Elevated levels of arsenic and trace metals in drinking water of Tehsil Mailsi, Punjab, Pakistan

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ABSTRACT

Trace metal contamination in drinking water poses severe threat to human health through long-term exposure. The present study highlighted the elevated arsenic (As) and trace metal concentrations in drinking water and associated potential health risk to local residents of Tehsil Mailsi (Punjab), Pakistan. Our results showed that concentrations of As, Cd, Fe, Cr and Pb exceeded the WHO limits in drinking water, whereas Cu, Mn, Co, Ni and Zn concentrations were below the safe limits. The calculated estimated daily intake (EDI) of metals from local drinking water had the order of Zn > As > Cu > Pb > Cd > Ni > Mn > Cr, and the consequent target hazard quotient (THQ) above 1 was observed for As and Cd, which employed high potential health risk to local residents. Spatial distribution of As and trace metals in drinking water were related to the local anthropogenic sources, due to intensive application of agrochemicals. The study area presents high potential health risk associated with As and trace metals pollution in drinking water. The local wells have never been tested for metal concentrations prior to use, and necessary processes should be taken to test the wells with respect to As and trace metals contamination.

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1. Introduction

Trace metal pollution in water is one of the serious concerns worldwide due to their persistence, accumulation, and ecological toxicity in the aqueous environment (Yu et al., 2008; Qiao et al., 2013). Trace metals are present in various environmental compartments in broad concentrations ranging from ultra-trace (μg/L) to higher levels (mg/L), sometimes as a result of increasing anthropogenic inputs, thereby entering into soil and groundwater. The anthropogenic sources of trace metals include industrial waste discharges (Muhammad et al., 2010) and extensive use of agro-chemicals (Abbas et al., 2014). Other than anthropogenic sources, natural occurrences of trace metals as a result of chemical weathering of bed rocks and minerals also produce metal pollution in water (Khan et al., 2008; Krishna et al., 2009). Multivariate statistical analyses such as cluster analysis (CA), inter-metals correlation and principal component analysis (PCA) are usually helpful for source discrimination of trace metals in water (Wunderkind et al., 2001; Muhammad et al., 2011). Therefore, the demand has been increased

to study the drinking water quality with respect to trace metal distribution, source, and exposure to health risk of trace metals.

It has been evidently reported that As consumption from drinking water has affected about 150 million people worldwide (Ravenscroft 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 et al., 2002). Additionally, >25 nations of the world are facing problem of As and trace metal pollution. These nations include China, India, Pakistan, Sri Lanka, Ghana, Ivory Coast, Senegal, Algeria, Kenya, Uganda, Tanzania, Ethiopia, Mexico and Argentina (Ravenscroft et al., 2009; Rahman et al., 2009; Smedley et al., 2002).

In Pakistan, As affected areas include Jamshoro, Sindh (Baig et al., 2009b), Manchar lake, Sindh (Arain et al., 2008, 2009), Lahore and Kasur, Punjab (Farooqi et al., 2007a), Muzaffargarh, Punjab (Nickson et al., 2005), D.G. Khan, Punjab (Malana and Khosa, 2011) and Tharparkar, Sindh (Brahman et al., 2013). In 2004, >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, trace 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), Nagar Parkar (Sindh) (Naseem et al., 2010), and Tharparkar (Sindh) (Brahman et al., 2013).

Moreover, Pakistan Council for Research in Water Resources (PCRWR) has declared six cities as the most affected areas of Punjab with respect to elevated levels of trace metals, 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 sharing the similar topography and geology. So far, little is known about anthropogenic or geochemical distribution of trace metals in local drinking water and associated health risk in Tehsil Mailsi. The anthropogenic contribution of trace metals has been resulted from extensive use of fertilizers, sewerage system, drainage system, solid waste management, and landfills/dumping sites (Abbas et al., 2014; Shah et al., 2010), whereas the geochemical contribution of metals is related to weathering and erosion of mafic and ultramafic rocks (Shah et al., 2010; Kavcar et al., 2009), which are affecting water quality of Tehsil Mailsi. Hence, the present study was designed to investigate As and trace metal distribution in drinking water of Tehsil Mailsi and consequent assessment of sources in regard of their potential health risks.

2. Materials and methods

2.1. Study area

Tehsil Mailsi (72°17′–72°19′E, 29°78′–29°92′N) is located in Southern Punjab, with an area of 1639 km² and a population of about 0.71 million (Fig. 1). The average annual precipitation is 243 mm and the mean temperature is 26 °C (DCR, 1998). Farming is the basic occupation of population with major cash crops including cotton, wheat, sugarcane, maize and rice. Mailsi is situated along river Sutlej, however, this river is dry in most part of the year and facing shortage of good quality drinking water. Additionally, groundwater accessed by either electric or hand pumps is the major source of drinking water in the study area.

The regional hydrology of Punjab including Mailsi has been described previously (Greenman et al., 1967). The aquifer of the study area is under alluvial plains with >340 m thick layer of Holocene and Pleistocene sediments transported by the River Sutlej (Greenman et al., 1967), originating from southern slopes of Kailash mountains near the lake of Mansarovarand, which 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 deposits and Aeolian deposits of Pleistocene to present age. Calcium carbonate concretions of irregular shape, but of regular size and distribution are associated with these sediments (Farooq et al., 2007). The study area towards southwestern part of Bari Doab (area between the two rivers, Sutlej and Chenab) contains relatively older alluvial deposits, which tend to coincide with zones of highly mineralized groundwater (Greenman et al., 1967). The geologic features influencing the permeability and transmissibility of water are lateral lithological changes, disparity in sand thickness, and grain size distribution (Farooq et al., 2007). The older Quaternary (i.e., Pleistocene) deposits are more widely distributed in the western sedimentary basin, thereby promoting more aerobic aquifer conditions in the study area over other locations (Mahmood et al., 1998; Tasneem, 1999).

2.2. Sampling and analysis

Two sites (Mailsi and Sargana) were selected for water sampling (Fig. 1). Sampling was conducted in December 2013 following the standard procedures of Khan et al. (2012). Initially, survey was conducted about the health hazards associated with drinking water, which revealed 14% hepatitis, 29% stomach pain, 20% kidney pain, 18% typhoid, 7% lung cancer, 9% liver cancer and 3% other common diseases in local
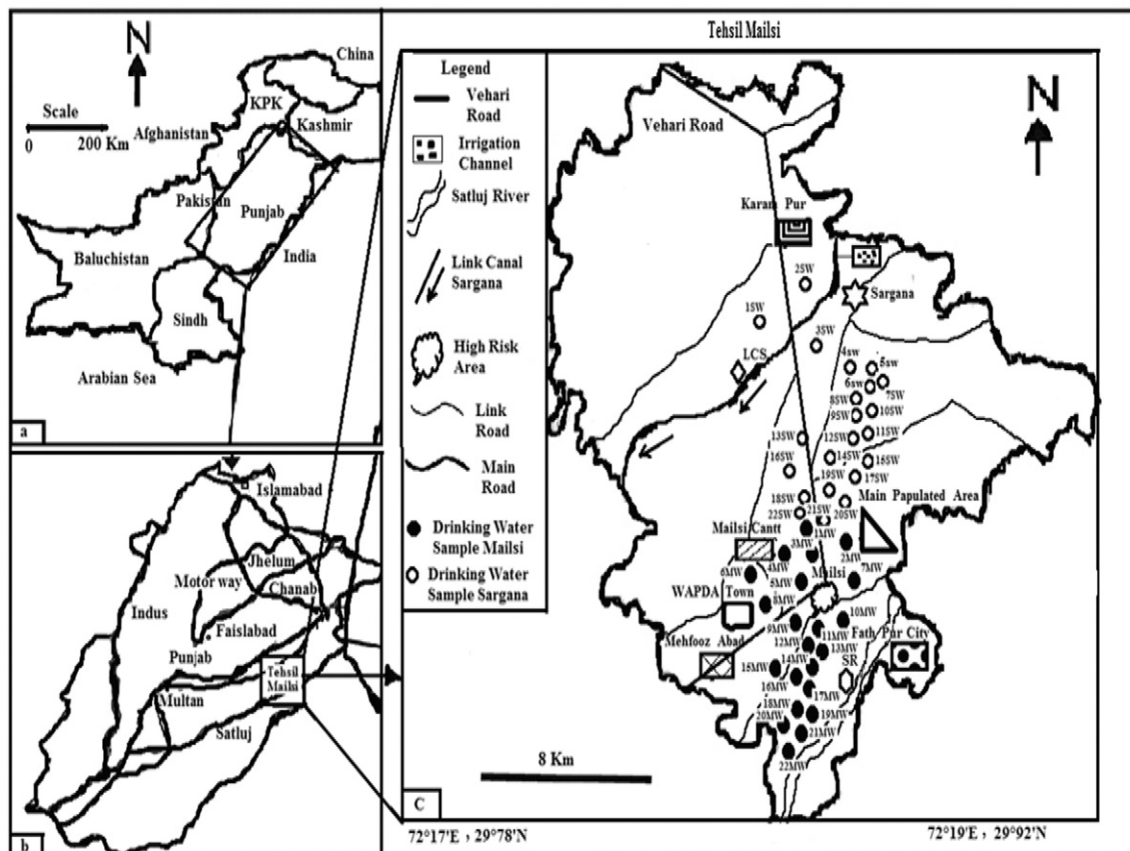

