



Toxicological & Environmental Chemistry

ISSN: 0277-2248 (Print) 1029-0486 (Online) Journal homepage: http://www.tandfonline.com/loi/gtec20

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To cite this article: Sadia Bibi, Abida Farooqi, Mehwish Ramzan & Asif Javed (2015) Health risk of arsenic in the alluvial aquifers of Lahore and Raiwind, Punjab Province, Pakistan: an investigation for safer well water, Toxicological & Environmental Chemistry, 97:7, 888-907, DOI: 10.1080/02772248.2015.1066175

To link to this article: https://doi.org/10.1080/02772248.2015.1066175



Published online: 25 Jul 2015.

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Health risk of arsenic in the alluvial aquifers of Lahore and Raiwind, Punjab Province, Pakistan: an investigation for safer well water

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(Received 16 June 2015; accepted 18 June 2015)

Environmental pollution has generated release of high amounts of arsenic (As) which ultimately are detected in the water of Indus Basin Punjab, Pakistan. The area is characterized by a semiarid climate, and alluvial deposits. This investigation, an extension of previously reported As-affected area in Lahore and Kasur, aimed to (1) assess the extent of water contamination in this area and (2) determine possible safer sites for future water use. In a comparative study, total As contamination of underground water from individual dwellings and community water supply of some villages located at the boundary of the Sheikhopura and Lahore districts, Pakistan were measured to compare with previously published data of villages located at the boundary of the Lahore and Kasur districts. The results showed variable levels of As in shallow drinking water wells and average concentration exceeding WHO guidelines value. As levels ranged from below 5.2 to 80 µg/L and mean 45.5 µg/L. The As concentrations were higher than WHO limits but lower than previous studied area. In addition, high salinity was found to be a serious concern for deteriorating groundwater quality rendering it unsuitable for drinking. Groundwater is predominantly of the $Na-HCO_3$ type with slightly alkaline pH. High pH values and competition of As with HCO3 may serve as an important process for mobilization of As in the shallow groundwater of the region. Continuous monitoring and expansion of monitoring systems are necessary to establish safer wells within As-contaminated areas.

Keywords: arsenic; groundwater; risk assessment; safer wells; continuous monitoring; blanket testing

Introduction

The quality of groundwater depends on various chemical constituents and their concentrations, which are mostly derived from geological data of the particular region. It is estimated that approximately one-third of the World's population use groundwater for drinking (Dalal-Clayton, and Sadler 2005). The widespread switch from microbiologically unsafe surface water to microbiologically unsafe groundwater has led to unanticipated poisoning of large numbers of individuals in the developing world who have consumed various toxic trace elements. Arsenic (As) is a naturally occurring contaminant in ground water found largely as the result of minerals associated with previous volcanic activity dissolving from weathered rocks, ash and soils (Bernstam and Nriagu 20000). However, the presence of As can also be attributed to anthropogenic activities, including the use of herbicides. As is classified as one of the most toxic and carcinogenic chemical elements (Bernstam and Nriagu

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2000; Abernathy, Thomas, and Calderon 2003; Safiuddin and Karim 2001; Welch et al. 1999). In drinking water, it predominantly occurs as inorganic (As^{3+} and As^{5+}) and organic forms (methyl and dimethyl As compounds) (Kazi et al. 2009b; Smedley and Kinniburgh 2002). The major metabolic pathway for inorganic As in humans is methylation (Hughes 2002). The enzymatic conversion of inorganic As to mono- and dimethylated species was considered a major mechanism for detoxification of inorganic As. However, compelling experimental evidence obtained from several labs suggests that biomethylation, particularly production of methylated metabolites that contain trivalent As, is a process that activates this metal as a toxin and carcinogen.

Underdeveloped countries have been suffering from water contamination due to disordered industrial growth. In many parts of the world, groundwater is contaminated with As (Chowdhury et al. 2000; Mandal and Suzuki 2002). As is recognized as carcinogenic (class A), producing skin, lungs, and bladder cancer and these effects are primarily due to the consumption of As contaminated drinking waters (Tsai, Wang, and Ko 1998; Arain et al. 2009; Tokar et al. 2010). The World Health Organization (WHO) and United State Environmental Protection Agency (USEPA) revised the maximal contaminant level of As in drinking water as10 mg/L (World Health Organization 1996; Rice 2004). Highly As-contaminated (450 mg/L) groundwater was reported in various parts of the world (Gunduz, Simsek, and Hasozbek 2010; Mukherjee and Bhattacharya 2001; O'Reilly et al. 2010; Rahman and Hasegawa 2011). Similar to other South Asian countries, in Pakistan researchers and Agencies Pakistan Council of Research in Water Resources (PCRWR) and UNICEF noted the level of As >100 mg/L in ground water (Ahmed Baig et al. 2010; Brahman et al. 2013; Farooqi, Masuda, and Firdous 2007a). High As concentrations in various parts of the country and physiochemical processes that control the heterogeneous As distribution in groundwater were reported (Kolachi et al. 2011; Muhammad et al. 2013; Sultana, Farooqi, and Ali 2013). The recommended permissible limit for As in drinking water is 50 µg/L by Pakistan Environmental Protection Agency.

The present study is a series study and study area is the extended area from alreadyreported area from Lahore and Kasur (Farooqi, Masuda, and Firdous 2007a; Farooqi et al. 2007b). Objectives of the present study were to (1) determine the distribution of As in groundwater samples collected from the districts of Lahore and Sheikhopura, Pakistan and compare it with previously published data of the Lahore and Kasur districts, (2) investigate the mutual relationship of As with different physiochemical parameters, (3) determine carcinogenic and non-carcinogenic risks among the populations exposed to As through groundwater drinking pathways, and (4) examine safer wells within the highly contaminated area to use as alternative source of water.

