

Arsenic and heavy metals contamination, risk assessment and their source in drinking water of the Mardan District, Khyber Pakhtunkhwa, Pakistan

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ABSTRACT

The present study was conducted to investigate the physico-chemical characteristics in drinking water of Mardan District, Pakistan. Furthermore, water quality was evaluated for the risk assessment of arsenic and heavy metals (HMs) and their contamination sources. Representative groundwater samples of shallow and deep sources were collected in the study area. These samples were analyzed for physical parameters, anions, light metals (LMs) and HMs. Results were compared with the drinking water guideline values set by the World Health Organization and the US Environmental Protection Agency. Average concentrations of anions, LMs and HMs were found within the maximum allowable contaminant levels except for bicarbonates, Fe, Cu, and Pb. Results revealed that hazard quotients >1 were observed for shallow groundwater for 10% samples only, suggesting potential health risk from water consumption. Correlation analysis and principal component analysis showed a relationship among various physico-chemical parameters in both shallow and deep groundwater. Statistical analyses suggested the geogenic and anthropogenic sources for possible enhancement of various physico-chemical parameters in the aquifer system of the study area.

Key words | arsenic, drinking water, heavy metals, light metals, Mardan District, statistical analyses

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ABBREVIATIONS

AAS	atomic absorption spectrophotometer
ADI	average daily intake
Cl	chloride
CR	cancer risk
EC	electrical conductivity
HRA	health risk assessment
HMs	heavy metals
HQ	hazard quotients
LMs	light metals
MCL	maximum contamination levels
PCA	principal component analysis
TDS	total dissolved solids
US EPA	US Environmental Protection Agency
WHO	World Health Organization

INTRODUCTION

Drinking water contamination both of biological and chemical origin has received great attention by scientific studies all over the world (Muhammad *et al.* 2011; Chappells *et al.* 2014; Lotter *et al.* 2014; Singh *et al.* 2014; Khan *et al.* 2015a). The presence of heavy metals (HMs) in drinking water up to toxic levels in aquatic environments is a matter of great concern due to their deleterious impacts on the lives of plants, animals, and humans (Binning & Baired 2001; Khan *et al.* 2011, 2013, 2015b; Muhammad *et al.* 2013; Sultana *et al.* 2014). These metals are contributed by both natural and anthropogenic sources to drinking water (Shah *et al.* 2012). Major natural sources of these metals are the weathering and oxidation of rocks, and the presence of geothermal waters and river sediments (Macklin & Klimek 1992;

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Buchet & Lison 2000). However, a large number of anthropogenic activities, such as mine drainage, industrial discharge, wastewater effluents, agricultural runoff and land fill disposals have resulted in multifold increases of these metals in aquatic life (Panero *et al.* 1995; Ritter *et al.* 2002; Hussain *et al.* 2014). Light metals (LMs) such as sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg), and some of the HMs like iron (Fe), copper (Cu), chromium (Cr), and zinc (Zn) are required in specific amounts, and their deficiency may result in impairment of biological processes and functions, while their high concentrations may cause toxicity (Shah *et al.* 2012; Khan *et al.* 2014). For example, Cu is an essential metal for many physiological processes but its elevated concentration may cause hepatocellular toxicity, methemoglobinemia, intravascular hemolysis, kidney failure, gastrointestinal bleeding, and Wilson disease (Agarwal *et al.* 1990). Some of the HMs including lead (Pb) and cadmium (Cd), and metalloids such as arsenic (As) are considered to be extremely toxic due to their persistent, bio-accumulative and hazardous nature (Buchet & Lison 2000; Muhammad *et al.* 2010; Shah *et al.* 2012). For example, drinking water contaminated with As may cause serious health hazards, such as hypertension, cancer, skin lesions, hyperkeratosis, melanosis, gangrene, and peripheral vascular disease, as well as having a carcinogenic effect on lungs and skin (Rahaman *et al.* 2008; Fatmi *et al.* 2009; Muhammad *et al.* 2010).

The extent and magnitude of the adverse impacts caused by contamination depend upon the quantity of contaminant and the age as well as the gender of the consumer. Women and children are more vulnerable to HM contamination, e.g., Pb has both carcinogenic and teratogenic properties and adversely affects the reproductive system of women and can lower the neuropsychological and neurobehavioral development of young children (Needleman & Bellinger 1991; Tong *et al.* 2000). HMs are also capable of crossing the placental barrier and can cause permanent structural changes to respiratory and central nervous system of the fetus (Sly & Flack 2008). It has also been reported that Cd exposure may result in osteoporosis, diabetes, and breast cancer in women (Smedley & Kinniburgh 2002; Jarup & Akesson 2009). As well, the adverse impacts of other HMs, As contamination in drinking water have also become a challenge for scientists throughout the world. As contamination

has been reported in tube wells and other drinking water supplies of South East Asian countries like Bangladesh, India, and Pakistan (Bhattacharyya *et al.* 2002). It has been estimated that about 100 million people in these countries are at risk due to consumption of As contaminated water (Nordstrom 2002; Sun *et al.* 2002). Chronic effects of As on humans generally include skin diseases (pigmentation, dermal hyperkeratosis, skin cancer), cardiovascular, neurological, hematological, renal, and respiratory disorders (Morton & Dunette 1994; Smith *et al.* 1999).