Fig. 1. Location maps showing the sampling points of drinking water from Sargana and Mailsi sites.

residents. A total of 44 household water samples from hand pumps and electric pumps used for drinking purposes were collected at the depth of 75 to 120 ft. Water of hand pumps and electric pumps was allowed to run for 2 to 5 min before collection. Half of the water samples (22) were collected from site Mailsi city, whereas the others from Sargana site of Mailsi. Each water sample of both sites was collected from different locations.

All the water samples for geochemical analysis were filtered on sites using Millipore Sterivex syringe capsules containing 0.45 μm cellulose acetate filters. Two filtered sub-samples were sealed in pre-cleaned 60 mL Nalgene1 bottles, one for anion analysis and the other for cations (preserved with 10% ultra-pure HNO_3 to acidify the sample pH to 2.0). For validation of results, duplicate sample was collected at every 10th site of sampling. The temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) and dissolved oxygen (DO) in drinking water samples were also recorded. The latitudes and longitudes were recorded via global positioning system (GPS) at the time of sample collection. The pH, EC, and TDS in all water samples were determined by pH/EC meter (W2015, Sinowell Company, Shanghai, China). The DO meter was also used for the determination of DO in all water samples. All the instruments were calibrated with standard solutions before measurements. All the samples were sealed with screw caps and stored at 4 °C for further analysis. Calcium and magnesium were analyzed by volumetric titration with ethylene diamine tetra acetic acid (EDTA, 0.05 N) and alkalinity (Sultana et al., 2014). Anions including nitrates (NO_3^-) and sulphate (SO_4^{2-}) were determined spectro-photometrically using UV/VIS-Spectrophotometer (Shimadzu model UV 1601, Shanghai, China) at a wavelength of 220 nm. Chloride (Cl^-) was determined by titration method (APHA, 1998). As and other trace metals were determined using Atomic Absorption Spectrophotometer (Spectra AA 220 FS, Varian, New Jersey, USA). Quality control of metal determination was assessed with standard references, blank and duplicate samples, and reproducibility of the analytical data was within 5% and the analytical error was estimated to ≤10%. The charge balance of total cations and anions (meq L^{-1}) is secure to be 2.4%, and the ion balance was better than ± 5%.

2.3. Approaches for assessing human health risk

The estimated daily intake (EDI) of metal through water ingestion was calculated with the following equation:

$$EDI = C_m \times D_w / B_w \qquad (1)$$

where, C_m means concentration of metal (μg/L) in water, D_w is the daily average intake of water (L/d, assumed to be 2 L/d for adult and 1 L/d for child) (US-EPA, 2011), and B_w is the body average weights (kg, assumed to be 72 kg for adult and 32.7 kg for child), respectively (Muhammad et al., 2011; Rasool et al., 2015a, b).

The THQ for non-carcinogenic health risk was calculated with the following equation:

$$THQ = EDI / RfD \qquad (2)$$

where the oral toxicity reference dose (RfD) values for Cd, Cr, Cu, Mn, Ni, Pb, As and Zn are 5.0E−01, 1.5E + 03, 3.7E + 01, 1.4E + 02, 2.0E + 01, 3.6E + 01, 3.0E−01 and 3.0E + 02 μg/kg·d, respectively (Shah et al., 2012; Rasool et al., 2015a, b). The THQ value less than one is considered safe for consumers (Khan et al., 2008).

2.4. Statistical analyses and graphical tools

All the calculations were obtained 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. Major ion chemistry of groundwater samples were determined by Gibbs diagrams (Gibbs, 1970). Arc Geographic Information System software version 10 was used to mapping metal concentration distribution.

3. Results

3.1. Major ion chemistry

Physical and chemical properties were determined in order to check the drinking water quality (Table 1). The pH was slightly alkaline in the range of 7.31 to 8.1 and 6.8 to 8.2 in Sargana and Mailsi city, respectively. The mean pH values were higher in groundwater samples of Mailsi than those of Sargana site, however, remained in the WHO permissible limits (6.5–8.5). Dissolved oxygen (DO) values ranged from 6.8 to 8.2 and 6.7 to 8.3 mg/L, respectively. The EC values ranged from 0.85 to 2.80 and 0.78 to 2.45 mS/cm in Sargana and Mailsi city, respectively (Table 1). A total of 41% samples exceeded the WHO permissible limits (1.5 mS/cm) for EC. Total dissolved solids (TDS) ranged from 578 to 1910, and 524 to 1653 mg/L in Sargana and Mailsi city, respectively. Major ions like calcium (Ca^{2+}) concentration ranged from 82.6 to 353.5 mg/L in Sargana site, while 61.4 to 401.6 mg/L in site Mailsi. Sodium (Na^+) concentration ranged from 250.5 to 430.5 and 177 to 634.5 mg/L in water samples of sites Sargana and Mailsi, respectively. Overall, 98% of the samples from both sites exceeded the WHO permissible limit of 200 mg/L for Na^+ and 89% exceeded the WHO permissible limit of 100 mg/L for Ca^{2+}. Magnesium (Mg^{+2}) concentrations ranged from 34.7 to 85.9 mg/L in water samples of site Sargana, while 31.6 to 86.5 mg/L in water samples of site Mailsi. Our results revealed that 41% samples of drinking water of Mailsi and Sargana were lower, while 59% higher than permissible limits for Mg^{+2} according to WHO standard limits (50 mg/L). Potassium (K^+) ranged from 3.2 to 9.72 and 31.1 to 18.82 mg/L in water samples of Sargana and Mailsi city, respectively. Overall, K^+ concentrations were lower than the WHO permissible limits (12 mg/L) in studied area except sample 16 of Mailsi site where it approached to 18.82 mg/L.

