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Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area

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Highlights

- First detailed inorganic and organic arsenic speciation data for ground water in Pakistan (As^{+5}, As^{+3}, MMA, DMA and AsB) with the highest level of total arsenic up to 3090 µg L^{-1}.
- As^{+5} found to be the major species in groundwater while As^{+3} was dominant at a small number (13) of sources only.
- Mean ratio of As^{+3} to total arsenic slightly higher than found in Bangladesh.
- Highest average daily dose of 236.51 µg kg^{-1} day^{-1} for total arsenic through drinking water ingestion.
- Average daily dose of 15.63 µg kg^{-1} day^{-1} (children) and 15.07 µg kg^{-1} day^{-1} (adults) for As^{+5} and, 0.09 µg kg^{-1} day^{-1} and 0.26 µg kg^{-1} day^{-1} for As^{+3}.

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Abstract

Understanding arsenic speciation in water is important for managing the potential health risks associated with chronic arsenic exposure. Most arsenic monitoring studies to date have only measured total arsenic, with few looking at arsenic species. This study assessed 228 ground water sources in six unstudied villages in Pakistan for total, inorganic and organic arsenic species using ion chromatography inductively coupled plasma collision reaction cell mass spectrometry. The concentration levels approached 3090 µg L^{-1} (*95% CI*, 130.31, 253.06) for total arsenic with a median of 57.55 µg L^{-1}, 3430 µg L^{-1} (median=52) for arsenate (As^{+5}) and 100 µg L^{-1} (median=0.37) for arsenite (As^{+3}). Exceedance of the WHO provisional guideline value for arsenic in drinking water (10 µg L^{-1}) occurred in 89% of water sources. Arsenic was present mainly as arsenate (As^{+5}). Average daily intake of total arsenic for 398 residents living in the sampled houses was found up to 236.51 µg kg^{-1} day^{-1}. This exposure estimate has indicated that 63% of rural residents exceeded the World Health Organization's provisional tolerable daily intake (PTDI) of 2.1 µg kg^{-1} day^{-1} body weight. Average daily intake of As^{+5} was found to be 15.63 µg kg^{-1} day^{-1} (*95% CI*, 5.53, 25.73) for children ≤ 16 and 15.07 µg kg^{-1} day^{-1} (*95% CI*, 10.33, 18.02) for adults. A mean daily intake of 0.09 µg kg^{-1} day^{-1} was determined for As^{+3} for children and 0.26 µg kg^{-1} day^{-1} for adults. Organic arsenic species such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and Arsenobetaine (AsB) were found to be below their method detection limits (MDLs).

1. Introduction

The natural occurrence of arsenic in ground and surface water poses a health risk for approximately 200 million people globally (Naujokas et al., 2013). Epidemiological studies have indicated an association between chronic exposure to inorganic arsenic via drinking water and cancer of the skin, liver, lung, kidney, prostate and bladder (ATSDR, 2007a). The toxicity and carcinogenicity of arsenic is strongly associated with its oxidation states and chemical forms. Arsenic species in water consist of inorganic species such as arsenate ($H_2AsO_4^-$ or As^{+5}), arsenite (H_3AsO_3 or As^{+3}) and organic species like monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AsB). As^{+3} was found to be 10 times more toxic than As^{+5} and 70 times more toxic than MMA^{+5} and DMA^{+5} (Squibb and Fowler,1983). Higher exposure to inorganic arsenic species is reported to be linked with various toxicities including cardiovascular disorders due to oxidative stress (Singh et al. 2011). Organic arsenic species in the trivalent oxidation state (MMA^{+3} and DMA^{+3}) may induce higher cytotoxic and genotoxic effects than pentavalent species (MMA^{+5} and DMA^{+5}) and inorganic arsenicals due to their higher membrane permeability. This has been exemplified in Chinese hamster ovary cells (Dopp et al. 2004).

Metabolism of inorganic arsenic to trivalent methylated arsenic species plays an important role in increasing the toxic effects as MMA^{+3} has shown higher toxicities than As^{+3} (Petrick et al. 2001; Petrick et al. 2000). Based on these studies, the International Agency for Research on Cancer considers DMA and MMA as possible carcinogens to humans (IARC, 2012). Despite this, there is no definitive understanding of the mechanism for carcinogenic effects of arsenic species. It is important to measure their concentrations in the environment and biological systems after ingestion to help understand their roles in the development of cancer (Hughes, 2009).

Organic forms of arsenic such as DMA have been used as ingredients in some pesticides such as monosodium methanearsonate (MSMA) or disodium methanearsonate (Ahuja, 2008; Hughes et al., 2011). Following the identification of organic arsenic species in surface waters or aquifers and associated carcinogenic effects, policy has been developed to limit exposure. For example, the US EPA produced the organic arsenical product cancellation order (USEPA, 2009) and EU pesticide legislation was developed i.e. Commission Directive 2003/3/EC: Regulation

(EC) No 304/2003 (Official Journal of the European Union, 2003). Nevertheless, few studies, particularly in arsenic affected regions, exist on inorganic arsenic speciation in water (Chen et al., 1994; Bhattacharya et al., 2006). In such regions, exposure assessments of inorganic and organic arsenic species may assist in identifying the likely sources associated with cancer clusters. These may include arsenic contaminated ground water used for drinking, food preparation, cooking and irrigation purpose. Previous studies undertaken in Pakistan have only determined inorganic arsenic using commercial field testing kits (Mahar et al., 2015; Uqaili et al., 2012; Ahmed et al., 2004) or validated a small percentage of samples in the laboratory for inorganic arsenic (Haque et al., 2008; Farooqi et al., 2007). Whereas, arsenic speciation studies (Zahir et al., 2015; Brahman et al., 2013 and Baig et al., 2016) have only analysed As^{+3} using simple spectrophotometry or Graphite Furnace Atomic Absorption Spectrometery (GFAAS). As^{+5} has been determined only as the difference between total inorganic arsenic and As^{+3}, whilst organic arsenic species (DMA, MMA and AsB) have not been analysed in water.

Considering the unknown extent of arsenic species in ground water and uncertainties regarding the species dependent arsenic toxicity, the aim of this study was to conduct an exposure assessment for different arsenic species in the groundwater of six previously unexplored rural settings. The specific objectives were to; 1) assess the spatial distribution of total arsenic, inorganic (As^{+3} and As^{+5}) and organic arsenic species (DMA, MMA and AsB) in ground water aquifers; 2) determine the magnitude of arsenic exposure from domestic ground water and associated health implications.

2. Methodology

2.1 Sampling design and study area characteristics

This study uses a population based probability design within four districts of Pakistan (Kasur, Sahiwal, Bahawalpur and Rahim Yar Khan). Six villages within these four districts were selected for sampling, where at least one groundwater source was found to contain arsenic concentrations >50 µg L^{-1}. The prevalence of arsenic associated health symptoms among the native residents of at least 1% of houses was also used. Ground water (obtained from hand pumps and dug wells) is the major water source in the study villages in the alluvial plain of the south-flowing

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Indus river and its five major tributaries (Pakistan paedia, 2008). These consisted of 1776 households, with a population of 15647 (51% men; 49% women) and an average of 7 family members per house (Pakistan Bureau of Statistics, 2014). The detailed sampling design is published elsewhere (Rasheed et al., 2016b). A sample size of 223 households was selected, derived from a formula for estimating sample proportions (Collet, 2003). Accordingly, a 95% confidence level and standard error of 0.05 assumes a statistically significant sample size. Ground water sampling for this study was conducted randomly depending on the willingness of 223 households simultaneously with data collection on daily water intake rate, body weight, and age from 398 residents of such houses. Five additional households were willing to participate only in water sampling; hence a total of 228 water samples were collected.