Previously, a number of research studies regarding drinking water quality and HM contamination have been conducted in different parts of Pakistan, such as Lahore and Kasur Districts (Farooqi *et al.* 2007), Jamshoro (Baig *et al.* 2009), Muzaffargarh District (Nickson *et al.* 2005), Peshawar basin (Shah & Tariq 2006), Manchar Lake Sindh (Kazi *et al.* 2009), and Kohistan region (Muhammad *et al.* 2010, 2011), and the Mohmand Agency (Shah *et al.* 2012). It can be concluded from these studies that drinking water in many parts of Pakistan is poor quality due to different kinds of contaminants, either sourced by natural processes or anthropogenic activities.

The present research work was aimed at physico-chemical characterization and health risk assessment (HRA) of the drinking water in Mardan District, Khyber Pakhtunkhwa, Pakistan. Results were compared with US Environmental Protection Agency (US EPA) and World Health Organization (WHO) drinking water guideline values. Multivariate statistical analyses and field observations were used for the identification of contamination sources.

MATERIALS AND METHODS

Study area

Mardan District is a part of the Peshawar basin and lies between latitude 34°05' to 34°32' North and longitude 71°48' to 72°25' East (Figure 1), with a total area of 1,632 km² (District Census Report (DCR) of Mardan District 1998). Mardan District can be broadly divided into two parts, the south-western plain area and northern hilly area. The southern part comprises fertile plain with hundreds of meters of thick quaternary deposits. The plain part of Mardan District was once to be the bed of the lake

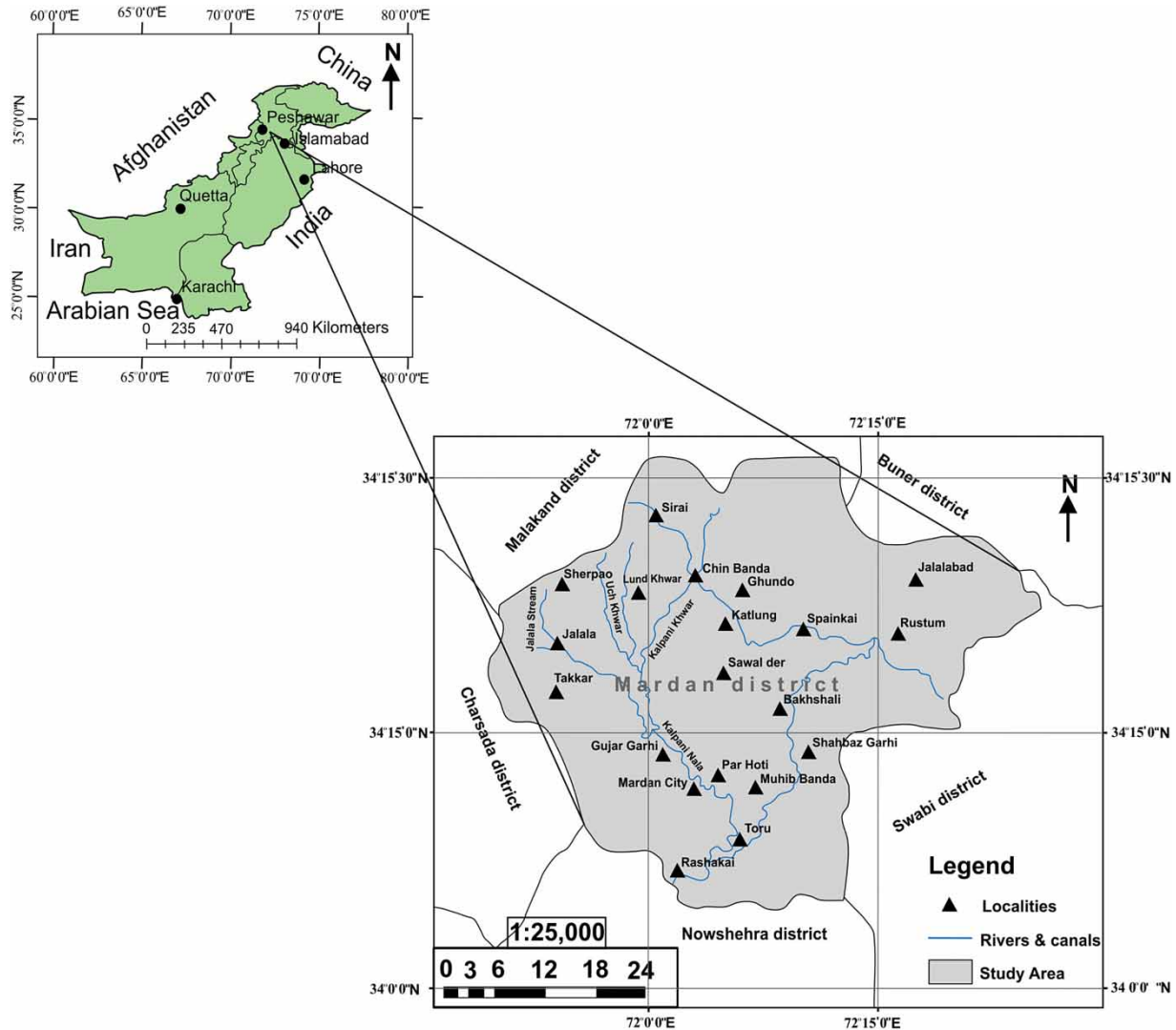


Figure 1 | Location map of the study area (Mardan District).