Nitrate (NO_3^-) concentrations were high, as ranged from 8.9 to 53.2 and 10.1 to 54.5 mg/L in water samples of Sargana and Mailsi, respectively. Only samples 4(S) contain NO_3^- values below the WHO standard for drinking water (10 mg/L). Bicarbonates (HCO_3^-) concentration ranged from 25 to 1266 and 390 to 1169 mg/L in water samples of Sargana and Mailsi, respectively. The highest HCO_3^- concentrations (1266 mg/L) were observed in sample location 12 (SDW) of site Sargana. WHO maximum permissible limit for HCO_3^- in drinking water is 500 mg/L. In Sargana site, 95% of water samples crossed the WHO permissible limits (500 mg/L), while in Mailsi site 91% of the water samples crossed the WHO permissible limits (500 mg/L). Similarly, sulphate (SO_4^{2-}) concentrations ranged of 205.8 to 1053 and 238.7 to 1185 mg/L in water samples of sites Sargana and Mailsi, respectively. WHO maximum permissible limit for sulphate ions in drinking water is 250 mg/L. In both sites, 5% of water samples exhibited lower sulphate concentrations, while 95% of the water samples crossed the WHO permissible limits (250 mg/L). Cl^- concentrations ranged from 55.1 to 225.3 and 30.1 to 305.3 mg/L in water samples of Sargana and Mailsi, respectively. WHO permissible limit for chloride in water is 250 mg/L. In both sites, 5% drinking water samples exceed chloride concentrations, while 95% below WHO permissible limit. Although the groundwater geochemistry from Mailsi and Sargana did not show any considerable variation, concentrations of SO_4^{2-} and NO_3^- were slightly higher in samples from the urban site of Mailsi. Efforts were made to obtain a mechanistic relationship for hydro-geochemistry using Gibbs plot (Fig. 2).

3.2. As and trace metal concentrations in drinking water

The water analysis results of trace metals were listed in Table 2. In general, trace metal concentrations in Mailsi were significantly higher

Table 1
Concentrations of field parameters and major ions of drinking water in the Sargana and Mailsi study area.

Sample ID	Latitude	Longitude	Depth	pH	EC	TDS	DO	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	NO_3	HCO_3^-	SO_4^{2-}
SDW1	29.926	72.196	75	7.55	1.81	1231	7.3	122.2	48.7	429	7.25	70.1	13.2	1005	551
SDW2	29.926	72.197	78	7.31	1.53	1040	6.8	111.4	51.9	403.5	7.35	55.1	14.4	829	584
SDW3	29.926	72.196	82	7.45	0.97	660	7.4	122.9	44.4	382.5	9.72	85.1	13.8	849	379
SDW4	29.924	72.197	85	7.74	1.21	823	7.6	114.6	38.3	426	3.53	65.1	8.9	927	551
SDW5	29.923	72.197	65	7.59	1.06	721	7.5	315.5	67.8	402	3.34	110.1	52.7	771	889
SDW6	29.924	72.195	78	7.45	1.13	768	7.9	183.1	48.2	366	5.41	165.2	35.5	878	444
SDW7	29.925	72.194	100	7.58	1.05	707	8.1	348.8	85.9	412.5	3.83	105.1	32.4	752	1053
SDW8	29.925	72.195	90	7.61	1.92	1306	7.6	153.9	59.9	430.5	3.68	75.1	20.7	1074	206
SDW9	29.922	72.189	72	7.74	0.92	626	7.5	104.9	40.7	402	4.04	65.1	53.2	576	642
SDW10	29.922	72.191	65	7.92	1.8	605	7.7	82.6	39.2	408	4.32	70.1	30.7	713	272
SDW11	29.926	72.188	80	8.1	0.85	578	7.8	199.9	51.2	250.5	5.56	75.1	25.6	517	1012
SDW12	29.926	72.188	85	7.62	2.8	1910	7.3	138.9	41.5	426	3.61	90.1	27.5	1266	198
SDW13	29.924	72.178	110	7.48	2.43	1652	7.6	284.2	75.2	286.5	4.01	175.2	15.2	732	1029
SDW14	29.924	72.177	90	7.7	2.56	1741	7.4	286.7	74.7	385.5	3.39	60.1	14.5	1210	1004
SDW15	29.922	72.171	102	7.51	2.38	1618	8.2	236.2	64.1	250.5	5.67	70.1	40.3	1064	700
SDW16	29.922	72.17	78	7.74	1.27	864	7.9	138.9	34.7	424.5	4.96	85.1	17.8	683	247
SDW17	29.922	72.171	78	7.3	1.99	1353	8.1	206.7	55.7	423	5.73	170.2	28.6	1220	815
SDW18	29.92	72.172	84	7.5	0.99	673	7.6	218.2	59.4	280.5	5.53	225.2	40.8	537	337
SDW19	29.917	72.172	75	7.47	1.4	952	7.9	353.5	85.7	409.5	8.66	210.2	48.7	878	1012
SDW20	29.909	72.174	80	7.56	1.09	741	7.6	176.6	55.1	388.5	6.17	175.2	15.2	752	280
SDW21	29.747	72.153	115	7.66	0.98	667	7.8	132.5	44.9	337.5	4.11	65.1	39.5	25	708
SDW22	29.748	72.154	77	7.8	1.87	1285	7.5	144.1	50.1	261	3.2	75.1	32.4	791	675
MDW1	29.749	72.155	85	7.61	1.08	734	8	401.6	78.6	420	6.32	170.2	52.6	966	1185
MDW2	29.758	72.154	80	7.89	1.85	1258	7.8	85.8	37.8	411	10.01	125.1	18.9	1103	313
MDW3	29.761	72.155	75	7.9	1.9	1292	8.1	108.2	42.2	424.5	6.02	110.1	38.7	1169	444
MDW4	29.769	72.155	88	8.2	1.64	1115	7.6	202.9	56.9	331.5	4.06	75.1	28	585	840
MDW5	29.769	72.156	75	7.29	0.93	632	7.9	183.7	54.6	417	3.99	225.2	13.9	771	749
MDW6	29.776	72.154	78	7.5	1.01	687	7.7	158.7	53.8	418.5	3.76	50.1	10.1	722	1004
MDW7	29.781	72.155	80	7.9	1.21	823	7.4	81.3	39.1	403.5	3.12	110.1	30.4	722	395
MDW8	29.781	72.155	115	7.45	0.87	571	7.8	318.7	80.9	634.5	3.86	125.1	54.5	653	774
MDW9	29.786	72.157	90	7.86	0.98	666	7.3	161.3	48.8	400.5	6.11	305.3	18.7	546	436
MDW10	29.787	72.157	95	7.6	1.13	768	6.7	74.9	39.1	435	5.14	40.1	14.4	819	337
MDW11	29.797	72.167	75	7.17	2.01	1367	7.8	366.4	86.5	394.5	4.35	210.2	24.2	732	996
MDW12	29.798	72.167	90	7.81	2.22	1299	7.4	269.4	72.1	402	3.34	100.1	13.1	683	971
MDW13	29.812	72.164	102	7.4	1.91	1170	6.9	235.5	61.5	408	3.63	130.1	18.4	703	1177
MDW14	29.813	72.164	84	7.54	1.61	1095	8.2	61.4	31.6	445.5	3.68	45.1	44.3	683	239
MDW15	29.812	72.161	120	7.3	1.39	945	7.8	127.4	46.6	177	3.87	30.1	11.7	390	255
MDW16	29.818	72.151	85	7	0.87	592	7.6	195.8	53.6	346.5	18.82	205.2	44.8	634	914
MDW17	29.847	72.106	78	7.44	1.67	528	8.1	165.1	57.6	249	3.067	80.1	32.4	1044	412
MDW18	29.875	72.081	85	6.8	2.45	1653	7.6	167.7	50.8	444	3.57	270.3	12.8	829	469
MDW19	29.923	72.189	90	7.12	1.85	1258	7.9	180.5	58.1	424.5	6.41	160.2	10.5	439	996
MDW20	29.922	72.191	75	7.92	1.79	1217	8.3	135.1	45.8	451.5	4.23	70.1	14.4	654	247
MDW21	29.786	72.157	95	6.82	1.72	598	6.8	120.3	45.5	399	3.61	120.2	17.7	664	741
MDW22	29.797	72.167	100	7.74	0.78	524	7.5	114.6	41.2	372	4.31	60.1	22.9	517	239
WHO (mg/L)				6.5–8	1.5	1000		100	50	200	12	250	10	500	250