Materials and methods

Description of study area

In the present study sampling was conducted in villages located at the boundary of Lahore and Sheikhopura adjacent to the previously reported As-contaminated area at the boundary of Lahore and Kasur (Farooqi, Masuda, and Firdous 2007a) (Figure 1). The Punjab Province occupies part of the Indus Plain, located on a fluvial plain made up of sediments derived from the Ravi and Satluj Rivers, as well as Pleistocene Aeolian terrace deposits. The surface soils consist mainly of permeable, organic-poor Aeolian sediment on the terraces and layers of sand and silt on the alluvial flood plain. The alluvial sediments occasionally reach several thousand feet in thickness (Farooqi, Masuda, and Firdous 2007a).

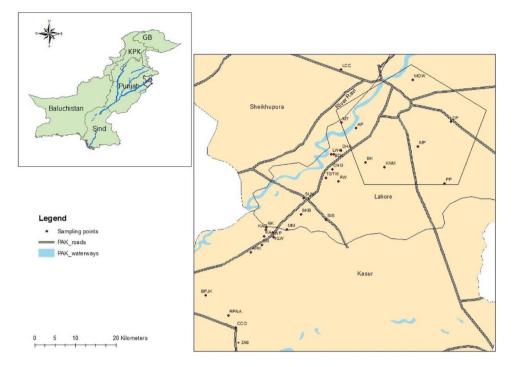


Figure 1. Study area; area in pentagon shows the present study area.

The Lahore and Sheikhopura districts are drained by the Ravi and Satluj Rivers, which flow into Pakistan from India (Figure 1). Groundwater is an important water source in the study area: 80% of the village water supply is obtained via hand pumps installed by private households in areas of shallow groundwater. Individuals in this area mostly rely on groundwater for drinking and irrigation as well as livestock purpose. The underground water is available at the depth of 10-12 m. The socioeconomic condition of people is poor and health and other necessities for life are limited.

Sample collection

Sixty-two (62) groundwater samples were collected from the study area from individual dwellings and community water supply in February 2012. Geographical coordinates were taken at each sampling site with a handheld GARMIN[®]GPS 12TM and then plotted in a map (Figure 1). Information about the depth was obtained from the owner. The groundwater sampling was carried out according to the Standard Methods (Directive 1998). Sampling was conducted based upon the accessibilities to tube wells and respondent claims of tube well after 5-10 min of flushing in order to remove any standing water from the tube and to avoid the addition of suspended solids from the pipe and to ensure a representative sample of the borehole. Samples were filtered using 0.45 μ m filters and water samples were collected in two replicates from each site: one for the cation and As analysis and was acidified with 0.1 ml ultra-pure 14 M HNO₃ ([®]Merck). Other sample was non-acidified for the anion analysis. The collected water samples were kept in well stopper polyethylene plastic bottles previously soaked in 10% nitric acid for 24 hr and

rinsed with ultrapure water (Gong et al. 2002). Prior to collection for total As analysis, each bottle was rinsed 2-3 times with the subsequent water sample to minimize potential elemental contamination from the bottle during storage. During field sampling, all of the collected water samples were kept in an ice box and then transferred to a refrigerator where they were stored at 4 °C for processing and analysis (Kazi et al. 2009b). All glasswares were kept overnight in 5 M HNO₃, then rinsed with deionized water before use. All chemicals and reagents were of analytical grade, Merck (Darmstadt, Germany).

Analytical procedures

Different water-quality parameters, their units, abbreviations and methods of analysis are summarized in Table 1. Water temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and alkalinity using thermometer, pH and conductivity meter, respectively, were measured in field (Kazi et al. 2009a). Total hardness was measured by EDTA complexometric titration; the indicators were Erio-chrome Black T and Murexide at pH 10 and 12, respectively, with an analytical error <2 %. HCO₃⁻ ions concentration was determined by titration with 0.02 M HCl. The concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺ and Fe were determined by Flame Atomic Absorption Spectrophotometer (Varian).

Quality control

In order to prevent the precipitation of As and adsorption of other elements to container surfaces during field storage, samples were acidified with concentrated HNO_3 to reach 1% of acidic aliquot. Field portable instruments were calibrated daily, and calibration standards were applied before each reading. All equipment in contact with the water was washed three times with well water prior to the measurements. For quality control, field blanks, reagent blanks and spiked samples were prepared and analyzed.

Variables	Abbreviations	Units	Analytical methods
pН	pH	pH Unit	pH-meter
Electrical conductivity	EC	μS/cm	Conductivity meter
Turbidity	Turbidity	NTU	Conductivity meter
Total dissolved solids	TDS	mg/l	Conductivity meter
Alkalinity (as HCO ₃) (mg/l)	A-HCO ₃	mg/l	Conductivity meter
Total hardness (as CaCO ₃)	T- hardness (as CaCO ₃)	mg/l	Titrimetric
Calcium	Ca ²⁺	mg/l	FASS
Magnesium	Mg^{2+}	mg/l	FASS
Chloride	Cl ⁻	mg/l	Spectrophotometer
Sulphate	SO_4^{2-}	mg/l	Spectrophotometer
Nitrate	NO_3^-	mg/l	Spectrophotometer
Arsenic	As	μg/l	GFAAS
Sodium	Na ⁺	mg/l	AAS
Potassium	K ⁺	mg/l	AAS
Iron	Fe	mg/l	AAS

Table 1.	The water-quality parameters	associated wit	h their abbreviations,	units and analytical
method.				

Health risk assessment model

A health risk assessment model derived from the USEPA (Integrated Risk Information System (IRIS): As CASRN 7440-38-2, 1998) was applied to compute the non-carcinogenic and carcinogenic effects to individuals who consume groundwater as their drinking water source,

$$ADD = \frac{C \times IR \times EF \times ED}{AT \times BW},$$
(1)

where ADD is average daily dose from ingestion (mg kg⁻¹ d⁻¹); C is As concentration in ground water (mg L⁻¹); IR is water ingestion rate (L d⁻¹); EF is exposure frequency (d y⁻¹); ED is exposure duration (y); AT is average time/life expectancy (d); BW is body weight (kg). Thus, we have

$$HQ = \frac{ADD}{RFD},$$
 (2)

where HQ is hazard quotient (HQ) (toxic risk is considered occurring if HQ > 1.00); RfD is oral reference dose (RfD = 3×10^{-4} mg kg⁻¹d⁻¹); and

$$CR = 1 - \exp(-SF \times ADD), \qquad (3)$$

where SF is the slope factor, equal to 1.5 mg kg⁻¹ d⁻¹.