which was gradually filled up by the load of river (District Census Report (DCR) of Mardan District 1998). The northern side of Mardan District is bounded by hills consisting of rocks of the Shewa Shahbazgarhi complex (Kazmi & Jan 1997). This complex can be divided into felsic and mafic rocks. Minerals in the basic rocks include hastingsite, clinopyroxene, orthopyroxene, biotite, and epidote, while the acidic rocks have orthoclase, plagioclase, and ferromagnesian minerals. These rocks and minerals may be playing an important role in the contamination of groundwater of Mardan District as the aquifer in the district is replenished with the rainwater percolating through these rocks. The

plain parts of the district are rich in agricultural activities irrigated by an extensive canal system. Drinking water in Mardan District is mainly available from shallow groundwater sources (dug wells and hand pumps); however, deep groundwater is also available where tube wells are installed by the municipal corporation (District Census Report (DCR) of Mardan District 1998).

Sampling

Representative drinking water samples were collected from shallow groundwater (5–15 m deep) and deep groundwater

(100–150 m deep) sources of Mardan District for the hydro-geochemical study. Locations of samples were recorded with global positioning system. In the field, each sample was collected in two bottles; one was kept un-acidified, while the other was acidified with a few drops of concentrated (68%) nitric acid (HNO₃) for LM and HM analyses. pH, electric conductivity (EC), and total dissolved solids (TDS) were determined on the spot using electrochemical analyzer, C931.

Chemical analyses

Anions, such as sulfates (SO₄), nitrates (NO₃), chlorides (Cl), and bicarbonates (HCO₃), were determined in the filtered and un-acidified shallow and deep groundwater samples using HACH DR 2800 spectrophotometer. Concentrations of LMs (i.e., Ca, Mg, Na, K) were determined using atomic absorption spectrophotometer (AAS) and for HMs (i.e., Fe, Mn, Cu, Pb, Zn, Ni, Cr, Cd) the AAS were equipped with graphite furnace. As was determined on AAS equipped with mercury hydride system (MHS). The measurement of the total As concentrations was carried out by taking 10 mL of each water sample mixed with 10 mL of 5 M HCl and 1 mL of KI. All the acids and reagents used were of analytical grade. Samples were analyzed in triplicate and the accuracy was found at 95% confidence level. All these analyses were performed in the Geochemistry Laboratory of the National Centre of Excellence in Geology, University of Peshawar.

HRA

HRA was carried out in order to understand the chronic (non-carcinogenic) and carcinogenic effects of HMs and As on the health of humans. Chronic effects are assumed to be based on threshold limits (reference dose), while carcinogenic responses are based on non-threshold limits. The non-threshold limit means that each dose would be able to cause a cancer risk (CR) (US EPA (United States Environmental Protection Agency) 1989). To measure the potential risk level of the selected HMs and As in drinking water, average daily dose (ADD) and hazard quotients (HQs) were calculated for Fe, Mn, Cu, Pb, Zn, Cr, Cd, and As. CR was also calculated for As only.

Chronic risk

Humans' exposure to HMs and As is mainly occurring through oral intake and, to a lesser extent, through several other pathways including dermal contact, inhalation and the food chain. ADD was calculated according to the equation (US EPA (United States Environmental Protection Agency) 1989)

$$ADD = C \times IR \times ED \times EF / BW \times AT$$

where *C* represents concentration of metals (μg/L), *IR* is the ingestion rate (2 L/day), *ED* is exposure time in years (considered here to be 72 years), *EF* is the exposure frequency in terms of days/year (365 days), *BW* is the average body weight in kg (72 kg), while *AT* is the average time in days of the whole life time = 25,550 days (72 years × 365 days). Chronic risk levels were determined according to the equation (US EPA (United States Environmental Protection Agency) 1989)

$$HQ = ADD / RfD$$

where *HQ* is hazard quotients and *RfD* (mg/kg-day) represents reference dose of a particular metal, e.g., 3×10^{-1} , 1.4×10^{-1} , 3.7×10^{-2} , 3.6×10^{-2} , 3×10^{-1} , 2×10^{-2} , 1.5×10^0 , 5×10^{-4} , 3×10^4 mg/kg-day for the Fe, Mn, Cu, Pb, Zn, Ni, Cr, Cd, and As (US EPA (United States Environmental Protection Agency) 1989).

CR

CR was calculated by the equation

$$CR = ADD \times CSF$$

Here, *CSF* represents cancer slope factor which is 1.5 for As (US EPA (United States Environmental Protection Agency) 2005). All the results were classified in accordance with US EPA (United States Environmental Protection Agency) (1999); however, standards were changed with other scales accordingly (US EPA (United States Environmental Protection Agency) 2005).

Statistical analyses

Statistical analyses such as mean, range, standard deviation, inter-elemental correlation and principal component analysis (PCA) were carried out by using statistical software SPSS 21 (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Physico-chemical characteristics

The average concentrations of various physico-chemical parameters of the different kinds of water are presented in Figure 2(a)–2(c). Average values of pH, EC, and TDS were found within the drinking water guidelines set by WHO (World Health Organization) (2011). Only 4% of shallow groundwater samples were found with high values of TDS,

while 25% of shallow groundwater samples showed relatively higher values of EC (Figure 2(a)). This suggests that water in the study area has a great potential to dissolve salts and minerals.