The abbreviations give the different types of water samples as follows: SDW, drinking water from Sargana and MDW, drinking water from Mailsi. All the values are expressed in mg/L^{-1} except EC in (mS/cm) and depth (feet). n = Number of samples.
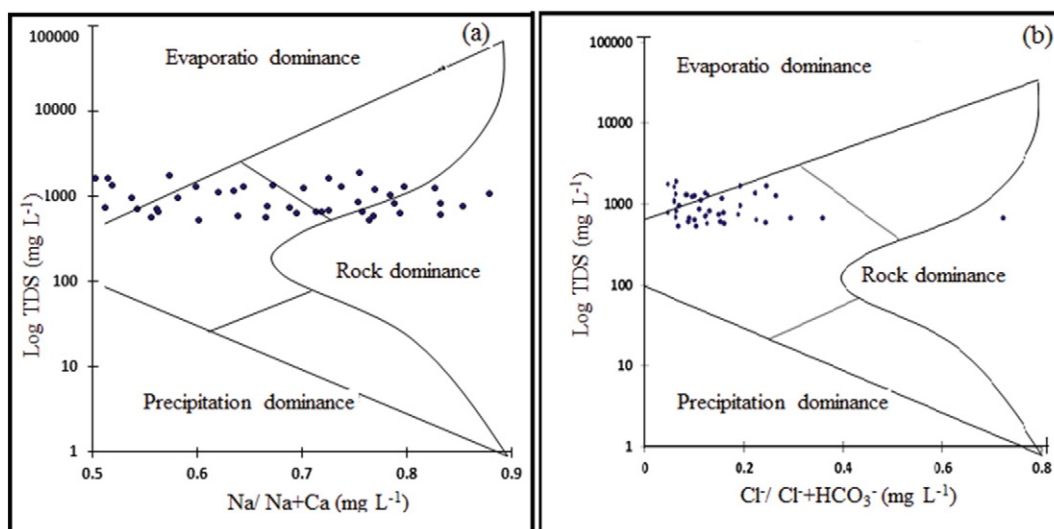

Fig. 2. Major ion chemistry of groundwater exhibiting (a) evaporation dominance and rock interactions for $Na^+/Na^+ + Ca^{2+}$ salts, and (b) only evaporation dominance for $Cl^-/Cl^- + HCO_3^-$. n = 44.

Table 2
Concentration (μg/L) of trace metals in drinking water $n = 44$.

Samples ID	Latitude	Longitude	Depth	Fe	Mn	Co	Cu	Zn	Cr	Ni	Pb	Cd	As
SDW1	29.926	72.196	75	1047	63	0.9	21	195	33	45	150	49	123
SDW2	29.926	72.197	78	1592	14	1.1	13	150	51	49	200	58	32
SDW3	29.926	72.196	82	1840	13	0	20	918	50	97	110	61	88
SDW4	29.924	72.197	85	712	10	0.1	139	11	43	33	70	58	18
SDW5	29.923	72.197	65	1988	89	0.4	3.6	1813	28	34	120	57	62
SDW6	29.924	72.195	78	1591	15	0.7	3.9	1063	40	12	90	101	33
SDW7	29.925	72.194	100	2515	12	0.6	125	972	51	71	100	76	31
SDW8	29.925	72.195	90	1534	7	0	33	21	52	25	50	63	543
SDW9	29.922	72.189	72	2834	11	0.1	3.6	1445	51	37	160	85	61
SDW10	29.922	72.191	65	1121	5	0	12	1223	61	49	110	110	670
SDW11	29.926	72.188	80	889	2	0	3.7	426	51	38	60	89	14
SDW12	29.926	72.188	85	2245	3	0.2	3	1129	53	32	160	85	270
SDW13	29.924	72.178	110	1506	8	0.1	3	582	40	28	70	86	34
SDW14	29.924	72.177	90	2072	7	0.8	256	1794	53	42	180	48	762
SDW15	29.922	72.171	102	1928	10	0.5	178	961	54	49	90	74	271
SDW16	29.922	72.17	78	2918	61	0	198	73	52	73	30	92	14
SDW17	29.922	72.171	78	1918	15	0.6	45	855	50	23	210	74	642
SDW18	29.92	72.172	84	835	68	0.4	2.9	14	56	33	40	68	62
SDW19	29.917	72.172	75	1716	13	0	3	865	30	31	130	58	121
SDW20	29.909	72.174	80	1884	14	0.7	3.9	359	52	59	100	102	32
SDW21	29.747	72.153	115	2121	6	0.1	39	1374	59	17	90	103	21
SDW22	29.748	72.154	77	1178	7.9	0.2	1.6	103	52	21	70	68	274
MDW1	29.749	72.155	85	2110	11	1.5	23	786	64	39	230	111	19
MDW2	29.758	72.154	80	776	45	0.2	24	262	51	35	140	106	272
MDW3	29.761	72.155	75	46	2	0.2	39	21	50	13	90	64	122
MDW4	29.769	72.155	88	1350	3.8	0	23	46	38	40	40	89	33
MDW5	29.769	72.156	75	1989	10	0	5	1466	56	11	100	56	86
MDW6	29.776	72.154	78	1970	81	0.7	41	25	49	23	70	53	63
MDW7	29.781	72.155	80	253	29	0	23	377	51	50	10	80	34
MDW8	29.7812	72.155	115	513	11	1.4	22	2325	52	18	90	106	32
MDW9	29.786	72.157	90	563	7.5	0	123	1313	54	49	40	67	115
MDW10	29.787	72.157	95	469	6.7	0	24	72	55	12	100	34	87
MDW11	29.797	72.167	75	3255	21	0	84	1090	51	14	120	89	172
MDW12	29.798	72.167	90	1988	10	0.4	84	1813	52	33	130	58	812
MDW13	29.812	72.164	102	1349	11	0	6	3661	43	95	60	90	22
MDW14	29.813	72.164	84	184	9	0	5	143	51	31	80	46	31
MDW15	29.812	72.161	120	231	1	0	273	65	20	71	130	60	12
MDW16	29.818	72.151	85	55	10	0.8	28	56	51	23	100	80	33
MDW17	29.847	72.106	78	935	6	0.2	49	26	14	87	110	52	538
MDW18	29.875	72.081	85	2520	13.9	0.1	73	91	26	26	120	59	268
MDW19	29.923	72.189	90	1440	21	0.7	24	49	50	58	50	50	12
MDW20	29.922	72.191	75	1920	18	0.2	53	1188	13	24	100	105	750
MDW21	29.786	72.157	95	74	16	0.9	43	4877	53	11	90	63	340
MDW22	29.797	72.167	100	1509	7	0.4	52	1431	51	28	160	64	63
WHO				300	400	10	2000	3000	50	70	10	3	10

The abbreviations give the different types of water samples as follows: SDW, drinking water from Sargana and MDW, drinking water from Mailsi. n = Number of samples.

as compared to the Sargana site. Chromium (Cr) concentrations were 28–61 and 13–64 μg/L in Sargana and Mailsi, respectively. A total of 73% samples exceeded the WHO permissible limit at 50 μg/L. Lead (Pb) ranged at 30–200 and 10–230 μg/L in Sargana and Mailsi, respectively, and all the samples exceeded the WHO limit of 10 μg/L. Ni ranged at 12–97 and 11–95 μg/L in Sargana and Mailsi, respectively (Table 2), and about 14% samples exceeded WHO permissible limit (70 μg/L). Similarly, Cd ranged from 48 to 110 and 34 to 111 μg/L in Sargana and Mailsi, respectively, exceeding the WHO limit 3 μg/L (Table 2). Fe^{2+} ranged from 712 to 2918 and 46 to 3255 μg/L in Sargana and Mailsi, respectively. Total 86% samples exceeded the WHO permissible limit of 300 μg/L for Fe^{2+}. As concentrations ranged from 14 to 762 and 12 to 812 μg/L in Sargana and Mailsi, respectively (Table 2). All the water samples of both sites exceeded the WHO permissible limit of 10 μg/L. The observed concentrations of other trace metals like Co, Cu, Zn and Mn (Table 2) in local groundwater were all in the WHO safe limits.