If HQ > 1 adverse non-carcinogenic effects of concern cancer risk

HQ < 1 acceptable level (no concern of cancer risk)

For the carcinogenic effect, calculated cancer risk used the following equation:

$$risk = CDI \times SF.$$
 (4)

If level is 10^{-6} , means the probable possibility that about 1 cancer patients among 1,000,000 people happen.

Statistical analysis

Multivariate statistical methods for classification, modeling and interpretation of large datasets from environmental monitoring programs allow the reduction of dimensionality of the data and extraction of information that will be helpful for water assessment (Sotiriou et al. 2003). Statistical data analyses were performed using SPSS for Windows (version 13.0) and XLSTAT (version 2014). As concentrations in groundwater, individual average daily dose (ADD) of metal, and risk indices in terms of HQ and cancer risk probability (*R*) were determined. The strength of inter-correlation between pH, EC, and total As and other parameters was measured by the Pearson correlation coefficients (r). The values below the limit of detection (LOD) were substituted by one-half of the respective LOD and used in the computations of mean, median and other statistical analyses. Data were considered significant at p < 0.05.

Results

Major chemical composition of groundwater

The minimum, maximum, mean and standard deviation values of each parameter are shown in Table 2(a), while for community water these values are given in Table 2(b). To evaluate the correlations between levels of variables, Pearson correlation coefficients (*r*) were calculated. Analysis of collected samples indicated that most of the variables were significantly from regulated standard values of WHO for drinking water. The water type identified in the study area is $Na^+-HCO_3^--SO_4^{2-}$ type (Figure 2).

The pH values fluctuated between 7 and 9 in groundwater samples, which were slightly above WHO-regulated values for drinking water. In general, high pH of the groundwater is produced by weathering reactions (silicate hydrolysis) and associated with increase in salinity (Smedley et al. 2002).

TDS and EC in all groundwater samples were in the range of 420-3675 mg/L and $561-4900 \ \mu\text{S/cm}$, respectively. The high values of EC were attributed to the high salinity and soluble electrolytes in underground water samples (Kazi et al. 2009b). The alkalinity was found in the range of 403-1610 mg/L, due to the presence of HCO_3^- . In groundwater, the concentrations of Ca^{2+} and Mg^{2+} were found in the range of 40-225 and 5-125 mg/L, respectively, which are higher than the previous study (Farooqi et al. 2007b). The range of SO_4^{2-} was 81-1390 mg/L, while Cl^- ranged from 43 to 618 mg/L. The NO_3^- were observed in the range of 3-87 mg/L. Na⁺, K⁺ and Fe were calculated in the range of 34-784 mg/L, 2-47 mg/L and 0-1 mg/L, respectively. The major chemical composition of the extended area is similar to previously reported findings, high SO_4^{2-} , NO_3^- and HCO_3^- except higher concentrations of Ca^{2+} and Mg^{2+} .

The physiochemical parameter's correlation matrices in groundwater are given in Table 3. In ground water, the correlation matrices show that various parameters displayed significant positive correlations such as $TDS-SO_4^{2-}(r = 0.96)$, $TDS-Cl^-(r = 0.96)$, $TDS-HCO_3^-(r = 0.880)$, $EC-Na^+(r = 0.93)$, $EC-SO_4^{2-}(r = 0.95)$, $EC-HCO_3^-(r = 0.880)$, $EC-Cl^-(r = 0.95)$, $HCO_3^--Cl^-(r = 0.74)$, $HCO_3^--SO_4^{2-}(r = 0.93)$, $HCO_3^--Na^+(r = 0.85)$, $Cl^--SO_4^{2-}(r = 0.86)$, $Cl^--Na^+(r = 0.90)$, $SO_4^{2-}-Na^+(r = 0.88)$.

Data indicated wide variations in the levels of all physical chemical parameters may be due to the complex geochemical involvement factors in studied areas. Other waterquality parameters of samples revealed that in some areas water was hard, consistent with the presence of high levels of sulfate and chloride (Table 2a). The EC and TDS are significantly correlated with Cl^- and SO_4^{2-} in groundwater samples, which might be the result of ion exchange in the aquifer (Kazi et al. 2009b). The groundwater is usually basic in nature with high EC due to elevated levels of TDS reflecting high mineral dissolution (Farooqi et al. 2007b).

Arsenic concentrations

Spatial distribution of arsenic in present and previous study: safer wells distribution

Table 4(a) summarizes As concentrations of the Lahore and Sheikhopura area districts, the present study and Table 4(b) presents As concentrations in drinking water of the Lahore and Kasur area districts. In the present study, As concentrations in the groundwater samples ranged widely from 5 to 80 μ g/L (Table 4(a)). In Patha Pind (n = 10 and c), water samples exceeded the WHO guideline of 10 and 50 μ g/L of National

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Table 2a. Physio-chemical water-quality parameters collected from the study area.