Concentrations of all anions were found within the drinking water guidelines suggested by WHO (World Health Organization) (2011) except for HCO_3^- . The majority of the shallow and deep groundwater samples showed elevated values of HCO_3^- above the drinking water guidelines of 250 mg/L given by WHO (World Health Organization) (2011) (Figure 2(a)). In shallow groundwater, HCO_3^- concentrations ranged from 160 to 1,000 mg/L with average value 474 mg/L and 240 to 660 mg/L with average concentration 405 mg/L in deep groundwater samples (Figure 2(a)). This indicates that dissolution of carbonate minerals could be the cause of elevated concentration of HCO_3^- in water samples of the study area.

Among LMs, the average concentrations of Ca, Mg and K were generally found within the drinking water guidelines set by WHO (World Health Organization) (2011). Only 29% of the shallow groundwater samples were found with higher concentrations (>75 mg/L) of Ca in comparison with drinking water guidelines of WHO (World Health Organization) (2011) (Figure 2(b)). These high Ca concentrations are consistent with the HCO_3^- , which is suggesting the contribution from leaching of carbonate phases of limestone deposits (SDNP (Sustainable Development National Programme) District Websites 2003). The range of Na concentrations varied from 91 to 616 mg/L with average concentration 323 mg/L in shallow groundwater samples and from 130 to 561 mg/L with an average value 328 mg/L in deep groundwater samples (Figure 2(b)). A majority of water samples from both shallow and deep groundwater showed relatively high (>200 mg/L) Na concentrations (Figure 2(b)). Higher concentrations of Na can be attributed to saline and water-logged soil conditions of the study area (Gul 2012).

Concentrations of Fe ranged from <0.05 to 956 $\mu\text{g/L}$ with average concentration 76 $\mu\text{g/L}$ in shallow groundwater, while in deep groundwater samples it ranged from 7 to 99 $\mu\text{g/L}$ with average content 43 $\mu\text{g/L}$ (Figure 2(c)). Only 7% of shallow groundwater samples were observed with relatively high Fe content (>300 $\mu\text{g/L}$) in comparison with WHO (World Health Organization) (2011) and US EPA

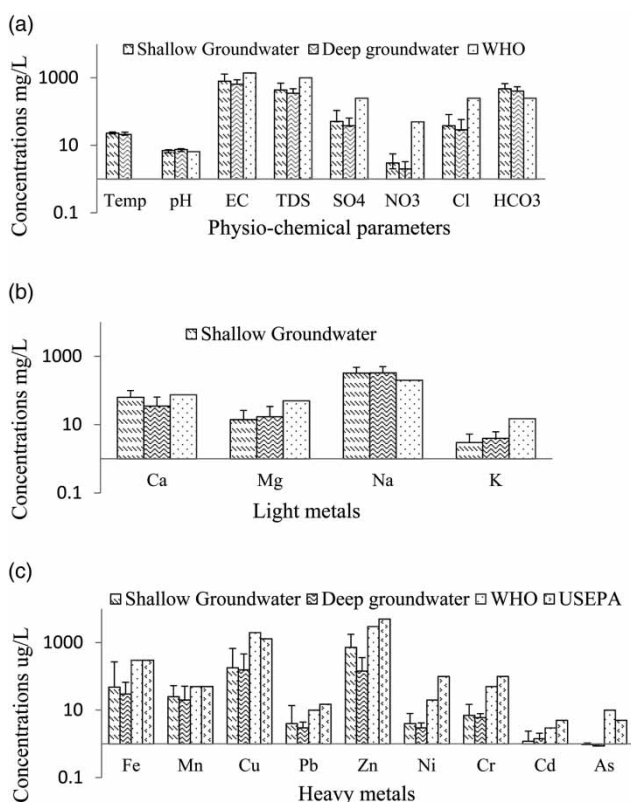


Figure 2 | (a–c) Comparison of physico-chemical parameters in drinking water of Mardan District with the drinking water guidelines of WHO (World Health Organization) (2011) and MCL of US EPA (United States Environmental Protection Agency) (2009).

(United States Environmental Protection Agency) (2009). Manganese in shallow groundwater samples ranged from 2 to 132 µg/L with average value 25 µg/L, while it ranged from 2 to 90 µg/L, with average content 20 µg/L in deep groundwater samples. Manganese was also found within the drinking water guidelines of 50 µg/L according to WHO (World Health Organization) (2011) and US EPA (United States Environmental Protection Agency) (2009). However, 10% of shallow groundwater and 13% of deep groundwater samples showed relatively high Mn content. Average value of Cu in shallow groundwater samples was 180 µg/L with a range of 1–2,496 µg/L. In deep groundwater samples, Cu content ranged from 30 to 845 µg/L with average value 156 µg/L. Only 10% of groundwater samples showed relatively high Cu values. The concentrations of Pb in shallow groundwater samples ranged from <0.05 to 34.60 µg/L with average value 4.00 µg/L, while in deep groundwater samples Pb ranged from 0.12 to 3.10 µg/L with average content 1.04 µg/L. A majority of the samples showed Pb concentrations within the drinking water guidelines of 10 µg/L and 15 µg/L by WHO (World Health Organization) (2011) and US EPA (United States

Environmental Protection Agency) (2009) respectively, except for 10% of shallow groundwater samples showing relatively higher Pb. Other metals like Zn, Ni, Cr, Cd, and As were found within the drinking water guidelines of WHO (World Health Organization) (2011) (Figure 2(c)). Higher concentrations of Fe, Mn, Pb, and Cu in some of the water samples of Mardan District could be due to the presence of sulfide seams in the area.