The spatial distribution patterns of As and trace metals (Cd, Cr, Pb, Fe^{2+} and Ni) in local drinking water of Tehsil Mailsi using contour maps have been presented in Fig. S1. The spatial distribution of higher concentrations of As were mainly compared between the northwest and the southeast sections, and similar pattern was observed for Pb (Fig. S1). Moreover, a significant positive correlation between Pb and

As was observed (Table 5). Cd and Cr showed similar spatial distribution pattern (Fig. S1) and belonged to first group in the hierarchical clustering analysis (Fig. S2).

3.3. Correlations for the interrelationship of measured ions and trace metals

The correlation matrix of As and trace metals and physiochemical parameters drinking water samples were listed in Table 5. The correlation matrix showed that numerous parameters had significant positive correlations with each other such as TDS-EC ($r = 0.99$), Ca^{2+}-Mg^{2+} ($r = 0.95$), Ca^{2+}-SO_4^{2-} ($r = 0.73$), Mg^{2+}-SO_4^{2-} ($r = 0.72$), HCO_3^--As ($r = 0.54$). Furthermore, the co-relationship of trace metals and physico-chemical parameters were supported by dendrogram of CA in drinking water of both sites (Fig. S2).

The clustering procedure generated three groups of sites, as the sites in these groups have similar characteristic features and same source of contamination as well as their range of correlation coefficient (Table 5). The group (G1) includes DO, pH, K^+, EC, Mn, Cr, Ni, Cu, Cd, Co, Mg^{2+} and NO_3^-, whereas the second group (G2) includes Pb, As, Na^+, Ca^{2+} and Cl^-. Third group (G3) includes Fe^{2+}, Zn, TDS, HCO_3^-, TH and SO_4^{2-} (Fig. S2). In order to assess the enrichment of trace metal contamination and other major ions in drinking water samples, scores plots

were also drawn between factors; F1 and F2 (Fig. S3). The scores plots obtained from drinking water samples analyses showed the dominancy of trace metals and other water quality parameters like major ions. The right side quadrants either upper or lower revealed that groundwater samples of both sites; Sargana and Mailsi city were highly enriched with trace metal contamination as well as the major ions. Sample distribution in the left quadrants either upper or lower was enriched with Ni (Fig. S3).

3.4. Daily intake of metals and human health risk assessment

The local residents cannot afford processed water, instead they use hand-pump, electric pump and tube well water for drinking and cooking purposes. Therefore, these available sources of drinking water in studied area were analyzed for the potential health risk assessment through exposure assessment and risk assessment. The estimated daily intake (EDI) values of selected for trace metals have been presented in Table 3. Our results indicated that in both sites; Sargana and Mailsi, where people consumed drinking water contaminated with heavy metals, EDI values ranged from 0.78 to 1.69 and 0.36 to 1.78 μg/kg·d for Cr. The EDI for Cu ranged from 0.04 to 7.1 and 0.14 to 7.6 μg/kg·d in water samples of Sargana and Mailsi. Similarly, the people in Sargana and Mailsi had EDI values ranged from 0.07 to 2.5 and 0.03 to 2.26, 0.83 to 5.56 and 0.28 to 6.39 μg/kg·d for Mn and Pb, respectively. In Sargana and Mailsi area, the calculated EDI values for the people that consumed drinking water contaminated with heavy metals ranged from 0.31 to 50.4 and 0.58 to 135.5, 0.33 to 2.7 and 0.31 to 2.64, 1.33 to 3.1 and 0.94 to 3.1, 0.38 to 21.2 and 0.31 to 22.56 μg/kg·d for Zn, Ni, Cd and As, respectively.

The target hazard quotient (THQ) indices were also calculated to assess health risk in the study area. In Sargana and Mailsi locations, THQ index for Cd and Cr in drinking water was ranged from $3.00E+02$ to $6.00E+02$ and $2.00E+02$ to $6.00E+02$, $5.00E-02$ to $1.10E-03$ and $2.40E-02$ to $1.20E-03$, respectively (Table 4). In both sites; Sargana and Mailsi, the THQ index value for Cu in people were ranged $0.01E-01$ to $1.90E-01$ and $0.04E-01$ to $2.10E-01$, respectively. The trace metals contaminated drinking water showed that THQ index values for Mn, Pb and Zn were $0.05E-02$ to $1.80E-02$ and $0.02E-02$ to $1.6E-02$, $0.23E-01$ to $1.50E-01$ and $0.08E-01$ to $1.80E-01$, $0.1E-02$ to $17E-02$ and $0.19E-02$ to $45E-02$, respectively. Similarly, in Sargana and Mailsi, the drinking water THQ index values for Ni and As ranged from $0.17E-01$ to $1.40E-01$ and $0.15E-01$ to $1.30E-01$, $0.13E+01$ to $7.10E+01$ and $1.00E+02$ to $7.50E+01$, respectively. The drinking water quality (EDI) indices for trace metals in the study area were found in the following order; Zn > As > Cu > Pb > Cd > Ni > Mn > Cr. Similarly, THQ of the selected heavy metals were found in the order of Cr < Zn < Mn < Ni < Pb < Cu < As < Cd through the consumption of drinking water in both sites; Sargana and Mailsi city.

Table 3
Estimated daily intake (EDI) of trace metals in μg/kg day^{-1} though drinking water consumption in studied area.

Metals	Statistics	Sargana	Mailsi
		Drinking water ($n = 22$)	Drinking water ($n = 22$)
Cr	Range (Mean)	0.78–1.69 (1.34)	0.36–1.78 (1.25)
Cu	Range (Mean)	0.04–7.1 (1.4)	0.14–7.6 (1.42)
Mn	Range (Mean)	0.07–2.5 (0.58)	0.03–2.26 (0.44)
Pb	Range (Mean)	0.83–5.56 (3.1)	0.28–6.39 (2.7)
Zn	Range (Mean)	0.31–50.4 (20.6)	0.58–135.5 (26.8)
Ni	Range (Mean)	0.33–2.7 (1.13)	0.31–2.64 (0.99)
Cd	Range (Mean)	1.33–3.1 (2.1)	0.94–3.1 (1.1)
As	Range (Mean)	0.38–21.2 (4.6)	0.31–22.56 (4.1)

4. Discussion

4.1. Overall groundwater quality and geochemistry

The pH of water is considered as one of the most significant water quality parameters in aquatic system, hence, high pH range is responsible for bitter taste of water. In the current study, pH values of drinking water samples were in the order of Mailsi > Sargana. Alkaline pH of water in the study area was due to the presence of HCO_3^-, a weathering product of carbonaceous rocks (Breit and Wanty, 1991; Lopez Pazos et al., 2010). Relatively higher values of dissolved oxygen in water samples were might be due to the cumulative effect of higher wind velocity coupled with rainfall and mixing with freshwater, which is rich in DO (Mahananda, 2010). Similar to pH, EC of the water is considered as an important parameter for determining the water quality of different aquifers (Roscoe, 1990). In the current study, higher EC values were resulted due to the presence of higher contents of dissolved salts in water (Abdullah and Musta, 1999). High TDS in ground water were probably attributed to wastewaters from residential and dyeing units, which are discharged into the pits, ponds and lagoons (Shyamala et al., 2008). Majority of the water samples were not fit for drinking purpose, as TDS values crossed the WHO limits (values1000 mg/L), which is harmful for drinking purpose (WHO, 1993). Variation in EC and TDS values of water from site Mailsi was attributed to the fact that wells located near the Sutlej river are recharged by the river resulting in low EC, while wells away from the river are least recharged. There is increasing evidence that EC of water increases in response to residence time and more rock water interaction (Abbas et al., 2014).

