7 had contributed 6.88% to total variance with high loading on Cr (r=0.403), the source could be the presence of mafic rock in study area (Khan et al., 2010). Factor-8 has contributed 5.54% with high loading on As (r=0.624), which indicates the involvement of both geogenic and anthropogenic sources (Liu et al., 2003). Factor-9 contributed 4.89% with high loading on NO₃⁻ (r=0.213) and Ni (r=0.311). The source these parameters may be due to the anthropogenic and geogenic inputs (Mico et al., 2006).

The results of cluster analysis (CA) well approved with PCA. The results of CA helped in interpreting the data and indicating patterns of similar objects. In tube well water samples four groups of elements were recognized. The clustering behavior of tube well water in dendrogram showed that there is one large and three small clusters of parameters (Fig. 4). In cluster analysis, similar objects fall into the same class and dissimilar group fall into another group (Chen et al., 2007; Danielsson et al., 1999). The first group includes Ca²⁺, Cd, Fe, Pb, SO₄²⁻, Na⁺, Mn and Mg²⁺ parameters as shown in (Fig. 4), suggesting all these parameters are from the same source, mainly anthropogenic activities, (industrial and natural activities). The second group includes EC, TDS, Ni and Cl⁻ as shown in (Fig. 4). It is possible that the source of second group parameters may be originated from the mafic rocks. The third group includes HCO₃⁻, Cu, pH and As as shown in (Fig. 4). It is possible that all of the ions of third group may be originated from the parent rock mate-

rial. Elevated HCO_3^- , As, and pH concentrations were caused by the interaction of ground water with aquifer sediments rich in carbonate (Ahmed et al., 2004). The fourth group includes K^+ , DO, Co, Cr, NO_3^- and Zn as shown in (Fig. 4). Similar to group first, the elements of this group may be originated from anthropogenic, natural and parent rock materials. Similar aspects have been reported previously (Arain et al., 2009; Simeonov et al., 2003).

4. Global perspectives

The As and HMs contamination in groundwater were determined in different countries of the world, such as Bangladesh, India, China, Germany, Pakistan, Thailand, Argentina, Chile, Hungary, Nepal, USA, Mexico, Vietnam, Finland, Romania, Turkey, Kenya, Ethiopia, South Africa, Tanzania, and the USA. According to the (USEPA, 2011; WHO, 2011) water guidelines for HMs, more than 100 million people are at risk globally, with about 45 million of those belonging to developing countries (Ravenscroft et al., 2009). The situation is worse in Pakistan, where many of the regions exceed WHO limits. Ashraf et al. (1990) reported elevated concentrations of As in the water reservoirs of Pakistan, i.e., Tarbela (620 ppb), Chashma (750 ppb), and Lloyd (620 ppb). Excessive and long-term (6–10 years) human intake of toxic As above the 10 ppb level, leads to arsenicosis, which is the term used for arsenic health effects including skin problems, skin cancer, internal cancers (bladder, kidney, lung), and diseases of the blood vessels of the legs and feet (Ravenscroft et al., 2009; Karim, 1999; WHO, 2011). However, a recent report, (Smith et al., 2000), revealed that, despite the daily consumption of good nutritious food, some people have developed arsenic poisoning, such as the small populations of Chiu village (Chile) and, Eruani village of Laksam (Bangladesh), where drinking water contains As levels of 750–800 ppb and 250–260 ppb, respectively. Worldwide, elevated As and HMs concentrations are usually associated with calcareous minerals, or high alkaline and carbonate conditions where sodium ions instead of calcium ions dominate (Amini et al., 2008). In addition to natural dissolution of minerals, industrial operations such as fertilizer plants, metallurgical industries, semiconductor production generate effluents with high HMs. The sources of HMs in Pakistan include phosphate fertilizer, insecticides, herbicides, semi-conductors, timber preservatives, mining and smelting, and coal combustion (Mondal et al., 2006; Bundschuh et al., 2011; Brahman et al., 2013a,b, 2014).

5. Conclusions

This study concluded that majority of the physico-chemical parameters were found within the safe drinking water guidelines set by Pak-EPA and WHO. The type of tube well water that predominates in the study is Ca^{2+} - Mg^{2+} - HCO_3^- , which is the best reflection of geology and climate of the study area. The important parameters such as SAR, RSC and MAR reveal as good quality of tube well water for irrigation purpose while KI and % Na concluded that tube well water in the study area was not suitable for agriculture and domestic use. The values of EDI were highest for Zn, whereas THQ values for highest for Cd and As. This higher intake of toxic metals in tube well water may pose chronic toxicity and carcinogenic risks to the local inhabitants. The statistical approaches (HCA and PCA) tracing out the possible source of contamination of HMs and other physicochemical parameters in tube well water due to local geochemistry, weathering of rocks and agricultural activity in the study area. Monitoring of heavy metal levels in the soil profile of the region and remediation programs are recommended for future management strategies in worldwide. Moreover, in the study area future research should be focused on assessing the health risk of As and heavy metals in food and fodder crops that human and animals

consume for their daily diet and how metals can be transferred from water to crops. Different crop rotations will be the prime focus of future investigations.

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