2.2 Samples collection procedure

Groundwater samples were collected from hand-pumps and dug wells at depths of 10 to 31 m following typical practice of purging for 5 to 10 minutes to obtain fresh groundwater. The groundwater samples were collected in duplicate in high density polyethylene (HDPE) bottles (125 mL each). One water sample was filtered and acidified on-site by adding 2 to 3 drops of concentrated nitric acid (HNO_3) to stabilize arsenic and reduce precipitation (USEPA method 200.8-modified; US Environmental Protection Agency, 1994). The acidified water samples were used to analyse total arsenic. For arsenic speciation, the second sample was filtered and preserved with 0.125 M ethylenediaminetetraacetic acid (EDTA) (Garbarino et al. 2002). Samples were kept in an insulated cooler containing ice and transported to the local laboratory for storage at 4 °C. They were then transferred to Brooks Applied Laboratory (BAL), USA by FedEx courier with dry ice under strict quarantine regulations and stored at 4 °C prior to analyses.

2.3 Samples processing for total arsenic and speciation

The pH of water samples was measured in the field using a pH meter (Model 350, Jenway). Total arsenic concentrations were obtained using an inductively coupled plasma mass spectrometer with Dynamic Reaction Cell (DRC™) technology (USEPA method 200.8, modified). Arsenic speciation data were obtained by analysis of samples using ion chromatography inductively coupled plasma collision reaction

cell mass spectrometry (IC-ICP-CRC-MS). Peak integration was performed by automated integration. Chromatographic peaks were integrated using the ICP-MS plasma lab software.

2.4 Quality Assurance

The quality of analytical work was checked by the analysis of NIST (National Institute of Standards and Technology) traceable standard reference materials (SRMs-1640A, trace elements in natural water), blanks and duplicates (Tables 1). Data quality in terms of precision, accuracy, method detection limits (MDLs), and completeness met the criteria established in the BAL's quality assurance project plan (QAPP), i.e., relative percent difference (RPD) of <25%, percent recovery of 75 to 125% and completeness of 80%.

Table-1: Summary of Quality Control Data of six analytical batches

Parameter	Method Detection Limits (MDLs)			Calibration Standard (CAL)		Initial Calibration Verification (ICV)		Duplicate (DUP)		Matrix Spike (MS)		Certified Reference Material (CRMs) NIST 1640a		Laboratory Fortified Blank (BS)		
	% Rec.	Results	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	SD	% Rec.	Results	SD
Total As	84	0.31	0.28	100	3.16	98	8.01	117	2.46	98	10.57	96	6.91	86%	0.62	0.56
As^{+3}	97	0.36	0.05	104	7.28	108	4.08	106	3.83	103	4.89	-	-	89%	0.78	0.37
As^{+5}	109	0.12	0.03	101	9.5	98	1.63	102	7.66	107	7.72	-	-	98%	1.07	0.16
MMA	90	0.18	0.04	97	7.21	75	14.29	109	4.4	109	7.35	-	-	97%	1.24	0.21
DMA	96	0.27	0.04	103	6.47	113	1.63	106	4.69	106	6.93	-	-	97%	1.1	0.17
AsB	100	0.37	0.03	-	-	107	8.57	-	-	-	-	-	-	99%	1.08	0.09

Expected percent recovery: 75-125%

2.5 Arsenic Exposure Assessment

The average daily dose (ADD) of total arsenic and arsenic species was calculated using Eq. (1) (USEPA, 1997).

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

Where **ADD** is average daily dose (as µg kg^{-1} day^{-1}), C represents the arsenic concentration in ground water (in µg L^{-1}), **IR** is the drinking water intake rate (L day^{-1}), **EF** is the exposure frequency (365 days year^{-1}); and **ED** is the exposure duration (years of using the ground water source). **BW** is the body weight (kg), and **AT** is the averaging time and is equal to (ED x 365 days/year). For children (≤16 years), the specific age class is considered as the ED.

The chronic daily intake and health risk was assessed for the study population by comparing the individual exposure to the reference level i.e. (RfD) and provisional tolerable daily intake (PTDI) via a ratio known as the "hazard quotient (HQ)". In this study, the HQ is quantified for total arsenic and inorganic arsenic species for each study participant (Rasheed et al. 2016b) using Eq. (2) (USEPA, 1997).

$$HQ \quad = \quad \frac{ADD}{RfD} \qquad (2)$$

Where;
  HQ   Hazard quotient
  ADD   Average daily dose of arsenic from the oral ingestion (µg kg^{-1} day^{-1})
  RfD   Reference dose: 0.0003 mg kg^{-1} day^{-1} (USEPA, 1992) for total inorganic
               arsenic

ADD values were compared with the World Health Organization's (WHO) provisional tolerable daily intake (PTDI) of 2.1 µg kg^{-1} day^{-1} (WHO 1985). If the calculated HQ is equal to or less than 1, the human health effect is assumed to be negligible, while a HQ greater than 1 suggests that there may be health concerns (USEPA, 2011). To provide a conservative estimate of health risk for this study, the ratio between ADD and the oral RfD set by USEPA and between ADD and PTDI for total arsenic (JECFA/WHO guidelines) were considered. Considering the absence of RfDs for arsenic species, it was assumed that inorganic arsenic is primarily As^{+5}, hence the RfD of 0.0003 mg kg^{-1} day is also used for As^{+5}. Based on 1.5 orders of magnitude

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of higher toxicity of As^{3+} than As^{+5}, an estimated RfD of 0.000006 mg kg^{-1} day^{-1} is used for As^{3+} (Markley et al. 2009).

2.6 Statistical analysis

Arsenic data distributions for total arsenic, As^{+5} and As^{+3} was found to be positively skewed in this study, hence the data set was normalized by log transformation prior to statistical analysis. Following the log-normal distribution, arithmetic mean (AM), geometric mean (GM), median, upper confidence limit (UCL), upper baseline concentration (UBC) were then calculated. Median and the geometric mean (GM) were expected to better represent the natural level of arsenic in ground water by minimizing. Microsoft Excel and SPSS 17.0 (IBM, New York, NY, USA) were used for generating descriptive statistics and Pearson partial correlation analysis. Nonparametric Pearson's correlation coefficients were used to assess the relationship between concentrations of total arsenic and arsenic species. Statistical significance was two-tailed and set at α = 0.05.

3. Results and Discussion

3.1 Total arsenic and arsenic species

Statistical observations across the six villages imply non-uniform distribution of total arsenic, As^{+5} and As^{+3} in groundwater. This observation is supported by large differences among mean and median followed by positive skewness of the original data (skewness: total arsenic (4.04), As^{+5} (4.12) and As^{+3} (4.11). Log-transformation of arsenic concentrations significantly reduced the skewness as 0.34, 0.29 and 1.86 for total arsenic, As^{+5} and As^{+3} respectively. The distribution of total arsenic examined graphically is given in Supplementary Information (Figures SI-1a and SI-1b, Table SI-1).

Village-wise summary statistics of total arsenic and inorganic arsenic species has shown the median values closer to the central tendency. The highest median concentration for total arsenic was found to be 1670 µg L^{-1} (*95% CI*, 1013.91, 2016.67) in groundwater of village Badarpur (n= 16) followed by 154 µg L^{-1} (*95% CI*, 159.26, 361.16) in village Chak-48 (n=45) and 65.30 µg L^{-1} (*95% CI*, 53.82, 74.68) in village Chak-46 (n=57) as shown in Table-2. Median total arsenic across all samples

(n=228) of study area was found to be 57.55 µg L^{-1} (95% CI, 130.31, 253.06) and a range of 0.48 to 3090 µg L^{-1} as given below in Table-2.