HRA

In the study area, HRA was carried out for shallow and deep groundwater samples that were used for drinking and other domestic purposes. For this purpose, basic information regarding drinking water sources was collected in the field.

Chronic risk assessment

The HRA data for shallow and deep groundwater are presented in Table 1. The average ADD values for HMs in shallow groundwater were found as follows: Fe (1.3×10^{-3}), Mn (6.8×10^{-4}), Cu (4.6×10^{-3}), Pb (7.1×10^{-5}), Zn ($1.7 \times$

Table 1 | HRA through drinking water consumption in the Mardan District

Metals	Source	ADD (mg/kg-day)		HQ		CR	
		Range	Average	Range	Average	Range	Average
Fe	SW	2.78×10^{-7} – 2.66×10^{-2}	1.3×10^{-3}	9.26×10^{-7} – 8.85×10^{-2}	4×10^{-3}		
	DW	1.94×10^{-4} – 2.75×10^{-3}	7×10^{-4}	6.48×10^{-4} – 9.17×10^{-3}	$<1 \times 10^{-3}$		
Mn	SW	5.56×10^{-5} – 3.67×10^{-3}	6.8×10^{-4}	3.97×10^{-4} – 2.62×10^{-2}	5×10^{-3}		
	DW	5.56×10^{-5} – 2.5×10^{-3}	6×10^{-4}	3.97×10^{-4} – 1.79×10^{-2}	4×10^{-3}		
Cu	SW	2.78×10^{-5} – 6.93×10^{-2}	4.6×10^{-3}	7.51×10^{-4} – 1.87×10^0	1.2×10^{-1}		
	DW	8.33×10^{-4} – 2.35×10^{-2}	4×10^{-3}	2.25×10^{-2} – 6.34×10^{-1}	1×10^{-1}		
Pb	SW	2.78×10^{-7} – 9.61×10^{-4}	7.1×10^{-5}	7.72×10^{-6} – 2.67×10^{-2}	1.9×10^{-2}		
	DW	3.33×10^{-6} – 8.61×10^{-5}	1.41×10^{-5}	9.26×10^{-5} – 2.39×10^{-3}	$<1 \times 10^{-3}$		
Zn	SW	2.78×10^{-7} – 1.16×10^{-1}	1.7×10^{-2}	9.26×10^{-7} – 3.87×10^{-1}	5.9×10^{-2}		
	DW	1.67×10^{-4} – 1.69×10^{-2}	4×10^{-3}	5.56×10^{-4} – 5.64×10^{-2}	1×10^{-2}		
Ni	SW	3.53×10^{-5} – 4.66×10^{-4}	1×10^{-4}	1.76×10^{-3} – 2.33×10^{-2}	5×10^{-3}		
	DW	3.19×10^{-5} – 1.18×10^{-4}	2.5×10^{-5}	1.6×10^{-3} – 5.92×10^{-3}	4×10^{-3}		
Cr	SW	4.66×10^{-4} – 1.12×10^{-3}	1×10^{-3}	2.59×10^{-6} – 7.46×10^{-4}	$<1 \times 10^{-3}$		
	DW	1.20×10^{-4} – 2.53×10^{-4}	1.5×10^{-5}	7.98×10^{-5} – 1.69×10^{-4}	$<1 \times 10^{-3}$		
Cd	SW	1.58×10^{-6} – 1.2×10^{-4}	2×10^{-4}	3.17×10^{-3} – 2.39×10^{-1}	6.2×10^{-2}		
	DW	5.56×10^{-7} – 3.97×10^{-5}	1.6×10^{-5}	1.11×10^{-3} – 7.94×10^{-2}	3×10^{-2}		
As	SW	$<1.0 \times 10^{-5}$ – 2.15×10^{-4}	2.5×10^{-5}	$<1.0 \times 10^{-5}$ – 7.17×10^{-1}	83×10^{-2}	0.0 – 3.15×10^{-4}	3.7×10^{-5}
	DW	1.11×10^{-6} – 7.94×10^{-5}	2.17×10^{-5}	3.7×10^{-3} – 2.65×10^{-1}	6×10^{-2}	1.98×10^{-6} – 1.16×10^{-4}	3.24×10^{-5}

SW, shallow water; DW deep water.

10^{-2}), Ni (1.0×10^{-4}), Cr (1.0×10^{-3}), Cd (2.0×10^{-4}), and As (2.5×10^{-5}) mg/kg-day (Table 1). Average ADD values for HM concentrations in deep groundwater samples were found as follows: Fe (7.0×10^{-4}), Mn (6.0×10^{-4}), Cu (4.0×10^{-3}), Pb (1.41×10^{-5}), Zn (4.0×10^{-3}), Cr (1.5×10^{-5}), Cd (1.6×10^{-5}), and As (2.17×10^{-5}) mg/kg-day (Table 1).