Higher sodium and calcium levels in groundwater were mainly because of the fact that infiltration of surface water contaminated by soluble salts of soils, which were resulted either through irrigation or precipitation. Drinking water pollution by sewage effluent can also cause high level sodium and calcium (Abbas et al., 2014; Ashraf and Foolad, 2007). Conversely, higher concentrations of Na^+ and Ca^{2+} in water samples were resulted due to the fact that weathering of silicate minerals releases Ca^{2+} and Na^+, which possibly accumulates these ions in groundwater through water rock interactions (Singh et al., 1999; Ramkumar et al., 2010). Lower K^+ concentrations as compared to the Na^+ are due to the fact that K^+ tends to be fixed onto the surface of clay minerals and rate of disintegration of K^+ is low as compared to the Na^+ minerals (Geleijnse et al., 2003). High concentrations of Mg^{2+} were resulted due to penetration of leachate from landfills, household or industrial sites (Abbas et al., 2014; Kahlown et al., 2006).

Higher NO_3^- concentrations in water samples were mainly achieved due to higher sewage discharges, animal excreta, decay of dead plants, feces and agricultural activities (Ahmed et al., 2004; Kahlown et al., 2006). In studied area, urea, DAP and numerous other fertilizers and pesticides are broadly applied on various cash crops including cotton, wheat, rice, maize and sugar − cane, which are contaminating the soil and water sources. According to FAO (2004), fertilizer consumption in Pakistan has been increased over the last 30 years and Punjab Province has shared the largest part due to its abundant agricultural area. There are two possibilities for higher SO_4^{2-} and Cl^- in water samples from the urban site of Mailsi. First, anthropogenic activities like sewage, municipal seepage and other biowaste contributed in groundwater contamination. Secondly, this might be resulted that Mailsi is located at lower altitude where water flows from North to South − West, thereby loading higher concentrations of SO_4^{2-} and Cl^- in groundwater. Overload of SO_4^{2-} imparts unacceptable taste and may be laxative and corrosive when combined with Na^+ or Mg^{2+} (Ashraf and Foolad, 2007). Anthropogenic sources like municipal seepage and use of detergents have been reported for sulphates contamination in groundwater (Pawar and Shaikh, 1995). Drinking water samples had higher HCO_3^- concentrations, possibly due to the result of local inputs from fertilizers and domestic waste materials. Due to increased rate of population, agricultural and domestic wastes have been increased considerably in

Table 4
Target hazard quotient (THQ) indices of trace metals through drinking water consumption of study area.

Metals	Statistics	Sargana	Mailsi
		Drinking water ($n = 22$)	Drinking water ($n = 22$)
Cr	Range (Mean)	$5.00E-02 - 1.10E-03 \ (8.90E-02)$	$2.40E-02 - 1.20E-03 \ (8.30E-02)$
Cu	Range (Mean)	$0.01E-01 - 1.90E-01 \ (0.380E-01)$	$0.04E-01 - 2.10E-01 \ (0.380E-01)$
Mn	Range (Mean)	$0.05E-02 - 1.80E-02 \ (4.10E-01)$	$0.02E-02 - 1.60E-02 \ (3.10E-01)$
Pb	Range (Mean)	$0.23E-01 - 1.50E-01 \ (0.860E-01)$	$0.08E-01 - 1.80E-01 \ (0.75E-01)$
Zn	Range (Mean)	$0.1E-02 - 17E-02 \ (6.90E-02)$	$1.90E-01 - 4.50E-03 \ (8.90E-02)$
Ni	Range (Mean)	$0.17E-01 - 1.40E-01 \ (0.6E-01)$	$0.2E-01 - 1.30E-01 \ (0.49E-01)$
As	Range (Mean)	$0.13E+01 - 7.10E+01 \ (1.50E+01)$	$1.00E+02 - 7.50E+01 \ (1.40E+01)$
Cd	Range (Mean)	$3.00E+02 - 6.00E+02 \ (4.20E+02)$	$2.00E+02 - 6.00E+02 \ (2.20E+02)$

studied area. Higher HCO_3^- in waters has been resulted due to weathering of carbonaceous rocks (Ahmed et al., 2004).

High Na^+, Ca^{2+} and HCO_3^- concentrations also make the water unacceptable for drinking purposes. The functional sources of dissolved ions can be assessed by plotting the samples, according to the variation in the ratio of Na/(Na + K) and Cl/(Cl + HCO3) as a function of TDS (Gibbs, 1970). The Gibbs plot of data from the study area (Fig. 2) indicated the interaction between rock chemistry and chemistry of percolation waters under subsurface. These plots suggested that the local groundwater quality is influenced more by weathering and least by evaporation. This suggests that concentrations of major ions Na^+, Ca^{2+}, Mg^{2+} in water increases 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).

4.2. Distribution of As and trace metals

Spatial distribution of trace metal is a useful indicator to evaluate the possible sources of enrichment as well as to identify different zones containing either lower or higher concentrations of metals (Li et al., 2012). In the current study, spatial distribution of higher concentrations of As was mainly cramped in the northwest and the southeast sections (Fig. S1). Moreover, similar pattern was observed for Pb, which was positively correlated with As ($r = 0.29$). Cd and Cr showed similar spatial distribution pattern and belonged to first group in the hierarchical clustering analysis (Fig. S2). These patches represented that higher concentrations of Cr and Cd are mainly distributed through the inflow of Sutlej River to the northeast zones of studied area, as both the sites exceeded the limits of coefficients of variation by 40%. Similar to Cd and Cr, distribution of higher concentrations of Fe^{2+} and Ni^{2+} were achieved through the inflow of Sutlej River, which was further distributed from north to south. Overall, results of the current study showed that As concentrations were higher than the other trace metals in regions near to Sutlej River as compared to the areas located far from it. This similar pattern was also observed in previous study of district Muzaffargarh and Multan (Nickson et al., 2005).

Additionally, major sources of Pb, Cd, Ni, Cr, Fe and As in local drinking water were associated with intensive application of agro-chemicals in the study area, which may influence As and trace metals concentrations at different depths. This practice is common, because farmers use fertilizers and pesticides to enhance crop yield. On the other hand, leachable As concentrations in fertilizer samples were found to be 7–10 mg/kg (Farooq et al., 2007) as fertilizer use has increased in Punjab province from 156.7 kg/ha in 2005–2006 to 185.5 kg/ha in 2009–2010 (NFDC, 2016). This is evident from the literature that high concentrations of metals as a result of extensive use of agro–chemicals pesticides and fertilizers may contaminate groundwater and affect human health (Singh, 2011). Hence, anthropogenic sources like use of agro–chemicals were also causing health problems associated with groundwater contamination. Our results are well supported by other studies where As and trace metals contamination in drinking water were posing severe health risk to all life forms (Muhammad et al., 2010, 2011; Shah et al., 2012; Khan et al., 2013).

4.3. 4.3. Source discrimination of arsenic and trace metals

Multivariate analysis was performed to discriminate the distinct groups of physico–chemical parameters as well as to identify the natural and anthropogenic sources for trace metal contamination. Analysis of the correlation matrix showed that As with physicochemical parameters had similar sources of contamination, such as agricultural activities, industrial activities, landfills, and household wastes (Khan et al., 2013). Cluster analysis (CA) has been proved to be effective tool for the identification of heavy metals sources and physico–chemical parameters (Mico et al., 2006; Muhammad et al., 2011). The main anthropogenic activities that may release As and trace metals into the environment include fossil fuel processing and combustion, wood preserving, pesticide production and application, and disposal and incineration of municipal and industrial wastes (Popovic et al., 2001 and Prosun et al., 2002). The use of As containing pesticides like lead arsenate $[Pb_3(AsO_4)_2]$, calcium arsenate $[Ca_3(AsO_4)_2]$, magnesium arsenate $[Mg_3(AsO_4)_2]$, zinc arsenate $[Zn_3(AsO_4)_2]$, zinc arsenite $[Zn(AsO_2)_2]$, and Paris green $[Cu(CH_3CCOO)_2 \ Cu(AsO_2)_2]$, is considered as a nonpoint anthropogenic source of As (Martin et al., 2000). Although data of pesticides used in the study area is not known from the literature, As prevalence was likely due to intensive use of pesticides especially for cotton crop. Moreover, As-rich water samples were collected from shallow groundwater, which was likely to be happened due to leaching process of pesticides and fertilizers from soils to groundwater (Sharma, 2006).