Table-2 Summary statistics of total arsenic and inorganic arsenic species (µg L^{-1}) in groundwater samples (n = 228)

Analyte	Statistics	Chak-46/12-L	Chak-48/12-I	Chak 49/12-I	Basti Balochan	Badarpur	Basti Kotla Arab	Overall
No of samples	n	57	45	50	31	16	29	228
As (Total)	AM	64.25	260.21	57.73	25.16	1515.29	14.52	191.68
	SD	39.30	336.01	26.42	8.35	940.92	13.23	470.31
	GM	49.76	145.29	49.10	23.25	1075.29	9.21	55.33
	Median	65.30	154.00	61.450	25.90	1670.00	11.40	57.55
	95% CI LB	53.82	159.26	50.22	22.19	1013.91	9.49	130.31
	95% CI UB	74.68	361.16	65.24	27.84	2016.67	19.56	253.06
	Minimum	3.56	8.50	7.11	8.25	43.60	0.48	0.48
	Maximum	228.00	1401.05	95.60	37.70	3090.00	51.40	3090.00
As^{+5}	AM	64.52	250.11	46.54	20.72	1690.18	16.48	199.22
	SD	38.99	361.88	29.15	7.32	1051.33	15.57	523.95
	GM	127.18	49.49	34.60	18.88	1198.53	9.59	49.08
	Median	64.00	124.00	46.20	21.20	1855.00	12.60	52.00
	95% CI LB	54.18	141.39	38.25	17.98	1129.97	10.56	130.85
	95% CI UB	74.87	358.83	54.82	22.92	2250.40	22.40	267.60
	Minimum	2.40	7.67	3.01	5.05	47.90	0.11	0.11
	Maximum	222.00	1440.00	106.00	29.60	3430.00	62.50	3430.00
As^{+3}	AM	0.39	3.79	19.22	1.24	0.91	0.62	5.37
	SD	0.08	11.41	30.05	1.21	0.78	0.51	16.61
	GM	0.38	0.81	3.87	0.83	0.70	0.51	0.88
	Median	0.37	0.37	2.73	0.61	0.60	0.37	0.37
	95% CI LB	0.36	0.36	10.68	0.76	0.49	0.43	3.20
	95% CI UB	0.41	7.22	27.76	1.68	1.32	0.82	7.54
	Minimum	0.37	0.37	0.37	0.37	0.37	0.37	0.37
	Maximum	0.96	57.50	100.00	4.82	3.26	2.27	100.00

n: Number of samples; AM: Arithmetic mean; SD: Arithmetic standard deviation; GM: Geometric mean; GSD: Geometric standard deviation; 95% CI: Confidence Interval, LB: Lower bound; UB : Upper bound;

The maximum level of total arsenic in ground water determined in this study is found to be higher than previous arsenic monitoring studies undertaken in Pakistan i.e. 0.2 to 2580 µg L^{-1} (Khattak et al., 2016; Rasool et al., 2015; Mahar et al., 2015; Shakoor et al. 2015; Zahir et al. 2015; Brahaman et al., 2013; Farooqi et al., 2007; Haque et al., 2008; Nickson et al., 2005). The highest level of inorganic arsenic discovered in this study is of the same order of magnitude as reported in other studies of arsenic rich zones of the world e.g. Bengal Basin, Argentina, Mexico, northern China,

Taiwan and Hungary, where arsenic in ground water was found up to 5000 μg L^{-1} (Smedley and Kinniburgh, 2002).

The percentage of total arsenic exceedance above the WHO provisional guideline value for arsenic in drinking water (10 μg L^{-1}) was found to be highest for the samples collected from the villages of Badarpur and Basti Balochan (100%) followed by Chak-48 (98%), Chak-49 (96%), Chak-46 (91%) and Kotla Arab (54%). 126 sources (56%) were also found to have total arsenic above Pakistan's water quality standard for arsenic (50 μg L^{-1}; PSQCA, 2010) as depicted in Figures 1a to 1c.
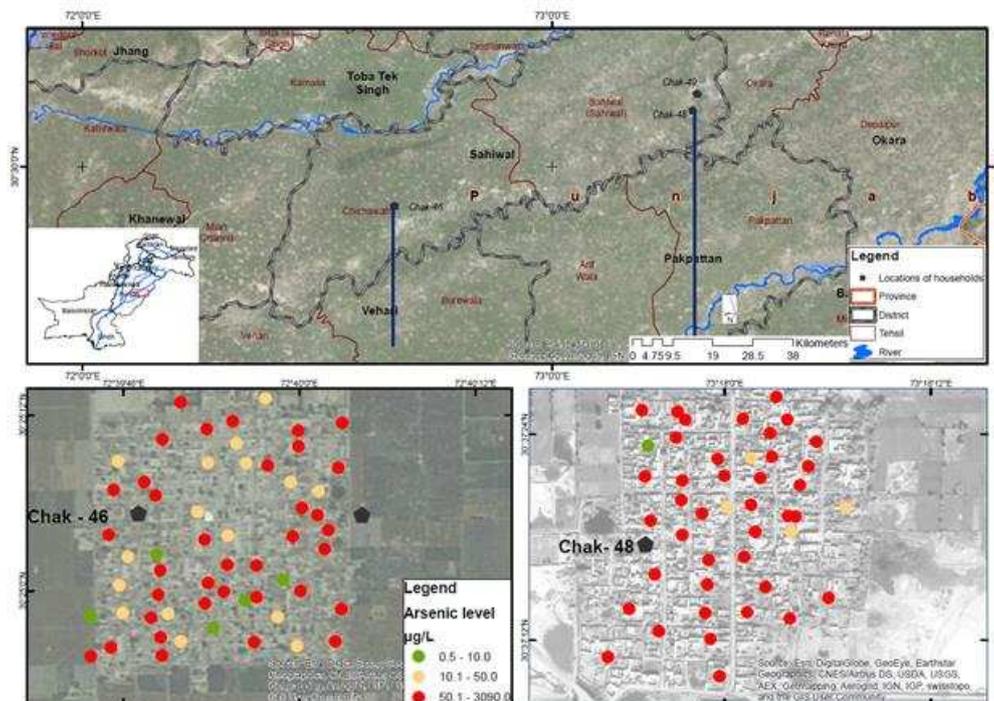
Figure 1a: Spatial distribution of total arsenic in villages Chak-46/12-L (*n=57*), Chak-48/12-I (*n=45*) in district Sahiwal
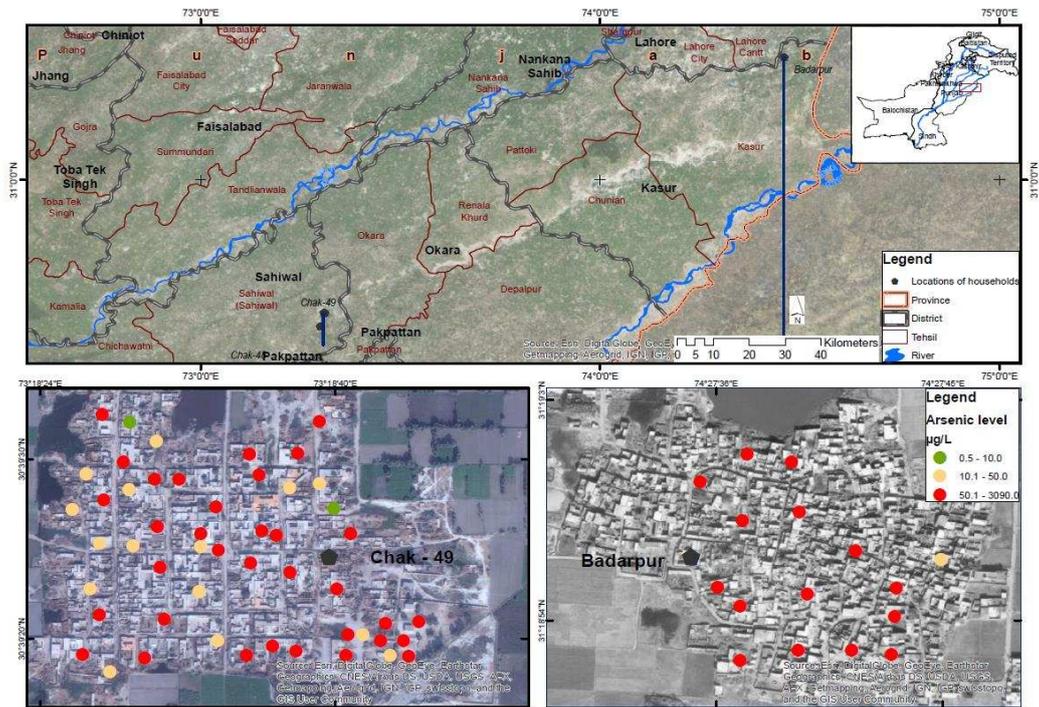
Figure 1b: Spatial distribution of total arsenic in villages Chak 49/12-I (n=50) and Badarpur (*n=16*) in Sahiwal and Kasur districts
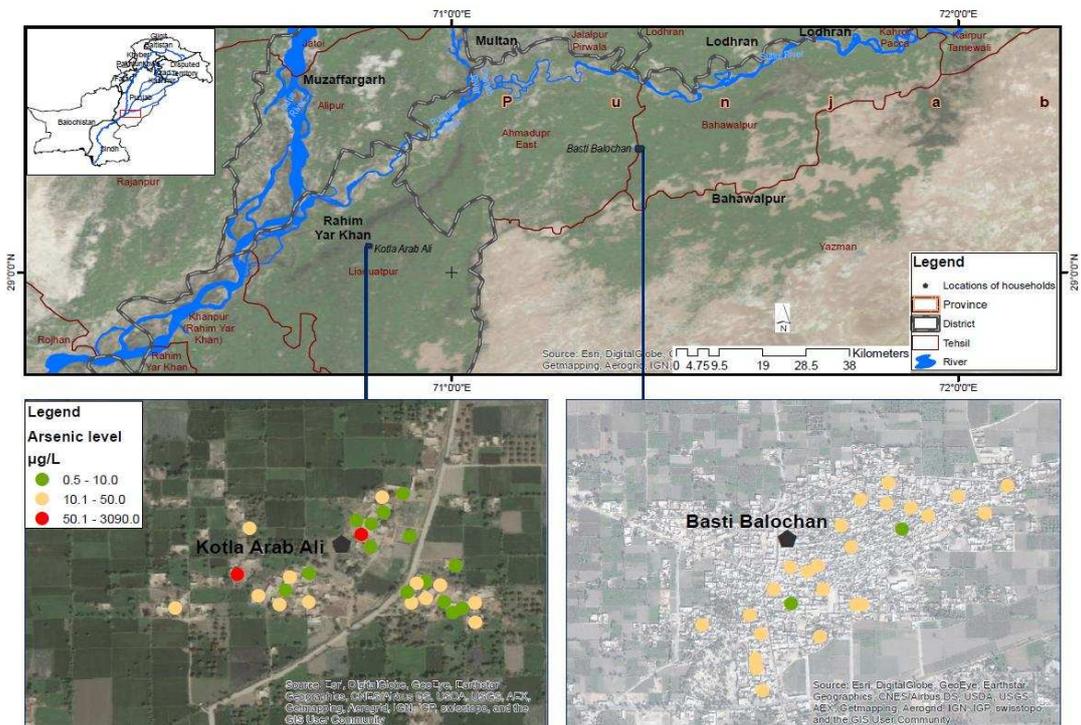
Figure 1c: Spatial distribution of total arsenic in villages Basti Kotla Arab (*n=29*) and Basti Balochan (*n=31*) in districts RYK and Bahawalpur