The HQ values for all the HMs of the shallow and deep groundwater samples are summarized in Table 1. Highest (1.87) HQ value was observed for Cu, followed by As in shallow water and the lowest (7.46×10^{-4}) for Cr. Results of drinking water revealed that shallow water showed higher HQ values in term of HMs to the exposed population as compared to deep water. Higher HQ values in shallow water were attributed due to the fact of their higher HM contamination. Considering the HQ values of individual samples, it was found that the majority of shallow groundwater showed no health risk when compared with the US EPA (United States Environmental Protection Agency) (1999) and Rapant & Krcmova (2007). However, samples collected from shallow groundwater of Chin Banda showed medium risk with high HQ value (1.87) for Cu. The lower HQ values of deep groundwater samples suggest no health risk to the exposed human population (Table 1).

CR

The cancer slope risk factor is available only for As, therefore, CR was calculated for As concentrations in drinking water of shallow and deep groundwater samples of the study area (Table 1). CR values ranged from 0.00 to 3.15×10^{-4} with an average value of 3.7×10^{-5} in shallow groundwater samples (Table 1) indicating very low risk. However, samples collected from Garhi Kapora had a high CR level (3.15×10^{-4}), which was only 3% of total shallow groundwater samples (Table 1). Similarly, in deep groundwater samples, CR values ranged from 1.98×10^{-6} to 1.16×10^{-4} with an average value of 3.24×10^{-5} (Table 1). Again, a majority of samples possessed very low carcinogenic risk except for samples collected from Katlung, which had a high CR value (1.16×10^{-4}) which constitutes 12% of the total deep groundwater samples (US EPA (United States Environmental Protection Agency) 1999; Rapant & Krcmova 2007) (Table 1). Therefore, CR assessment of the study area suggests that there is a very low health risk due to As contamination.

Statistical analyses

Tables 2 and 3 show the results of correlation analysis among various physico-chemical parameters in the shallow and deep groundwater sources, respectively. The correlation of physico-chemical parameters provided interesting information on metal sources and pathways (Manta et al. 2002; Muhammad et al. 2011). Shallow groundwater sources showed positive correlation for pH-Fe, pH-Pb, pH-As, EC-SO₄, EC-NO₃, EC-Cl, EC-HCO₃, TDS-SO₄, TDS-NO₃, TDS-Cl, TDS-HCO₃, TDS-Cr, SO₄-NO₃, SO₄-Cl, SO₄-K, NO₃-Cl, NO₃-Mg, NO₃-Mg, NO₃-K, Cl-HCO₃, HCO₃-Mg, K-Mn, Fe-Pb, and Fe-Zn, while some of the pairs also showed negative correlation such as pH-Ca, EC-Zn, TDS-Zn, HCO₃-Zn and Ca-As. In deep groundwater, some of the selected physico-chemical parameters showed strong positive correlation, such as pH-As, EC-TDS, EC-SO₄, EC-HCO₃, EC-K, TDS-SO₄, TDS-NO₃, TDS-HCO₃, TDS-K, SO₄-Cl, HCO₃-K, Mg-Cu, Cu-Pb, Pb-Cr, and Pb-As, while negative correlation was noted in pairs like pH-Ca, NO₃-Cr, K-Zn, and Ca-As. Correlation of natural associated and non-associated physico-chemical parameter pairs suggests that the parameters have both geogenic and anthropogenic contamination sources. These results of correlation analysis were further supported by the PCA.

PCA with Varimax normalization was applied to physico-chemical parameters for their qualitative evaluation. Table 4 summarizes the PCA results for physico-chemical parameters of shallow groundwater samples, having a total variance of 88.561% for five factors of association. Factor-1 contributed 31.033% to the total with high loading on pH ($r = 0.879$), Fe ($r = 0.903$), Cu ($r = 0.948$), Pb ($r = 0.846$), Zn ($r = 0.886$), and As ($r = 0.830$). The association of these parameters could be attributed to the presence of mafic rocks and agriculture activities present in the northern parts of the Mardan District, suggesting geogenic and anthropogenic sources. Factor-2 contributed 24.058% to total variance with high loading observed on EC ($r = 0.872$), TDS ($r = 0.852$), SO₄ ($r = 0.642$), NO₃ ($r = 0.846$), and Cl ($r = 0.857$). The sources of EC, TDS, SO₄, NO₃, and Cl can be the localized sulfide rich soil and also the use of agrochemicals. This indicates the involvement of both geogenic and anthropogenic sources. Factor-3 contributed 12.613% with high loading on Na ($r = 0.939$) suggesting the contribution from saline soil,

Table 2 | Correlation matrices of physico-chemical parameters of shallow groundwater in the Mardan District