0.2 (EU) (mg/l) Ь 0.00.0 0.0 0.0 0.0 0.0 0.0 0.20.1 0.1 0.1 0.1 0.1 0.0 0.3 0.1 0.1 0.1 0.1 (mg/l) (mg/l) (mg/l) (mg/l) \mathbf{K}^+ 27.3 15.0 7.8 0.0 3.9 46.8 3.9 8.6 2.6 7.6 5.9 7.8 7.8 11.6 1.54.7 11.7 11.1 5.1 15.1 12 Na^+ 221.0 372.0 287.9 157.0 64.0232.0 143.0 382.0 19.5 261.3 403.0460.0 40.3 56.0 586.0 314.5 46.2 44.3 431.5 167.3 200 \mathbf{As} 10.0 30.0 80.0 8.9 50.4 32.0 37.5 2.4 35.9 37.5 15.9 28.3 3.0 75.0 1.4 4.0 25.0 5.0 5.2 33.5 10 NO_{3}^{-} 28.0 7.0 19.8 17.6 15.2 38.2 11.7 41.4 15.8 16.0 12.0 8.8 5.5 14.3 18.2 1.7 29.0 5.1 6.3 29.3 50 $\mathrm{SO_4}^{2-}$ (mg/l) 88.4 58.9 64.6 346.8 532.6 612.5 56.5 572.5 87.0 465.6 276.6 409.8 55.8 465.1 233.8 50.7 381.3 230.5 532.2 528.1 500 Mg²⁺ Cl⁻ S (mg/l) (98.8 59.8 16.323.5 53.3 163.9 46.6 87.3 06.5 127.8 10.7117.3 138.5 191.7 37.7 05.8 296.9 71.2 80.0 165.1 250 80.0 20.0 35.0 28.3 60.090.0 75.0 45.0 125.0 33.2 41.6 55.0 68.0 7.6 21.2 0.00 71.5 10.019.2 9.1 50 Ca ²⁺ , 84.0 55.0 70.0 30.0 25.022.2 95.0 00.00 220.0 76.4 53.3 70.0 42.4 00.00 90.0 25.0 28.060.055.2 45.5 100 hardness (as HCO₃) (CaCO₃) Total mg/l 75.0 250.0 47.2 125.5 10.0 260.0 56.6 68.0 05.0 240.0 69.3 181.7 130.0 220.0 63.6 75.0 70.0 270.0 32.5 99.5 100 as Alkalinity (mg/l) 610.0 711.2 536.8 64.0 646.6 463.6 915.0 225.9 683.2 805.2 939.4 94.9 872.3 402.6 134.6 248.5 584.4 915.0 695.4 06.1 (mg/l) 749.3 208.3 150.2 950.3 609.8 925.5 129.8 818.4 573.8 220.3 323.6 906.0 262.3 490.3 161.2 616.0 010.0 532.7 120.2 TDS 1000 376 **Furbidity** (NTU) 4.3 7.3 5.4 0.3 5.0 4.6 6.00.6 5.4 4.3 4.8 0.34.5 6.2 7.1 0.6 6.7 1.2 5.8 6.5 - 9Ηd 7.0 0.37.0 7.5 7.5 8.0 8.2 7.2 8.2 0.4 7.0 7.7 7.9 0.1 0.0 7.1 8.0 0.3 7.0 Temp ς) 25.0 25.5 25.4 25.4 25.5 25.5 25.4 25.5 25.4 25.6 25.6 25.5 25.5 0.1 0.10.1 25.8 0.10.1 25.7 (mS/cm) 1627.0 215.0 0.999 190.0813.0 173.0091.2 765.0 431.5 1683.0 1987.0 234.0 822.0 2680.0 710.2 493.7 611.0 0 - 2501267 ВC 208 835 Limits Sample VHO code Mean Mean Mean Mean Min Max Min Max Min Max Min Max Min Mean Max ß S SD SD ß KNM (n = 3)BDK (n = 2)MP (n = 10)PP (n = 10)CP (n = 5)

(continued)

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Table 2a. (Continued)

								Total hardness									
	Sample code	EC Temp (µS/cm) (°C)	Temp (°C)	Hq	Turbidity (NTU)	TDS (mg/l)	Alkalinity (as HCO ₃) (mg/l)	as (CaCO ₃) mg/l	Ca ²⁺	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	$\mathrm{SO_4}^{2-}$ (mg/l)	NO ₃ ⁻ (mg/l)	As (µg/l)	Na ⁺ (mg/l) (K ⁺ (mg/l)	Fe (mg/l)
BK $(n = 8)$	Min	1129.0	25.6	7.3	7.7	846.8		95.0	55.0	30.0	94.5	245.3	4.7	5.0	198.0	5.9	0.0
	Max	3310.0	25.8	8.0	9.9	2482.5		205.0	140.0	90.0	319.5	1013.4	23.5	75.0	634.0	27.3	0.1
	SD	727.9	0.1	0.2	0.8	545.9		40.1	32.6	19.4	75.0	290.9	6.4	21.6	152.0	7.8	0.0
	Mean	1927.1	25.7		8.8	1445.3	857.1	145.0	91.3	53.8	177.1	569.4	4.4	26.5	405.0	15.0	0.0
RW $(n = 9)$	Min	582.0	25.5	7.5	4.8	436.5		50.0	40.0	10.0	53.3	199.2	5.8	10.0	34.0		0.0
	Max	4900.0	25.9	8.2	8.7	3675.0		190.0	120.0	80.0	615.6	1390.4	45.0	79.0	784.0		0.6
	SD	1593.3	0.1	0.3	1.1	1195.0		41.7	22.3	26.0	198.9	370.6	14.9	29.3	269.3		0.2
	Mean	2636	25.6	8.0	6.0	1977		131.7	90.6	41.1	263.9	820.7	8.2	49.7	486.1		0.1
MOW (n = 5)	Min	630.0	25.5		5.9	472.5		80.0	50.0	5.0	42.6	149.8	11.0	10.0	102.0		0.0
	Max	1253.0	26.1	8.3	7.1	939.8		220.0	135.0	90.0	105.9	501.3	19.2	75.0	202.0		0.2
	SD	288.6	0.2	0.3	0.4	216.5		57.0	36.6	31.9	25.5	161.8	3.1	31.5	45.0		0.1
	Mean	996.2	25.7		9.9	747.2		143.0	95.0	48.0	72.4	329.8	10.5	42.0	151.2		0.1
LKW (n = 4)	Min	1161	26.0		5.0	871.0		95.0	50.0	25.0	82.0	350.0	15.0	55.0	202.0		0.0
	Max	1781.0	26.3	8.5	7.0	1335.8		130.0	75.0	65.0	202.1	596.0	41.1	80.0	289.0		0.2
	SD	307.4	0.1	0.1	0.9	230.5		16.5	10.4	17.8	61.1	122.9	6.6	10.8	38.6	1.9	0.1
	Mean	1487	26.2	8.5	6.2	1115		111.3	62.5	50.5	135.3	491.5	41.1	70.5	253.3	12.7	0.1