An explorative hierarchical CA was performed on the normalized data set of physico–chemical parameters and heavy metal concentrations by mean of the Ward's method, using squared Euclidean distances as a measure of similarity. CA method is an informal classification procedure that involves measuring either the distance or the similarity between the objects to be clustered (Singh et al., 2004; Chen et al., 2007). First group of DO, pH, K^+, EC, Mn, Cr, Ni, Cu, Cd, Co, Mg^{2+} and NO_3^- suggested that all these parameters are from the same source, mainly resulted from agricultural activities, industrial activities and weathering of mafic and ultramafic rocks (Shah et al., 2010). As we have discussed above that either anthropogenic sources (agriculture activities) or rock water interactions with inflow of Sutlej River were associated with groundwater contamination. On the other hand, some studies discussed that evaporation enrichment was possible mechanism for trace metal contamination (Bhattacharya et al., 2006; Nickson et al., 2005). This is fact that evaporation is not a major mechanism responsible for groundwater contamination, as soluble salts and metals come on to the soil surface when water is evaporated. However, soil surface accumulated metals and other ions can be dissolved in water under rainfall conditions, but this effect is more common in humid or high rainfall regions. As present study area falls in semi–arid region of the country, groundwater contamination was resulted from sources other than evaporation enrichment.

Table 5
Correlation matrix of trace metals and physic−chemical parameters in drinking water (n = 44). Highlighted values indicate significance at P ≤ 0.05 levels.

Pmt	pH	EC	TDS	DO	Ca²⁺	Mg²⁺	HCO₃	Cl⁻	SO₄	NO₃⁻	Na⁺	K⁺	Co	Cu	Mn	Cr	Fe²⁺	Pb	Zn	Ni	Cd	As
pH	1																					
EC	−.05	1																				
TDS	−0.06	**0.99**	1																			
DO	0.14	0.01	0.04	1																		
Ca²⁺	−0.16	0.13	0.11	**0.23**	1																	
Mg²⁺	**−0.21**	0.17	0.16	0.16	**0.95**	1																
HCO₃	0.01	**0.48**	**0.49**	0.05	0.08	0.09	1															
Cl⁻	**−0.39**	0.01	0.01	0.07	0.4	0.34	−0.02	1														
SO₄	−0.19	0.08	0.05	0.01	**0.73**	**0.72**	−0.08	0.21	1													
NO₃⁻	0.09	−0.27	−0.26	0.34	0.34	0.24	−0.03	0.08	0.16	1												
Na⁺	−0.07	0.01	−0.01	−0.08	0.05	0.05	0.19	0.12	0.01	0.06	1											
K⁺	**−0.21**	−0.16	−0.15	0.01	−0.01	−0.04	0.05	**0.28**	0.06	0.13	0.21	1										
Co	**−0.31**	**−0.94**	−0.1	−0.04	0.35	0.36	0.16	0.04	**0.33**	0.19	−0.03	0.21	1									
Cu	−0.01	0.21	0.21	0.15	0.09	0.08	0.04	−0.2	−0.04	**−0.29**	**0.29**	0.03	−0.04	1								
Mn	−0.03	−0.13	−0.13	−0.03	0.05	−0.01	−0.01	0.03	0.02	0.01	**−0.23**	−0.03	0.16	−0.1	1							
Cr	0.25	−0.02	−0.03	−0.19	0.09	−0.02	−0.06	−0.1	0.11	−0.01	0.12	−0.1	0.05	−0.2	0.01	1						
Fe²⁺	−0.06	0.26	0.26	0.18	**0.41**	**0.35**	0.07	0.09	0.25	−0.04	0.09	**−0.2**	−0.02	0.11	0.15	0.16	1					
Pb	−0.19	0.18	0.18	−0.03	0.15	0.16	**0.39**	−0.1	0.09	0.08	0.1	0.15	**0.43**	0.04	−0.1	0.04	**0.29**	1				
Zn	**−0.21**	−0.07	−0.11	**−0.34**	0.23	0.21	−0.12	−0.2	**0.31**	0.08	0.12	−0.2	0.19	0	−0.1	0.13	0.05	0.01	1			
Ni	0.12	−0.14	−0.14	−0.04	−0.13	−0.11	0.001	0.07	−0.25	−0.17	0.24	0.1	−0.08	**0.33**	0.05	0.01	0.06	0.01	**−0.31**	1		
Cd	0.28	−0.1	−0.1	0.27	0.18	0.06	−0.16	0.13	0.02	**0.31**	**−0.31**	0.08	0.1	−0.2	−0.1	**−0.6**	0.21	−0.1	0.17	−0.1	1	
As	−0.04	**0.36**	**0.34**	0.12	−0.05	0.04	0.27	−0.2	−0.18	−0.25	−0.15	−0.22	−0.09	**0.41**	−0.21	−0.3	0.03	**0.29**	0.12	0.1	0.09	1

Bold correlation is significant at the P ≤ 0.05 level.
n = Number of samples Pmt = Parameters.

The metals of Cd and Ni have similar source, mainly from combustion and agricultural activities. The elevated Cd in drinking water could be achieved from phosphate fertilizers, sewage sludge, weathering of mafic and ultramafic rocks (Fleischer et al., 1974; Shah et al., 2010). Anthropogenic sources for Ni include the production of automobiles, batteries, coins, jewelry, surgical implants, kitchen appliances, sinks and utensils (Astor, 2005). This high Cr concentration in drinking water samples was probably due to local geochemistry of the study area, as influenced by weathering of mafic and ultramafic rocks, manure, fertilizer, and industrial (Shah et al., 2000; Strachan, 2010). The second group of Pb, As, Na⁺, Ca²⁺ and Cl⁻, possibly originated from parent rock material, agricultural and human activity. The raised Pb levels in the drinking water samples could be resulted from weathering/leaching of mafic and ultramafic rocks, use of agricultural insecticides and transportation (Clement et al., 2000; Nafees et al., 2009; Shah et al., 2010). Higher As level suggested that weathering of local mafic and ultramafic rocks, coal combustion, traffic activity, acid rain, pesticide use, fertilizer, and erosion of arseno-pyrite greatly influenced their releases (Nickson et al., 2005; Khan et al., 2012).

Third group of ions like Fe²⁺, Zn, TDS, HCO₃⁻, TH and SO₄²⁻ had similar sources like fertilizers, pesticides, sewerage waste and weathering of parent rock material. High SO₄²⁻ concentrations may be derived from leaching of chemical fertilizer, household waste and animals manure (Kahlown et al., 2006). HCO₃⁻ salts are added to water sources from weathering of carbonaceous rocks (Ahmed et al., 2004). Sources of higher Fe²⁺ concentrations in drinking water are Fe − sulfide bearing sedimentary rocks, municipal and industrial sewage (Mico et al., 2006; Nguyen et al., 2009; Bai et al., 2010).

4.4. The release of As in groundwater: oxidative dissolution versus evaporative enrichment mechanism

Natural enrichment of As in groundwater can be attained by several mechanisms (Welch et al., 2000), which include oxidative and reductive dissolution (McArthur et al., 2001; Nickson et al., 1998), hydrothermal volcanism, oxidation of arsenical sulfide minerals (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 to increasing pH (Robertson, 1989; Smedley et al., 2005), and finally evaporative enrichment (Nicolli et al., 1989; Welch et al., 2000). Last mechanism might pose a threat of As to groundwater of areas where natural evaporation over the long periods has produced solute concentrations in shallow groundwater or return irrigation flow affects the irrigation's source itself (Welch et al., 2000). This has also been reported that sorption of As onto the surface of soils has modifying effects on evaporative concentrations of metals (Jones et al., 2009) and aquifer sediments under toxic conditions (Nimick, 1998).