Parameters	pH	EC	TDS	SO ₄	NO ₃	Cl	HCO ₃	Ca	Mg	Na	K	Fe	Mn	Cu	Pb	Zn	Cr	Cd	As	
pH	1	-0.015	0.002	0.041	-0.262	0.150	-0.062	-0.721	-0.022	0.039	0.092	0.766	0.063	0.217	0.574	0.412	0.141	-0.33	0.617	
EC		1	0.992	0.588	0.639	0.773	0.805	-0.178	0.474	0.098	0.309	-0.344	0.115	-0.048	-0.346	-0.373	0.491	-0.159	0.335	
TDS			1	0.595	0.652	0.775	0.794	-0.198	0.491	0.115	0.337	-0.360	0.126	-0.061	-0.356	-0.393	0.503	-0.176	0.352	
SO ₄				1	0.740	0.749	0.422	-0.112	0.416	-0.048	0.568	-0.206	0.138	-0.156	-0.209	-0.326	0.213	-0.166	0.170	
NO ₃					1	0.648	0.342	0.188	0.815	0.244	0.588	-0.382	0.179	-0.052	-0.285	-0.380	0.439	-0.166	-0.220	
Cl						1	0.582	-0.195	0.272	0.011	0.304	-0.218	0.076	-0.126	-0.197	-0.357	0.423	-0.218	0.365	
HCO ₃							1	-0.051	0.618	0.145	0.124	-0.433	-0.026	0.034	-0.449	-0.461	0.440	-0.179	0.361	
Ca								1	-0.131	-0.189	-0.281	-0.209	-0.197	-0.126	-0.319	-0.147	-0.175	0.132	-0.563	
Mg									1	0.432	0.345	-0.330	0.054	0.149	-0.309	-0.328	0.334	-0.233	-0.090	
Na										1	0.212	0.018	-0.184	0.292	-0.012	0.028	0.231	0.021	-0.234	
K											1	-0.098	0.516	-0.073	-0.203	-0.062	0.169	-0.389	-0.038	
Fe												1	-0.151	0.296	0.715	0.740	0.069	-0.216	0.174	
Mn													1	-0.193	-0.077	-0.218	-0.178	-0.149	0.039	
Cu														1	0.283	0.110	-0.027	-0.175	0.047	
Pb															1	0.410	0.100	-0.075	0.239	
Zn																1	-0.025	-0.255	-0.005	
Ni																	1	-0.162	0.227	-0.185
Cr																		1	-0.258	0.200
Cd																			1	-0.345
As																				1

Bold correlation is significant at the 0.05 level (2-tailed). Italic correlation is significant at the 0.01 level (2-tailed).

Table 3 | Correlation matrices of physico-chemical parameters of deep groundwater in the Mardan District

Parameters	TDS	SO ₄	NO ₃	Cl	HCO ₃	Ca	Mg	Na	K	Fe	Mn	Cu	Pb	Zn	Ni	Cr	Cd	As
pH	0.020	0.300	-0.360	<i>0.450</i>	-0.210	-0.910	0.468	0.339	-0.040	-0.580	0.203	<i>0.459</i>	<i>0.882</i>	-0.030	0.294	0.402	0.376	<i>0.809</i>
EC	1	<i>0.900</i>	<i>0.767</i>	<i>0.640</i>	<i>0.751</i>	0.071	-0.460	0.172	0.799	<i>0.584</i>	<i>0.409</i>	-0.590	-0.630	-0.620	-0.650	-0.557	0.176	-0.076
TDS	1	<i>0.910</i>	<i>0.774</i>	<i>0.630</i>	<i>0.744</i>	0.075	-0.470	0.154	0.799	<i>0.552</i>	<i>0.429</i>	-0.600	-0.640	-0.610	-0.660	-0.573	0.139	-0.087
SO ₄		1	0.628	<i>0.749</i>	0.443	-0.140	-0.440	0.109	0.642	0.105	0.501	-0.470	-0.560	-0.540	-0.650	-0.476	0.009	0.166
NO ₃			1	0.160	0.525	0.555	-0.410	<i>0.491</i>	0.851	0.994	-0.030	-0.490	-1.000	-0.540	-0.690	-0.964	0.312	-0.603
Cl				1	0.197	-0.300	-0.310	0.146	0.178	0.534	0.053	-0.370	-0.760	-0.320	-0.300	-0.062	0.412	0.608
HCO ₃					1	0.207	-0.220	0.168	0.717	0.807	0.258	-0.500	-0.630	-0.350	-0.210	-0.544	0.278	-0.383
Ca						1	-0.500	-0.48	-0.060	0.538	-0.040	-0.460	-0.890	0.235	-0.390	-0.663	-0.450	-0.806
Mg							1	<i>0.459</i>	-0.170	-0.270	-0.040	0.934	<i>0.991</i>	0.158	0.469	0.634	<i>0.555</i>	0.309
Na								1	0.419	0.143	-0.410	0.252	0.600	-0.310	0.183	0.330	<i>0.698</i>	0.228
K									1	0.566	0.397	-0.320	-0.220	- 0.791	-0.540	-0.338	0.136	-0.247
Fe										1	-0.250	-0.550	-0.640	-0.680	-0.080	-0.399	0.521	-0.652
Mn											1	0.062	-0.190	-0.300	-0.520	-0.362	-0.300	-0.083
Cu												1	<i>0.975</i>	0.195	0.349	0.657	0.308	0.339
Pb													1	-0.080	0.360	0.971	0.513	-0.980
Zn														1	0.605	-0.133	-0.240	-0.153
Ni															1	0.434	0.312	0.224
Cr																1	<i>0.607</i>	<i>0.677</i>
Cd																	1	0.524
As																		1

Bold correlation is significant at the 0.05 level (2-tailed). Italic correlation is significant at the 0.01 level (2-tailed).