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Sample code	TGTW-1	AP-1	SIS-1	MT-1	DHA-1	LCC-1
EC	1078	1662	791	672	561	740
Temp	26	26	26	26	26	26
pН	8	8	8	8	8	8
Turbidity	5	5	10	6	5	6
TDS (mg/l)	809	1247	593	504	421	555
Alkalinity (as HCO ₃)	598	854	403	598	427	500
Total hardness (as CaCO ₃)	165	60	145	150	180	250
Ca ²⁺	100	50	95	90	115	125
Mg^{2+}	65	10	50	60	65	125
Cl ⁻	75	128	160	43	53	53
SO_4^{2-}	442	701	115	123	85	146
NO_3^-	15	12	4	10	8	8
As	75	75	8	38	25	38
Na ⁺	0.05	0.04	0	0.01	0.31	0.06
K ⁺	4.68	23.4	11.7	3.9	5.85	3.9
Fe	220	360	143	106	78	132

Table 2b. Physio-chemical water-quality parameters collected from the community water supply of study area.

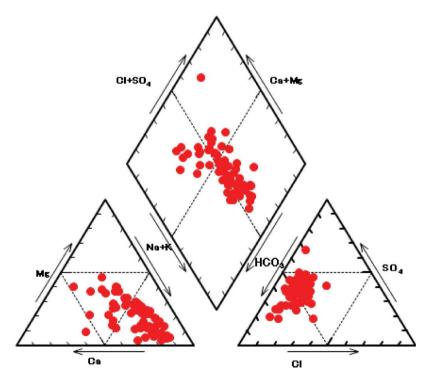


Figure 2. Piper plot showing the major water type in the area.

Table 3. Linear Pearson correlation coefficient matrix for different physicochemical parameters	n correlation	on coeffi	cient mat	rix for diffe	srent phys	sicochemica	ul paramete	ers.								1
	С Н	Temn	Hd	Turhidity	SUT	Total Alkalinity hardness (HCO.) (CaCO.) Ca ²⁺ Mo ²⁺	Total hardness (CaCO.)	Ca ²⁺ N	Λσ ²⁺	-10	SO_{s}^{2-}	_ ON	As	+ ^e N	к ₊	ت لت
		duina		1 month		(2001)	(2000)	7a 1	15		400	103		110		21
EC	1															
Temp	.154	1														
ЬН	.266	.400	1													
Turbidity	.376	.418	174	1												
TDS	1.000^{**}	.154	.266	.376	-											
Alkalinity (HCO ₃)	.888**	027	.323	.290	.888**	-										
Total Hardness (CaCO ₃)193	193	473	722*		193		1									
Ca^{2+}	220	549	710^{*}		220	278	.844**	1								
${ m Mg}^{2+}$.005	.067	135		.005	128	.431	119	1							
Cl ⁻	.957**	.110	.188	.310	.957**	.741*	050	070	.021	1						
$\mathrm{SO_4}^{2-}$.957**	.132	.442		.957**	$.930^{**}$	397			.865**	-1					
NO_3^-	371	.295	.040		371	547	.208				446	-				
As	.217	399	.879**		.217	.271	409			.122	.349	.111	1			
Na^+	$.931^{**}$	083	.169		.931**	.855**	.014	076	.145			376	.199	1		
K^+	-099	.300	500	.316	099	332	.409	.442	.032	.023	320	- 253 -	405 -	044	1	
Fe	.409	.263	.135	012	.409	.055	.039	127	.290		.354	.028 -	146	- 241	146	-
**Correlation is significant at the 0.01 level (two tailed) *Correlation is significant at the 0.05 level (two tailed).	it the 0.01 lo the 0.05 le	evel (two vel (two ta	tailed). ailed).													1

correlation coefficient matrix for different physicochemical parameters. Linear Pearson Table 3.

Table 4a. Ar	senic concentr.	ations in drink	Table 4a. Arsenic concentrations in drinking water samples along with HQ and CR values of study area.	s along with H	IQ and CR val	ues of study area.			
		As (µg/L)			Η			-	CR
Sample ID	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
PP	50.4	18.90	30 - 80	4.67	1.750	2,78-7.41	0.002	0.001	1.25E - 03 - 3.33E - 03
CP	35.9	2.43	32 - 37.5	3.32	0.225	2.96 - 3.47	0.001	0.000	1.33E - 03 - 1.56E - 03
KNM	28.3	15.88	10 - 37.5	2.62	1.470	0.93 - 3.47	0.001	0.001	4.17E - 04 - 1.56E - 03
BDK	74	1.00	73-75	6.85	0.093	6.76 - 6.94	0.003	0.000	3.04E - 03 - 3.13E - 03
MW	33.5	15.15	25-75	3.10	1.403	2.31 - 6.94	0.001	0.001	1.04E - 03 - 3.13E - 03
BK	26.5	21.55	5.1 - 75	2.45	1.997	0.46 - 6.94	0.001	0.001	2.08E - 04 - 3.13E - 03
RW	49.7	29.33	29129	4.60	2.716	0.926 - 7.31	0.002	0.001	4.17E - 04 - 3.29E - 03
MW	42.0	75.00	10.1 - 75	3.89	6.944	0.93 - 6.94	0.002	0.003	4.17E-04-3.13E-04
LWK	70.5	10.85	55 - 80	6.53	1.004	5.1 - 7.41	0.003	0.000	2.29E - 03 - 3.33E - 03
TGTW-1	75			6.94				0.00	
AP-1	75			6.94				0.00	
SIS-1	8			0.74				0.00	
MT-1	37.5			3.47				0.00	
DHA-1	25			2.31				0.00	
LCC-1	37.5			3.47				0.00	