Inorganic arsenic speciation results have shown the median As^{+5} concentration to be 1855.00 µg L^{-1} in Badarpur followed by 124.00 µg L^{-1} and 64.00 µg L^{-1} in Chak-48 and Chak-46 respectively. As^{+5} concentration across all samples ranged between

0.11 and 3430.00 µg L^{-1} with median value being 52.00 µg L^{-1} (*95% CI*, 130.85, 267.60). As^{+5} was the most dominant inorganic arsenic species and a strong relationship existed between total arsenic and As^{+5} (Pearson's r = 0.964, n = 228, *95% CI*, 0.929, 0.999).

Following As^{+5}, the second most prevalent inorganic species was As^{+3} (Table-2). Village-wise comparison of As^{+3} showed a highest median concentration of 2.73 µg L^{-1} in village Chak-49 with an overall range of 0.37 to 100 µg L^{-1} (Table-2). The overall median of As^{+3} was found to be 0.37 µg L^{-1} (*95% CI*, 3.20, 7.54). There were only 21 water sources discovered with co-existence of As^{+3} and As^{+5} and out of these, As^{+3} was dominant in only 13 sources (Figure 2).
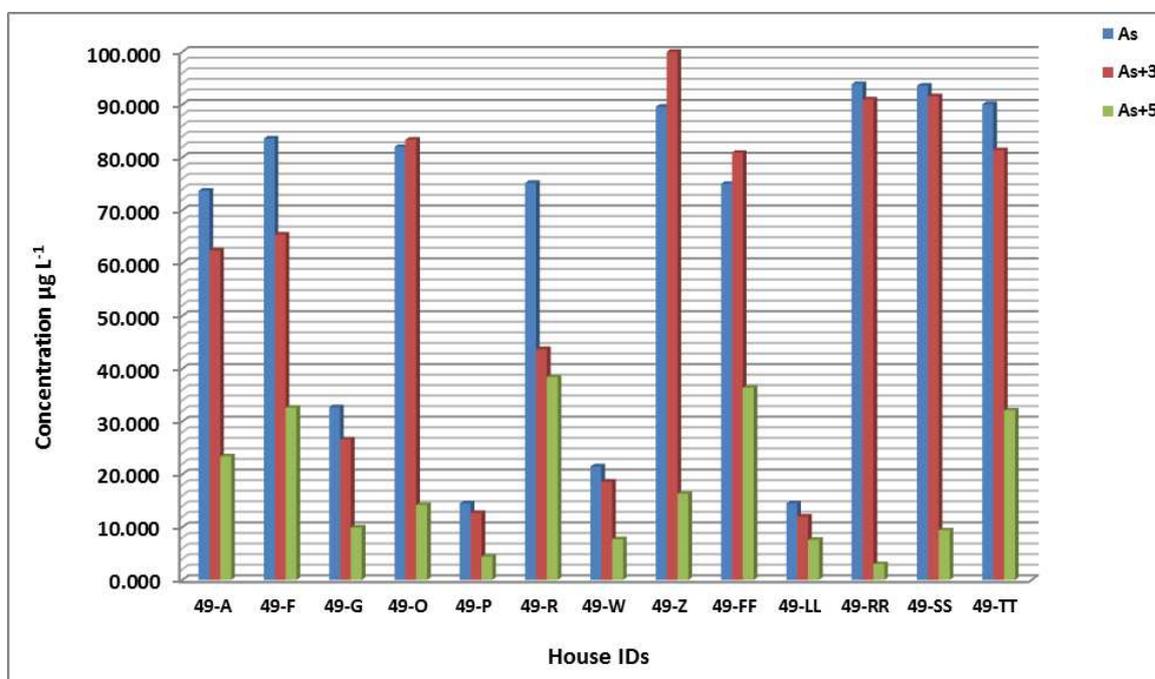
Figure-2: Pre-dominance of As^{+3} (µg L^{-1}) in some groundwater samples (n = 13) indicated by concentration levels of total arsenic, As^{+3} and As^{+5}

Other organic arsenic species (MMA, DMA and AsB) were found to be below or close to the method detection limits (MDLs) as shown below in Table-3

Table 3 Organic arsenic species (µg L^{-1}) in groundwater samples (n = 228)

Parameters	Statistics	District Sahiwal			district Bahawalpur	Kasur districts	district RYK	Overall
		Chak-46/12-L	Chak-48/12-I	Chak 49/12-I	Basti Balochan	Badarpur	Basti Kotla Arab	
		n=57	*n=45*	*n=50*	*n=31*	*n=16*	*n=29*	*n=228*
AsB	*Min*	0.37	0.37	0.37	0.37	0.37	0.37	0.37
	Max	0.37	0.37	0.37	0.37	0.37	0.37	0.37
	Mean±SD	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.00	0.37 ± 0.02

DMAs	Min	0.28	0.28	0.28	0.28	0.28	0.28	0.28
	Max	0.28	1.80	0.70	0.28	0.40	0.28	1.80
	Mean±SD	0.28 ± 0.00	0.31 ± 0.23	0.29 ± 0.06	0.28 ± 0.00	0.29 ± 0.03	0.28 ± 0.00	0.29 ± 0.11
MMAs	Min	0.20	0.20	0.14	0.20	0.20	0.20	0.14
	Max	0.20	0.20	0.14	0.20	0.20	0.20	0.20
	Mean±SD	0.20 ± 0.00	0.20 ± 0.00	0.14 ± 0.00	0.20 ± 0.00	0.20 ± 0.00	0.20 ± 0.00	0.19 ± 0.02