Table 4 | Factor loading for selected physico-chemical parameters in shallow groundwater

Parameters	Factor-1	Factor-2	Factor-3	Factor-4	Factor-5
pH	0.879	-0.277	0.073	0.283	0.163
EC	-0.331	0.872	0.157	0.096	-0.056
TDS	-0.347	0.852	0.196	0.122	-0.021
SO ₄	-0.342	0.642	-0.372	0.39	-0.01
NO ₃	-0.148	0.846	-0.114	-0.085	0.27
Cl	-0.239	0.857	-0.168	0.316	-0.108
HCO ₃	-0.538	0.544	0.506	0.29	-0.141
Ca	-0.527	0.189	-0.34	0.044	-0.715
Mg	-0.54	0.286	0.617	0.285	-0.025
Na	-0.039	-0.204	0.939	-0.014	-0.05
K	-0.164	0.504	-0.052	0.429	0.539
Fe	0.903	-0.154	-0.086	0.11	-0.188
Mn	-0.231	0.034	-0.301	0.07	0.762
Cu	0.948	-0.185	-0.018	0.05	-0.12
Pb	0.846	-0.292	-0.065	-0.093	0.005
Zn	0.886	-0.15	-0.088	-0.025	-0.174
Ni	-0.105	-0.096	-0.004	-0.936	0.026
Cr	0.242	0.647	0.37	0.082	-0.142
Cd	-0.282	-0.266	-0.182	-0.866	-0.196
As	0.838	-0.118	0.21	0.197	0.309
Eigen value	6.207	4.812	2.523	2.416	1.756
% of Variance	31.033	24.058	12.613	12.078	8.779
Cumulative %	31.033	55.092	67.705	79.782	88.561

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

Values of dominant parameters in each factor are reported in bold.

hence indicating A geogenic source. Factor-4 contributed 12.07%, while factor-5 contributed 8.779% with high loading on Mn ($r = 0.762$), which could be due to the mafic rocks. Table 5 summarizes the PCA results for deep groundwater samples, having a total variance of 95.292% for five factors. Factor-1 contributed 26.433% to the total variance with high loading found on EC ($r = 0.823$), TDS ($r = 0.818$), HCO₃ ($r = 0.847$), K ($r = 0.977$), and Fe ($r = 0.977$). The EC, TDS, HCO₃, K, and Fe could be due to the leaching from felsic, mafic and carbonate rocks, present in the northern parts of the district, suggesting geogenic sources. Factor-2 contributed 20.835% to the total variance with high loading on Mg ($r = 0.920$), Cu ($r = 0.932$), and Pb ($r = 0.953$). This could again be attributed to the geogenic source. Factor-3

Table 5 | Factor loading for selected physico-chemical parameters in deep groundwater

Parameters	Factor-1	Factor-2	Factor-3	Factor-4	Factor-5
pH	0.011	0.346	0.915	-0.15	0.089
EC	0.823	-0.417	0.256	0.017	-0.221
TDS	0.818	-0.421	0.253	-0.02	-0.238
SO ₄	0.576	-0.377	0.593	-0.205	-0.353
NO ₃	0.356	0.071	-0.139	0.852	0.327
Cl	0.168	-0.483	0.786	0.305	-0.101
HCO ₃	0.847	-0.234	-0.185	0.061	0.102
Ca	-0.156	-0.401	-0.835	0.067	-0.258
Mg	-0.092	0.92	0.143	0.212	0.213
Na	0.327	0.446	0.287	0.203	0.737
K	0.977	0.047	-0.015	-0.121	-0.042
Fe	0.756	-0.03	-0.513	0.383	0.13
Mn	0.411	0.189	0.129	-0.376	-0.771
Cu	-0.307	0.932	0.155	0.108	-0.022
Pb	-0.157	0.953	0.096	0.188	0.102
Zn	-0.735	-0.021	-0.181	-0.243	0.25
Ni	-0.362	0.22	0.091	-0.07	0.864
Cr	-0.2	0.335	0.125	0.876	-0.183
Cd	0.208	0.265	0.342	0.739	0.437
As	-0.16	0.1	0.914	0.324	0.019
Eigen value	5.287	4.167	4.113	2.811	2.681
% of Variance	26.433	20.835	20.565	14.054	13.406
Cumulative %	26.433	47.267	67.832	81.886	95.292

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

Values of dominant parameters in each factor are reported in bold.

contributed 20.565% to total variance with high loading on pH ($r = 0.915$), Cl ($r = 0.786$), and As ($r = 0.914$). Factor-4 contributed 14.054% with high loading on Cr ($r = 0.876$) and Cd ($r = 0.739$). The presence of mafic rocks could be the reason for Cr and Cd in factor-4. Factor-5 contributed 13.046% with high loading on Na ($r = 0.737$) and Ni ($r = 0.864$). This unnatural grouping of Na and Ni in factor-5 indicates their contribution by anthropogenic inputs.

CONCLUSIONS

This study concluded that a majority of the physico-chemical parameters were found within the drinking water guidelines

and maximum contaminant levels (MCL) of WHO and US EPA. However, elevated concentrations of HMs (Fe, Cu, and Pb) in some parts of Mardan District are significant from a health point of view, especially regarding women's health. The PCA results in both the shallow and deep groundwater suggest that the rocks exposed in the northern parts of the Mardan District and agriculture play a major role in the contribution of physico-chemical parameters in the aquifer system of the area. The study revealed that shallow drinking water has higher contamination than deep water. Therefore, this study suggests that deep groundwater should be encouraged for drinking purposes in the district.

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