Sample ID	N		As (μ/L)	HQ	CR
CNG	5	Mean	32	3	1.33E-03
		SD	26	2	1.10E-03
		Range	6.1-71	0.56 - 6.57	2.50E-04-2.96E-03
SUN	5	Mean	51	5	2.12E-03
		SD	40	4	1.67E-03
		Range	1.1 - 92	0.093-8.519	4.17E-05-3.83E-03
SKB	25	Mean	106	10	4.42E-03
		SD	107	10	4.46E-03
		Range	3.00-443.0	0.278-41.019	1.25E-04-1.85E-02
MM	17	Mean	100	9	4.15E-03
		SD	164	15	6.85E-03
		Range	4.00-611	0.37-56.57	1.67E-04-2.55-02
WP	11	Mean	152	14	6.33E-03
		SD	185	17	7.71E-03
		Range	33.0-677	3.056-62.685	1.38E-03-2.82E-02
KAD	12	Mean	81	7	3.36E-03
		SD	60	6	2.50E-03
		Range	10.00 - 171	0.926-15.83	4.17E-04-7.13E-03
KLW	29	Mean	106	13	1.21E-02
		SD	454	42	1.89E-02
		Range	23-2400	2.13-222	9.58E-04-1.00E-01
MPU	3	Mean	58	5	2.43E-03
		SD	6	1	2.51E-04
		Range	52-64	4.81-5.93	2.17E-03-2.67E-03
ARK	10	Mean	117	11	4.88E-03
		SD	270	25	1.12E-02
		Range	1.00-881	0.93-81.57	4.17E-05-3.67E-02
DN	6	Mean	26	2	1.08E-03
211	Ũ	SD	14	1	5.85E-04
		Range	8.00-38.00	0.741-3.52	3.33E-04-1.58E-03
NK	6	Mean	58	5	2.40E-03
		SD	21	2	8.63E-04
		Range	39-94	3.61-8.7	1.63E-03-3.92E-03
KA	3	Mean	397	37	1.65E-02
	5	SD	222	21	9.25E-03
		Range	177-621	16.4-57.5	7.38E-03-2.59E-02
BP	3	Mean	68	6	2.82E-03
DI	5	SD	36	3	1.52E-03
		Range	40-109	3.7-10.1	1.67E-03-4.54E-03
JK	2	Mean	55	5	2.27E-03
v11	2	SD	69	6	2.86E-03
		Range	6-103	0.56-9.54	2.50E-04-4.29E-03
D DNI Λ	2	Mean	6–103 47	0.36-9.34	
RPNA	2	wiean	4 /	4	1.94E-03

Table 4b. Arsenic concentrations in drinking water samples along with HQ and CR values of previous study.

(continued)

Sample ID	N		As (μ/L)	HQ	CR
		SD	33	3	1.38E-03
		Range	23 - 70	2.13 - 6.5	9.58E-04-2.92E-03
CCO	2	Mean	1	0	4.08E-05
		SD	0	0	1.17E-06
		Range	1.00 - 1.5	0.093 - 0.097	4.00E-05-4.17E-05
ZAB	5	Mean	30	3	1.26E-03
		SD	16	1	6.62E-04
		Range	14.00-56.00	1.296-5.19	5.83E-04-2.33E-03

Table 4b. (Continued)

Environmental Quality Standards (NEQS). While in CP, KNM and MOW the concentrations are higher than the WHO standard but lower than NEQS standards. Some samples showed As levels even less than the WHO limits, e.g., in BK-4, BK-1, and BK-2. Among community water samples, TGTW-1 and in AP-1 metal concentrations exceeded the WHO and NEQS standards, while in MT-1, DHA-1 and LCC-1 As levels exceeded the WHO limit of 10 but are lower than the NEQS limits. In one sample SIS, As concentrations were lower than the WHO and NEQS standards.

In the study area, the As concentrations in water were lower than those reported in Sindh (23.3–96.3 μ g/L) (Arain et al. 2009) and in Jamshoro groundwater (3–106 μ g/L); lower than Muzaffargarh district surface and groundwater (1–905 μ g/L) (Nickson et al. 2005) and lower than in Lahore and Kasur (Farooqi et al. 2007b) (<100–1900 μ g/L), as shown in (Figure 3).

Concentrations of previous and present study are plotted in Figure 3 to show the spatial distribution and to know the extent of safer wells. In the present study the proportion of low-As wells increased markedly from left to right, but there are a few safe wells available even in the most affected village of Kalalanwala (Farooqi et al. 2007b) distribution of As in hand pump water is that it is spatially variable, even with a single village. The key implication is that most households in rural Punjab live within walking distance of a safe well even if their own well is high in As (Figure 3). Studies carried out in Bangladesh showed that up about one-half of households informed that their hand pump is high in As seek a neighbor's hand pump that is low in As, despite cultural barriers to sharing wells that are likely to be comparable in Punjab (Ahmed Baig et al. 2010; George et al. 2012).

The main obstacle to well-switching, and therefore exposure reduction for millions of villagers is lack of information. The vast majority of hand pumps have never been tested. Field kits for testing the As of groundwater are available and effectively distinguish those wells that meet the WHO guidelines for As 10 ug/L (George et al. 2012). Only few wells in these villages were tested; blanket testing of all wells could therefore reveal additional safe wells.

Correlation of arsenic and release mechanism

Although higher concentrations are detected in shallower wells but deeper wells also contain As levels exceeding the WHO limit. This illustrates that As concentrations are independent of the depth (Figure 4), as shallow and deeper wells both contain metal levels higher than the WHO standard. In order to determine the source of As enriched

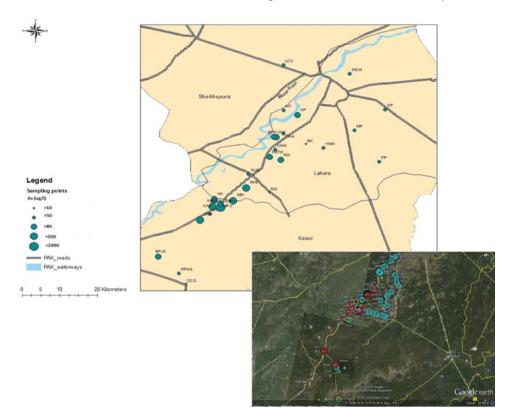


Figure 3. Spatial distribution of arsenic concentrations in present and previous study area.

groundwater correlation of metal parameters affecting the mechanism of release was carried out (Table 3). The As concentration rose with increasing pH in groundwater and metal showed strong positive correlation with pH (r = 0.88), slight positive with HCO₃⁻ (r = 0.27), and SO₄²⁻ (r = 0.35), while negative association with Fe (r = -0.146). The

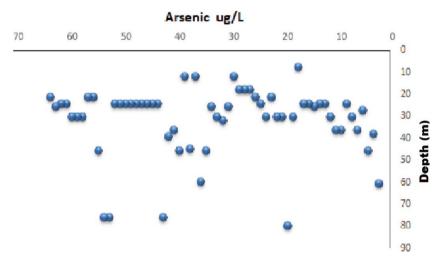


Figure 4. Relationship of arsenic concentration with depth.