A large number of aquifers in various parts of the world have problem of As contamination (50 mg/L). Such affected aquifers have been identified in some parts of Argentina, Chile, Mexico, USA, Hungary, Romania, Bangladesh, India, Nepal, Burma, Cambodia, Pakistan, China and Vietnam (Robertson, 1989; Smedley et al., 2002). In arid conditions, silicate and carbonate weathering occurs considerably, which results in the enhancement of evaporative dominance of As along with high pH values (Caceres et al., 1992; Smedley et al., 2002).

In order to understand the possible mechanism for groundwater As release in the study area, a comparison chart has been presented in the light of earlier studies where different mechanisms have been suggested (Nickson et al., 2005; Farooq et al., 2007; Halim et al., 2009). The Fig. 3 highlights possible mechanism prevailing for the release of As in groundwater in the study area (Fig. 3). A study by Halim et al. (2009) reported reductive dissolution mechanism for the enrichment of As in groundwater on the basis of following indicators; high pH, NO₃⁻ and SO₄²⁻. On the other hand, oxidative dissolution mechanism has been suggested when high concentrations of HCO₃⁻ (>500 mg/L) and SO₄²⁻ (>250 mg/L) and pH (>7.5) occurred in groundwater
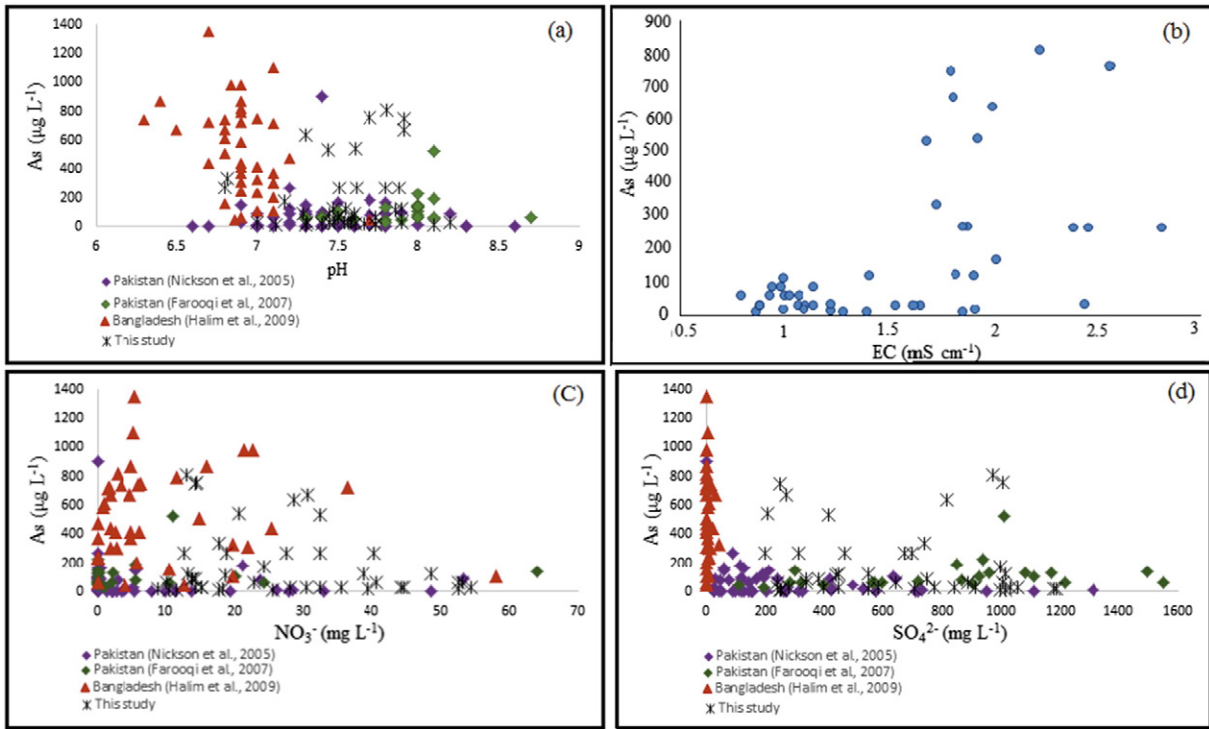
Fig. 3. Mechanism controlling the As release in studied area is related to (a) pH, (b) EC, (c) NO_3^-, and (d) SO_4^{2-}. Comparisons have also been made with earlier studies for better description of mechanism. $n = 44$.

(Smedley and Kinniburgh, 2002). In the present study, higher concentrations of HCO_3^-, SO_4^{2-}, 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).

In the present study, high Cl^- in some samples and high Na^+ concentrations are the indicators of high evaporation rates. This is consistent with dendrogram (Fig. S2), as Na^+, Cl^- and As are in the same group. The ground waters from the basins are greatly affected by evaporative concentrations and resulting in high TDS values (Fujii and Swain, 1995). Likewise, high EC is also related with high As concentrations in the study area (Fig. 3). This could be inferred from our results that As is released by oxidative dissolution under the influence of high alkaline water and high pH (Fig. 3) and to some extent by high evaporation rates.

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 heavy 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 been infrequently 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.

4.5. Human health risk assessment

There are several exposure pathways, which are mainly dependent on contaminated sources of air, water, soil, food and consuming population (Caussy et al., 2003). Among these pathways, exposure of human beings to contaminated water is one of the key pathways of heavy metals (Muchuweti et al., 2006). In drinking water, high EDI values of As, Zn, Cd, Cu, Ni and Pb may be attributed to the Pb—Zn sulfide mineralization, domestic sewage and agricultural practices such as fertilization and use of fungicides, while that of Cr and Ni may be resulted from the mafic and ultramafic bed rocks hosting chromites deposits (Shah et al., 2000). Moreover, most of the Zn, Mn, Cu estimated daily intake exceeded the respective toxicity reference dose (RfD) values, while that of Cr, Pb, Ni, As and Cd were within their respective RfD limits set by United States Environmental Protection Agency (US-EPA, 2005).

The human risk assessments of As and Cd obtainable THQ values exhibited adverse health risk in human beings (Table 4). The calculated THQ indices through consumption of trace metal contaminations in drinking water suggested high risk in local population of the study area (Khan et al., 2008). However, THQ indices of Cr, As, Pb and Cd metals were higher than those reported in drinking water by Kavcar et al. (2009). This study demonstrated that the THQ values in this study were not within safe limits (THQ <1), suggesting for potential health risk in this region. Similarly, Zn and Cu exhibited near unity, reflecting that they could have harmful effects on human health (Ikeda et al., 2000). Likewise, THQ for Cr, Zn, Pb and As were higher in this study compared to studies (Muhammad et al., 2011; Shah et al., 2012). Hence, the major contributors to carcinogenic health risk were As and Cd in drinking water of both sites.

The present study is important in terms of health perspectives indicating the health risk exposure of human beings to heavy metals consumption through drinking water. About 85% people in Mailsi area are using groundwater for drinking and household purposes, therefore, considered at high risk due to trace metals pollution of water. Only 15% people of the Mailsi area showed a medium risk when compared with the US EPA approach (US-EPA, 1999). These results indicate that

sampling sites have high levels of As, Cr, Pb and Cd in groundwater, which is not safe for drinking and other domestic uses.

5. 5. Conclusions

Drinking water of Mailsi and Sargana sites of Punjab province are severely polluted with Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^- and NO_3^-. Basic ion chemistry of groundwater was mainly influenced by evaporative enrichment of salts as well rock-water interactions. Trace metals like Cd, Cr, Pb, Fe and As concentrations exceeded the WHO permissible limits and exhibited THQ value >1, while Cu, Mn, Co and Zn concentrations were within their limits. Since As and Cd were related with each other, oxidative dissolution along with the evaporative enrichment were responsible for trace metal pollution in ground water. Moreover, CA results revealed that anthropogenic sources pronounced trace metal's contamination in ground water of both Sargana and Mailsi. Our results suggest that water from contaminated locations of Mailsi is not safe for drinking without proper treatment. Hence, drinking water quality tests and continuous assessment should be conducted at regular intervals to check the quality of drinking water.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2016.07.013.

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