SD: Standard Deviation

3.2 Geological impact on relationship between arsenic species

The co-existence of As^{+3} and As^{+5} possibly associated with variations in aquifer's redox conditions was also evidenced by past studies (Bhattacharya et al., 2006; Smedley and Kinniburgh, 2002). However, contrary to the dominance of As^{+5} in this study, As^{+3} (462 µg L^{-1}) has been found as the principal species in the water sources in Taiwan (Chen et al. 1995; Ko et al. 1997). In West Bengal India, 60% to 90% of total arsenic existed as As^{+3} (6.8 to 462 µg L^{-1}) and 20% to 60% as As^{+5} (7 to 185 µg L^{-1}) (Shraim et al.,2002). A mixed reduction-oxidation process associated with localized geology was concluded to be responsible for such variations in these past studies. A mean ratio of As^{+3} to total arsenic was found to be within the range 0.1 to 1.1. This is slightly higher than typically found in Bangladesh i.e. 0.5 to 0.6 (DPHE/BGS/MML, 1999) and closer to that found (0.7 to 0.9) in reducing groundwater of Inner Mongolia (Smedley et al., 2000).

This study data showed that arsenic in ground water aquifers appeared to increase in concentration from the southern region (district Bahwalpur) towards the central region (district Kasur) of Punjab province. This study area is located within the Indus plain having geogenic presence of quaternary alluvial-deltaic sediments derived from sedimentary rocks (Rasheed et al., 2016a; Nickson et al., 2005). Sedimentary rocks due to the slow formation over centuries allows for aggregation of iron with greater capacities for arsenic retention. Under oxidizing conditions (i.e. oxidation-reduction potential >0 millivolts), As^{+5} is generally found to be the dominant form, whereas, higher concentration of more toxic As^{+3} in ground water is expected under reducing conditions (i.e. oxidation-reduction potential <0 millivolts) (Sorge et al.,2014). Excessive iron causes the onset of reducing conditions in alluvium (anoxic conditions) resulting in higher mobility of As^{+3} (Smedley, 2008). Indeed, there was a strong relationship between iron and As^{+3} where detected in the current study (Pearson's r=0.954, n=21, *95% CI*, 0.755, 1.1533).

Consumption of ground water with an elevated As^{+3} concentration could make a significant contribution to the intake of toxic inorganic arsenic species, with possible long-term adverse effects on the human health. However, the WHO provisional

guideline value for arsenic in drinking water (10 µg L^{-1}) and any of international or national enforceable regulations do not differentiate among arsenic species.

Arsenic contamination has also been reported to be associated with shallow wells (Mahar et al., 2015; Brahman et al., 2013; Welch et al. 2000; Ahmed et al., 2004). This agrees with the current study with presence of arsenic at a depth of 10 to 31 meters. To remediate shallow well contamination, the strategy of development of deeper wells has been the most recommended option for arsenic affected areas. However, the presence of more toxic As^{+3} has been reported in wells deeper than 170 metres in Taiwan (Tseng et al, 1968; Chen et al.,1994; Guo et al., 1994), Bangladesh (Roychowdhury, 2010) and the Mekong Delta in Vietnam (Erban et al., 2013). Other studies did not find any correlation between arsenic concentration and wells depth (Boyle et al.1998; Nimick, 1998). The presence of As^{+3} in 21 shallow wells in this study suggests, nevertheless, that this contamination is not just associated with deeper wells. The transport of arsenic in groundwater is also reported to be influenced by pH (Lovley and Phillips, 1988). However, the pH of ground water in this study was determined to be between 6.50 and 8.10 and there was no significant relationship between inorganic arsenic species and pH (Pearson's correlation coefficient (r) as = -0.14 (total arsenic), 0.008 (As^{+3}) and -0.16 (As^{+5}).

3.3 Arsenic exposure assessment

Given the high levels of total arsenic in drinking water supplies than WHO provisional drinking water guideline value of 10 µg L^{-1}, an exposure assessment was carried out for the six villages. The principal factors that have been taken into account in the exposure assessment calculations are presented in Table 4.

The daily intake of total arsenic as an average daily dose (ADD) for 398 persons residing within the 223 houses was found to be 15.12 µg kg^{-1} day^{-1} (*95% CI*, 5.59, 24.66) and 14.18 µg kg^{-1} day^{-1} (*95% CI*, 10.33, 18.02) for age groups of ≤ 16 and >16 years respectively. Similar mean values were found for As^{+5} whereas, for As^{+3}, a very low average daily dose is shown in Table-4. Compared with the provisional tolerable daily intake (PTDI) value of 2.1 µg day^{-1} kg^{-1} body weight (World Health Organization, 1989) of inorganic arsenic, 51 of 66 children of age ≤ 16 were found to have an average daily dose (ADD) for total arsenic above this limit. 201 of 332 adults (>16 years) exceeded the daily intake of 2.1 µg day^{-1} kg^{-1} body weight. As the

provisional tolerable daily intake (PTDI) value of 2.1 µg day^{-1} kg^{-1} body weight (World Health Organization, 1989) is set on the basis of total inorganic arsenic no species based assessments can be made.

Table-4: Average daily dose (ADD) of total arsenic and arsenic species from drinking water

Age groups	n	Overall statistical parameters	Body weight (Kg)	*Total daily water intake	ED (years)	Average daily dose ($\mu g\ kg^{-1}\ day^{-1}$) (mean ± SD)						Population > 2.1 $\mu g\ kg^{-1}$ bw day^{-1} of total arsenic	
						Total arsenic	As^{+5}	As^{+3}	MMA	DMA	AsB	count	%age
Age 3-6	5	-	12 ± 3	1.94	5	8.12 ± 5.86	8.37 ± 6.044	0.06 ± 0.02	0.026 ± 0.0056	0.04 ± 0.011	0.06±0.014	5	8
Age 6-16	61	-	26 ± 8	2.92	12	15.70 ± 41.06	16.22 ± 43.485	0.09 ± 0.15	0.023 ± 0.0063	0.03 ± 0.009	0.04±0.012	46	70
Age ≤ 16	66	-	25 ± 8	2.85	12	15.12 ± 39.53	15.63 ± 41.858	0.09 ± 0.14	0.023 ± 0.0063	0.03 ± 0.010	0.04 ± 0.013	51	78
	-	95% CI, LB	-	-	-	5.59	5.53	0.05	0.02	0.03	0.04	-	-
	-	95% CI, UB	-	-	-	24.66	25.73	0.12	0.03	0.04	0.05	-	-
	-	Minimum	9	-	-	0.065	0.01	0.02	0.01	0.02	0.02	-	-
	-	Maximum	44	-	-	195.88	226.59	1.05	0.04	0.06	0.08	-	-
Male >16	206	-	68 ± 14	3.86	20	14.05 ± 33.65	14.73 ± 37.430	0.32 ± 1.01	0.011 ± 0.0045	0.02 ± 0.008	0.02 ± 0.008	144	43
Female >16	126	-	55 ± 13	3.18	20	14.40 ± 39.05	15.64 ± 44.022	0.17 ± 0.67	0.012 ± 0.0035	0.02 ± 0.005	0.02±0.006	57	17
Age>16	332	-	63 ± 15	3.6	20	14.18 ± 35.74	15.07 ± 39.997	0.26 ± 0.90	0.011 ± 0.0042	0.02 ± 0.007	0.02 ± 0.007	201	61
	-	95% CI, UB	-	-	-	10.33	10.77	0.17	0.01	0.02	0.01	-	-
	-	95% CI, LB	-	-	-	18.02	19.38	0.36	0.02	0.03	0.02	-	-
	-	Minimum	29	-	-	0.02	0.005	0.01	0.01	0.01	0.01	-	-
	-	Maximum	105	-	-	236.51	262.54	7.57	0.03	0.09	0.06	-	-

bw: body weight

Consumption of water with a total inorganic arsenic level below the WHO value (10 µg L^{-1}) has indicated a total daily intake of 0.37 ± 0.26 µg day^{-1} kg^{-1} for total arsenic which did not exceed the PTDI of 2.1 µg day^{-1} kg^{-1} body weight. However, at a concentration level of 10 to 50 µg L^{-1}, the average daily dose was found to be 2.01 ± 1.32 µg day^{-1} kg^{-1}. While, at an arsenic concentration of 50 to 100 µg L^{-1}, intake was found to be 5.09 ± 2.90 µg day^{-1} kg^{-1} and a higher intake of 59.62 ± 63.32 µg day^{-1} kg^{-1} was found at arsenic concentration levels above 100 µg L^{-1}. These findings have revealed that 63% (n=252) of the household members consuming arsenic contaminated water >10 µg L^{-1} also exceeded the PTDI of 2.1 µg day^{-1} kg^{-1} body weight. These results suggest that countries, including Pakistan, currently following a drinking water standard for arsenic of 50 µg L^{-1} would place many people at risk of developing adverse health effects in rural areas.