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	F1	F2	F3
EC	0.966	0.001	0.014
Temp	0.342	0.174	0.036
рН	0.022	0.574	0.320
Turbidity	0.088	0.627	0.207
TDS (mg/l)	0.966	0.001	0.014
Alkalinity (as HCO ₃)	0.821	0.069	0.007
Total hardness (as CaCO ₃)	0.699	0.172	0.048
Ca ²⁺	0.808	0.091	0.000
Mg ²⁺	0.572	0.226	0.125
Cl ⁻	0.220	0.619	0.030
SO_4^{2-}	0.949	0.036	0.001
NO ₃ ⁻	0.391	0.451	0.001
As	0.602	0.362	0.003
Na ⁺	0.102	0.048	0.760
K ⁺	0.695	0.177	0.005
Fe	0.953	0.001	0.020
Eigenvalue	9.193	3.630	1.592
Variability (%)	57.458	22.689	9.947
Cumulative (%)	57.458	80.147	90.095

Table 5. Factor loadings showing significant variables and their relationship in water samples.

Note: Values in bold correspond for each variable to the factor for which the squared cosine is the largest.

trend is similar to previous findings, which demonstrated the same mechanism of As release in the extended area, i.e., desorption of As from Fe oxides under alkaline pH (Stollenwerk 2003; Waychunas et al. 1993)

Principal component analysis: source extraction and relationship

Principal component analysis (PCA) is a powerful pattern recognition technique that attempts to explain variance of a large dataset of correlated variables with a smaller set of independent variables (Simeonova, Simeonov, and Andreev 2003). PCA was employed on our dataset to compare compositional patterns between the examined water systems and identify factors that influence each one. The majority of the variance (90.1%) of the scaled data was explained by three eigenvectors-principal components as shown in Table 5. The first principal component factor (PCF-1) explained 57.45%. PCF-1 had a significant correlation with EC (0.966), TDS (0.966), Fe (0.953), SO₄²⁻(0.949), Ca²⁺ (0.808), alkalinity as HCO₃ (0.821), total hardness as CaCO3 (0.699), K⁺(0.695) and As (0.602). The sources of EC, TDS, As, Fe, K^+ , SO_4^{2-} , alkalinity (as HCO₃) might be geogenic due to weathering of the sulfide's bearing minerals and Ca²⁺ hardness might be due to dissolution of Ca in water through sulfides bearing calc-silicate (Farooqi, Masuda, and Firdous 2007a). The second component (PCF-2), explaining 22.68 % of the total variance, has strong positive loadings with Cl^{-} (0.619), turbidity (0.627), pH (0.574) and NO_3^- (0.451). The sources of NO_3^- may be anthropogenic such as contribution of animal, manure and human waste to the ground water whereas sources of Cl⁻ may be geogenic, due to leaching of sedimentary rocks or dissolution of salt deposits (Guo et al. 2011; Khan and Ho 2011; Simeonova, Simeonov, and Andreev 2003). The correlation of pH with As and other minerals may be justified because changes in groundwater pH promote adsorption or desorption of As and other minerals (Dzombak 1990; Waychunas et al. 1993; Fuller and Davis 1989). The third component (PCF-3) of PCA shows 9.94% of the total variation has positive loading with Na⁺, suggesting natural geologic source (Shah 2000).

Arsenic health risk assessment

Hazard identification

In the areas of the Lahore, Kasur and Sheikhopura districts, groundwater is still the main source for drinking water. This is due to the lack of safe water supplies and water treatment systems in rural areas. In rural areas, the majority of people are actively consuming groundwater since they have no other alternate water sources. The survey results showed that residents in the study areas consumed groundwater for the whole year (365 days). Life expectancy of individuals is 67 years. Various symptoms of arsenicosis such as skin lesions, skin hyperpigmentation, hyperkeratosis and ulcers were found during a field survey in the study area, resulting from the consumption of groundwater over a decade.

Exposure assessment

Exposure assessment was conducted for the present and previous study (Table 4(a) and 4(b) and Figures 5(a) and 5(b)), toxic and cancer risk indices were calculated by expressions (2) and (3), respectively. Computational results displayed that the residents in the Lahore and Kasur districts' study areas had toxic risk indices (HQ) ranging from 1.11 to 7.407 (n = 64) 2.6 × 10⁻² to 2.08 × 10⁻⁴. In some study areas from the districts of Lahore and Kasur, residents exceed the toxic risk index 1.

In the present study, toxic risk indices (HQ) found in the Patha Pind ranging 2.8-7.41 and Cancer risk indices were between 1.2×10^{-3} and 3.33×10^{-3} . In Chamropur, HQ ranged from 2.96 to 3.47, while CR ranged from 1.3×10^{-3} to 1.5×10^{-3} . Kot Noor Muhammad HQ values were calculated in the range of 0.93-6.94, and CR ranged between 3.1×10^{-3} and 4.1×10^{-4} . In Malamwal, HQ values were calculated between 2.314 and 6.944, and CR ranged between 1.1×10^{-3} and 1.4×10^{-4} . In BhaiKot, HQ

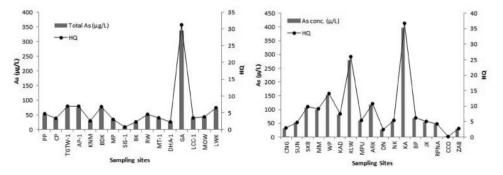


Figure 5. Total arsenic and HQ values in present study area (a) and total arsenic and HQ values in previous study area.