The maximum average daily dose of total arsenic in this study was found to be 236.51 µg kg^{-1} day^{-1} (for age group >16) which is higher than reported in all of the earlier studies of Pakistan i.e. 0 to 5.56 x 10^{-4} µg kg^{-1}day^{-1} (Muhammad et al., 2010), 0.11 to 3.7 µg kg^{-1}day^{-1} (Farooqi et al., 2007), 0.29 to 1.43 µg kg^{-1}day^{-1} (Memon et al., 2016), 0.036 to 5.6 µg kg^{-1}day^{-1} (Shakoor et al., 2015), 0.5 to 23 µg kg^{-1}day^{-1} (Rasool et al., 2015). This highest average daily dose of total arsenic is attributed to the higher geogenic arsenic concentration detected in the ground water sources. Exposure data from this study is also expected to be higher than those reported for other areas of the world such as 2.1 to 4.3 µg kg^{-1}day^{-1} (Nguyen et al., 2009) and 1 µg kg^{-1}day^{-1} (Bui et al., 2014) in Vietnam; 0.023 to 0.0521 µg kg^{-1}day^{-1} in Turkey (Caylak, 2012); 4.5 µg kg^{-1}day^{-1} (Valberg et al.,1997), 2.2 to 3.3 µg kg^{-1}day^{-1} (Meacher et al., 2002) and 177 µg kg^{-1}day^{-1} (Steinmaus et al., 2003) in USA; 73.9 µg kg^{-1}day^{-1} in India (Mazumder et al.,1998); 1.97 to 2.44 µg kg^{-1}day^{-1} in rural Bangladesh (Khan et al., 2009). Most of these studies have used the USEPA default body weight of 70 Kg and water intake of 2 litres per day (USEPA, 1989). Average daily dose determined in this study was found to be lower than those reported in Bangladesh as 50 to 500 µg kg^{-1}day^{-1} (Karim, 2000) with a body weight of 44 to 55 kg and a water intake of 2.37 to 3.89 litres per day, daily arsenic intake of 1060 µg kg^{-1}day^{-1} (Pokkamthanam et al., 2011) in India with 4 litres per day water intake. Arsenic occurrence in the ground water of Bangladesh i.e. 4227 µg L^{-1} (Chakraborti et al., 2010) was reported far above the Bangladesh drinking water standard of 50 µg L^{-1}. In addition to such an excessive levels of arsenic in water sources, water intake

values may also have influenced the higher average daily dose as explained in Rasheed et al. (2016b).

There are no set regulatory limits and reference dose (RfD) of organic arsenic species to compare the results, however, a very low concentration of organic arsenic species (below MDLs) have also resulted in very low average daily doses of MMA, DMA and AsB (Table-4). Comparing these findings with minimal risk levels (MRLs) defined by the Agency for Toxic Substances and Disease Registry (ATSDR, 2007b) has indicated the lower daily intake dose of MMA and DMA.

3.4 Ratio between average daily dose (ADD) and reference dose

The reference dose (RfD) is the daily chemical dose that results in no long-term harmful health effects from prolonged exposure (Lee et al., 2005). For water, the regulatory limits are set on the basis of total inorganic arsenic (i.e. RfD: 0.0003 mg/kg/day) rather than individual arsenic species. The ratio of average daily dose (ADD) to USEPA reference dose (RfD) has resulted in higher chronic non-cancer risk compared to the ratio between ADD and PTDI also set as HQ for total arsenic as given in Table-5.

HQ calculations for As^{+5} have indicated results closer to total arsenic due to the existence of total arsenic mainly as As^{+5} and using a similar level of estimated RfD. A HQ for As^{+3} was determined using the RfD for total arsenic (0.0003 mg $kg^{-1}day^{-1}$) and was found to be less than 1 for most of the study participants. However, with an estimated RfD (0.000006 mg $kg^{-1}day^{-1}$) based on reported relative toxicity magnitude, a higher level of HQ was depicted (Table-5).

Table-5: Mean Hazard Quotient (HQ) calculated using standard and estimated reference doses at *95% CI*

Age groups	Mean Hazard Quotient (HQ) at *95% CI*				
	Total arsenic		As^{+5}	As^{+3}	
	ADD/RfD	ADD/PTDI	ADD/RfD	ADD/RfD	ADD/est. RfD
	RfD for total arsenic: 0.0003 (mg $kg^{-1}day^{-1}$)	PTDI: 2.1 (µg day^{-1} kg^{-1} body weight)	RfD equivalent to total arsenic: 0.0003 (mg $kg^{-1}day^{-1}$)	RfD for total arsenic: 0.0003 (mg $kg^{-1}day^{-1}$)	est. RfD 0.000006 (mg $kg^{-1}day^{-1}$)
Age 3-6	27.07 (9.95, 44.18)	3.87 (1.42, 6.31)	27.89 (10.23, 45.55)	0.20 (0.14, 0.27)	10.07 (6.85, 13.28)
Age 6-16	52.33 (17.98, 86.68)	7.48 (2.57, 12.38)	54.07 (17.70, 90.45)	0.29 (0.17, 0.42)	14.69 (8.55, 20.83)
Age ≤ 16	50.42 (18.62, 82.20)	7.20 (2.66, 11.74)	52.09 (18.43, 85.75)	0.29 (0.17, 0.40)	14.34 (8.66, 20.03)
Male >16	47.98 (31.50, 62.14)	6.69 (4.50, 8.88)	49.08 (32.05, 66.12)	1.08 (0.62, 1.54)	53.85 (30.88, 76.82)
Female >16	47.26 (25.25, 70.72)	6.85 (3.61, 10.10)	52.15 (26.53, 77.77)	0.56 (0.17, 0.95)	28.09 (8.71, 47.47)
Age>16	47.26 (34.45, 60.08)	6.75 (4.92, 8.58)	50.25 (35.91, 64.59)	0.88 (0.56, 1.20)	44.08 (28.00, 60.15)

The difference of possible health risks estimation subjected to daily reference dose or estimated reference doses presses the need to set the regulatory limits for daily

intake level of total arsenic and arsenic species. This has also been shown in the Food Standards Australia New Zealand (FSANZ, 2002), where PTDI of 0.003 mg kg^{-1}day^{-1}bw has been recommended and it is higher by 50% than the JECFA/WHO PTDI of 2.1 µg day^{-1} kg^{-1} body weight for inorganic arsenic. Various levels of HQ as shown below in Table-6 have indicated that 95% of 398 persons living in surveyed houses are at risk of a chronic daily intake of arsenic, whereas this intake is expected mainly in the form of As^{+5} (92% of residents with HQ>1) as shown below in Table-6.