value was calculated between 0.46 and 6.944, and CR was between 3.1×10^{-3} and $2.0 \times$ 10^{-4} . Sheikhopura HQ ranged between 0.93 and 7.31, and CR ranged between 3.2 \times 10^{-3} and 4.1×10^{-4} . Mohnalwal HQ value was calculated between 0.93 and 6.94, and CR ranged between 3.2×10^{-3} and 4.1×10^{-4} . In Loharan Wala Koh study areas, HQ ranged between 5.1 and 7.407, and CR ranged between 2.2×10^{-3} and 3.3×10^{-3} . In community water supplies TGTW-1, AP-1, MT-1, DHA-1 and LCC-1 HQ and CR values were 6.94, 3.13×10^{-3} , 6.94, 3.13×10^{-3} , 3.47, 1.56×10^{-3} , 2.31, 1.04×10^{-3} , and 3.5, 1.56×10^{-3} , respectively. Health risk of As poisoning was more dependent on the metal levels in groundwater, ADD and other related factors of groundwater consumption such as exposure duration (ED) and ingestion rate (IR), rather than individual status such as gender and age. This study illustrates that some residents might ingest an excessive amount of As, not only through groundwater drinking pathway but also through daily diet. In fact, some residents in the study areas used As-contaminated groundwater to irrigate their farms. Therefore, the actual ingestion of metal content of this group would be higher than that of groundwater drinking pathway alone. Concurrently, in practice, some residents did not consume instantly pumped groundwater. Pumped groundwater may be stored for a period of time in traditional water storage containers, such as pitchers, which may lead to natural oxidation and precipitation and ion exchange processes that lower As levels (Smedley et al. 2002). In short, a number of factors may play a role in As accumulation in humans residing in the study area.

In comparison to present study, Table 4(b) summarizes As concentrations, HQ and cancer risk in ground water samples from previous investigation which was conducted in the districts of Lahore and Kasur adjacent to the present area in 2007. Study areas had toxic risk indices (HQ) ranging from 0.093 to 222 (n = 143) and CR ranging from 1 \times 10^{-1} to 4.17×10^{-5} . The upper end of the ranges for study area residents exceeds the typical toxic risk index 1, indicating significant adverse toxic health impacts. Toxic risk indices (HO) found in the CNG were in the range of 0.55-6.6 and cancer risk indices were between 9.58×10^{-4} and 1.88×10^{-3} . In SUN, HQ values were between 0.093 and 8.51, while CR values were between 4.17×10^{-5} and 3.83×10^{-3} . SKB HQ values were in the range of 0.278-41.01, and CR values were between 1.25×10^{-4} and 1.85×10^{-2} . In MM, HQ values were calculated between 0.37 and 56.5, and CR ranged between 1.67 \times 10⁻⁴ and 2.55 \times 10⁻². In WP, HQ ranged from 3.05 to 62.68, and CR ranged between 1.38×10^{-3} and 2.8×10^{-2} . In KAD, HQ ranged between 0.925 and 15.8, and CR ranged between 4.17×10^{-4} and 712×10^{-3} . KLW HQ value was calculated between 2.13 and -59.17, and CR value was calculated between 1.25×10^{-3} and 2.66×10^{-2} . In MPU study areas, HQ ranged between 4.81 and 5.92, and CR ranged between 2.17 \times 10^{-3} and 2.63 \times 10^{-3} . ARK HQ ranged between 0.0926 and 81.57, and CR ranged between 4.2×10^{-5} and 1.67×10^{-3} . In DN, HQ value was found between 3.5185 and 0.7407, and CR was found between 1.29×10^{-3} and 3.33×10^{-4} . In NK, HQ values were calculated between 8.7037 and 3.6111, and CR value was found between 3.92 \times 10^{-3} and 1.63×10^{-3} . At KA, HQ was found between 57.50 and 16.4, and CR was calculated between 1.63×10^{-2} and 7.4×10^{-3} . In BK, HQ was noted between 10.1 and 3.70, and CR was noted between 1.67×10^{-3} and 4.54×10^{-3} . JK HQ ranged between 9.54 and 0.56, and CR ranged between 4.29×10^{-3} and 2.5×10^{-4} . RPNA HQ value was calculated between 6.5 and 2.123, and CR was found between 2.92×10^{-3} and $9.58 \times$ 10^{-4} . CCO HQ ranged between 0.094 and 0.093, and CR ranged between 4.18×10^{-5} and 4.17×10^{-5} . ZAB HQ value was calculated between 5.18 and 1.3, and CR was calculated between 9.17×10^{-4} and 1.13×10^{-3} .

The CR value greater than one million (10^{-6}) was generally considered significant by US EPA. As shown in Figure 5(b), HQ is high at previous study sites which were located at the boundary of districts Lahore and Kasur as compared to present study area. HQ values were less but still higher than 1 in the present study. In some areas in previous study like Bhai Kot in the districts Lahore and Central Colony in the district Kasur HQ value was less than 1, as shown in Figure 5(b).

Conclusions

As concentrations in most of the underground water samples were higher than the permissible limits proposed by WHO. In comparison to areas located at the boundary of Lahore and Sheikhopura districts, analytical results demonstrated that groundwater in the Lahore and Kasur districts' study areas were significantly enriched with As. Consequently, the computation of risk through As consumption in drinking water indicated that residents in Lahore and Kasur areas might be exposed to more elevated toxic and carcinogenic risks than those of the present study areas. Rapid development of arsenicosis symptoms found during field sampling was closely correlated with risk factors such as extremely high As levels in groundwater, ADD, ED and IR. Data demonstrated that even in highly contaminated areas, some wells are safe with As values lower than WHO values, one possible and immediate remediation measure might be well switching to these wells which lie within walking distance of highly contaminated wells. Moreover, in order to find safer wells and reduce As health risk in the area, blanket testing of each and every well is an immediate need.

Acknowledgment

The authors acknowledge Fatima Jinnah Women University for the research support.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The research work is supported by the HEC [grant number 1267].

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