Table-6: Results for the chronic exposure assessment

Arsenic species	RfD	Unit	HQ<1 (No effect)		HQ 1-10 (Effect)		HQ >10 (Significant effect)		Overall HQ >1 (Effect)	
			n	%	n	%	n	%	n	%
Total arsenic	0.0003	mg kg^{-1}day^{-1}	20	5	181	45	197	49	378	95
	2.1(PTDI)	µg day^{-1} kg^{-1} body weight	146	37	210	53	42	11	252	63
As^{+5}	0.0003	mg kg^{-1}day^{-1}	30	8	185	47	183	46	368	92
As^{+3}	0.0003	mg kg^{-1}day^{-1}	362	91	25	6	11	3	36	9
	0.000006	mg kg^{-1}day^{-1}	0	0	291	73	107	27	398	100

The average daily intake of arsenic from drinking local domestic ground water in the study area is considerably higher than the levels reported to cause adverse health effects in the scientific literature. Chronic and acute health threats to the exposed rural communities are likely based on the dataset collected here. This is indicated as chronic and acute health complications such as black foot disease at a daily intake of 10 to 50 µg kg^{-1}day^{-1} bw (ATSDR, 1991), skin lesions, cardiac or kidney diseases, skin, lung, bladder, respiratory and other types of cancer at dose range of 10 to 40 µg kg^{-1}day^{-1} bw (Lasky et al., 2004; Lubin et al., 2000; Kurttio et al., 1999; Chiou et al., 1995; Hsueh et al., 1995;). Furthermore, the latency time between the onset of exposure and the appearance of chronic disease endpoints like cancer is reported to be 15 to 30 years depending on daily arsenic intake dose (ATSDR, 2007a). As such, the study area seems to be a high risk area where household ground water sources (hand pumps and wells) have never been tested for detailed arsenic species. There were general observations of arsenic associated skin problems in the villages Badarpur, Basti Balochan, Chak-46, Chak-48 and Chak-49 observed by the field sampling team with support of medical staff of basic health units. The skin manifestations like hyperpigmentation or hyperkeratosis probably associated with the chronic intake of As^{+5} by the local residents were identified following the guidelines of the UNICEF clinical diagnostic manual (Sun et al. 2004).

Very high arsenic concentrations found in groundwater might lead to other arsenic related health implications in the near future, if villagers continued to consume arsenic contaminated water and remedial measures are not taken. To provide the rural communities with arsenic free water for drinking and food preparation requires identification of alternative safe water sources and/or selection of arsenic treatment options capable of removing all the arsenic species. Arsenic free sources include surface water and rain water. Arsenic removal options based on oxidation, sedimentation, coagulation, flocculation, sorption and membrane filtration have been developed and adopted in several arsenic affected regions including Pakistan. Considering the economics, scalability and sustainability aspects, an overview of such technologies (Supplementay information: Table-SI-2) has revealed that most of these options can remove As^{+5} (Ahmed et al. 2006) but As^{+3} is comparatively more difficult to remove. As^{+3}, when present can be oxidized to As^{+5} for efficient removal in household or community level technologies as reported by Lan, 2013; Litter et al. 2010; Ramos et al. 2009; Garrido et al. 2007; Clifford and Ghurye, 2001; and, Pal, 2001. Studying arsenic speciation in drinking water sources is critical to understanding potential health risks and geochemical control is needed as an efficient water treatment solution. Understanding the contribution of individual arsenic sources to overall arsenic burden is important in developing the most appropriate risk management strategies.

4. Conclusions

Most studies evaluating human exposure to arsenic have focused on total arsenic and the role of individual arsenic species is still a pressing research need. Thus, this is the first study in Pakistan to characterise both the inorganic and organic arsenic species using ion chromatography inductively coupled plasma collision reaction cell mass spectrometry. The highest level of total arsenic in groundwater was found to be 3090 µg L^{-1} and is likely to be the most common pathway for long-term arsenic exposure. As^{+5} was the dominant inorganic arsenic species in 94% of samples across all the villages studied. Nevertheless, As^{+3} was identified in one village as the dominant pollutant, indicative of a reducing environment in the aquifer, and is considered the most toxic species as well as being difficult to remove using most of the arsenic remediation technologies. Organic arsenic species such as

monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AsB) were below detection limits, confirming that contamination of aquifers by human impacts (e.g. by use of arsenical pesticides and fertilizer) is low and the predominant source is geological arsenic release. An average daily intake of arsenic up to 236.51 µg kg^{-1} day^{-1} was determined which is the highest of all reported levels in Pakistan and of several other arsenic affected countries, other than Bangladesh and India. This level of arsenic intake is likely to be associated with potential health risks among exposed rural communities consuming ground water with arsenic above 10 µg L^{-1}. These results may prove useful for risk assessment and for regulatory agencies to reconsider the maximum contaminant level of arsenic in drinking water and define the regulatory limits for arsenic species. Further research efforts are needed to understand the spatial variation of arsenic species in various geological settings and their long term exposure assessment. The study findings also demand the adoption of efficient and sustainable remediation approaches to address the treatment of arsenite (As^{+3}) for the supply of arsenic free water to rural households.

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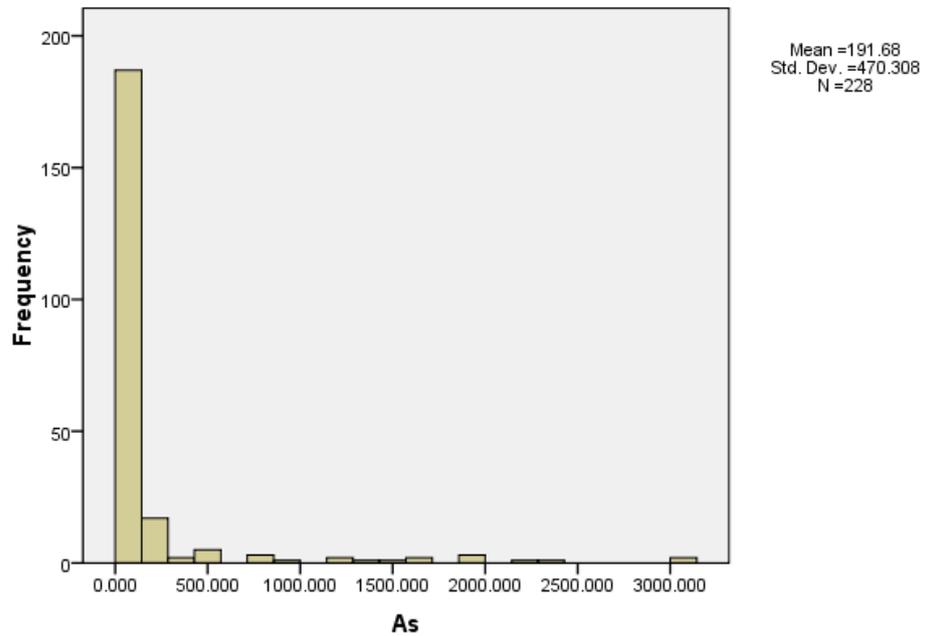
Figure SI-1a. Distribution frequency of total arsenic
(original data) concentrations in ground water
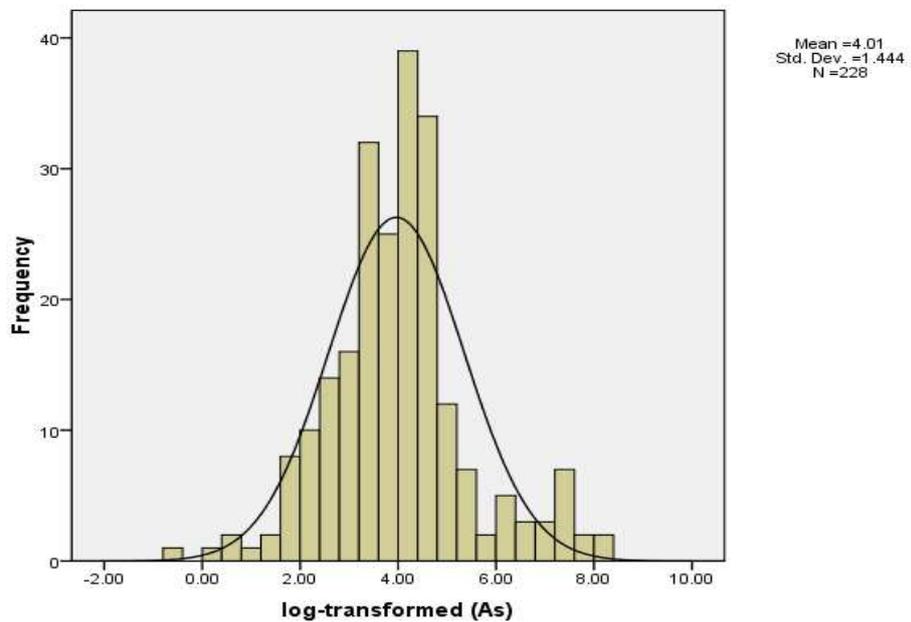
Figure SI-1b. Distribution frequency of total arsenic
(log transformed data) concentrations in ground water

Table-SI-1 Summary statistics of log transformed total arsenic and inorganic arsenic species (µg L^{-1}) in groundwater samples (n = 228)

Analyte	Statistics	Chak-46/12-L	Chak-48/12-I	Chak 49/12-I	Basti Balochan	Badarpur	Basti Kotla Arab	Overall
No of samples	n	57	45	50	31	16	29	228
As (Total)	AM	3.91	4.98	3.89	3.16	6.98	2.22	4.01
	SD	0.86	1.06	0.66	0.37	1.10	1.1	1.44
	GM	4.85	4.85	3.83	3.11	6.88	*	*
	GSD	2.35	2.97	1.93	1.58	2.98	3.02	4.24
	95% CI LB	3.68	4.65	3.71	3.02	6.40	1.80	3.82
	95% CI UB	4.13	5.31	4.08	3.31	7.56	2.64	4.20
	Log-Median	4.18	5.04	4.12	3.25	7.42	2.43	4.05
	Minimum	1.27	2.14	1.96	2.11	3.78	0.73	0.73
	Maximum	5.43	7.24	4.56	3.63	8.04	3.94	8.04
As^{+5}	AM	3.90	3.95	3.54	2.95	7.09	2.26	3.89
	SD	0.89	1.15	0.9	0.42	1.09	1.1	1.53
	GM	3.75	4.7	3.4	2.88	6.99	*	*
	GSD	2.429	3.159	2.449	1.651	2.984	3.717	4.617
	95% CI LB	3.67	4.5	3.29	2.78	6.51	1.76	3.69
	95% CI UB	4.14	5.19	3.8	3.12	7.67	2.76	4.09
	Log-Median	4.16	4.16	3.83	3.05	7.53	2.53	3.95
	Minimum	0.88	2.04	1.1	1.62	3.87	-2.21	-2.21
	Maximum	5.4	7.27	4.66	3.39	8.14	4.14	8.14
As^{+3}	AM	-0.96	-0.21	1.35	-0.18	-0.36	-0.68	-0.12
	SD	0.14	1.34	2.00	0.86	0.7	0.58	1.45
	GM	*	*	*	*	*	*	*
	95% CI LB	-1.00	-0.61	0.79	-0.52	-0.73	-0.90	-0.31
	95% CI UB	-0.92	0.19	1.92	0.16	0.02	-0.46	0.07
	Log-Median	-0.99	-0.99	0.99	-0.49	-0.51	-0.99	-0.99
	Minimum	-0.99	-0.99	-0.99	-0.99	-0.99	-0.99	-0.99
	Maximum	-0.04	4.05	4.61	1.57	1.18	0.82	4.61

n: Number of samples; AM: Arithmetic mean; SD: Arithmetic standard deviation; GM: Geometric mean; GSD: Geometric standard deviation; 95% CI: Confidence Interval, LB: Lower bound; UB : Upper bound; BDL: Below Detection Limit
Limit of detection (LODs): total arsenic (0.01 µg L^{-1}), As^{+5} (0.11 µg L^{-1}) and As^{+3} (0.37 µg L^{-1})

* Negative values due to very low log-transformed arsenic concentration, hence their GM and GSD could not be calculated.
Where negative values are given, it should be noted that they are in log and in actual represent low concentrations of arsenic.

Table-SI-2: An overview of household and community level arsenic removal technologies (ARTs)

ART name	Process/Removal mechanism	Year	Type	Removal efficiency	Region of Application	Cost (unit & yearly operation and maintenance (O&M)	Claimed life	Advantages	Drawbacks	Reference
Two Bucket Treatment Unit (2BTU)	Coagulation by addition of alum as a coagulant, potassium permanganate, added as an oxidizer, bind arsenic to the flocs, which are filtered out by sand layer at the bottom bucket.	1998	hh	60%	Bangladesh	Capital cost: USD 10 chemicals cost/year: USD15-20	.n.r	• 75% of the installed units removed arsenic to below 50 µg L^{-1}. • production from locally available material	issues in user's acceptability due to chemicals addition	Robinson (2000)
Three Kolshi Filter Unit (Adsorption and filtration)	Three traditional water filters or clay pitchers, stacked vertically in a frame. Top kolshi: contained a layer of iron filings and a layer of coarse sand, Middle kolshi: contains a layer of charcoal and a layer of fine sand, Bottom kolshi for the filtered water.	2000	hh	97%	Bangladesh	USD 40-50 capital cost	unit replacement after 3-5 years	• low cost and short term solution up for about 3-4 months • produced from locally available material.	• Solid lump formation after two weeks of usage and difficult to clean. • arsenic exceeds above 50 µg L^{-1}before 6 months	Munir et al. (2001); CAWST (2009)
Rama Krishna Mission (RKM) Filter Unit (Coagulation and filtration)	Powdered Ferric Alum is used as coagulant in combination with bleaching powder solution as an oxidant. Tripura candle filter is used to filter Arsenic flocs.	1999	hh	Initially removes arsenic to below 0.05 mg L^{-1}	West Bengal	USD 40-58	n.r	easy to use and low cost	• poor arsenic removal due to issues with continuous supply of high-grade chemicals,	Robinson (2000)
Amal Domestic Water Purifier (Adsorption)	Composed of conventional two-chamber domestic candle filter body, with a layer of Aluminum oxide in the top chamber.	1998	hh	n.r	West Bengal	USD 40-58	Two years (claimed life of activated alumina)	adsorbing media can be regenerated by flushing with sodium hydroxide and acid.	• media saturation and clogging in less than 6 months	Robinson (2000)
Kanchan Arsenic Filter (Adsorption)	Arsenic adsorbed on the rust of the iron nails. The rust and Arsenic flake off the nails, and are caught in the sand filter and retained	n.r	hh	85-95%	Bangladesh and India	USD12-40	More than 10 years	maintenance required at reduced flow rate	• Filter must be used almost every day to maintain the biological layer (maximum pause period is 48 hours). • Sand and iron nail selection and preparation are critical to ensure flow rate and treatment	CAWST (2009)
Passive Sedimentation (Aeration)	Aeration of water for 12 hours and then leaving to settle for 12 hrs.	n.r	hh	30-50%	Bangladesh	USD 5	n.r	easy to use and short term household solution	long storage duration increases chances of faecal contamination	CAWST (2009)
Tablet Reagents (Co-precipitation)	Handmade black coloured tablets made of ferric salt and activated charcoal	2000	hh	50%	Bangladesh	USD 2.00/year supply of tablets	n.r	higher arsenic removal efficiency of 95-100% in the lab with shelf life of 15 months	lower arsenic removal efficiency in the field	Das et al. (2000)
Sub-surface aerated water injection	Pumping the aerated water into the saturated zone of an aquifer, either through an abstraction point or an adjacent purpose-built well.	n.r	Comm	not efficient to remove arsenic below 10ug/L	Bangladesh	n.r	n.r	double-well designs have the advantage to use alternatively for arsenic removal	arsenic removal dependent on the groundwater properties such as; arsenic/iron ratio, effect of varying pH and interference by phosphorous.	Matthews (2014) Halem et al. (2010)
Alufloc	Household-level coagulant made of aluminium sulphite and ferric chloride	n.r	hh	98% with 100 µg/L	Bangladesh	USD 0.15 per bucket treated	n.r	effective in reducing arsenic content to safe levels	arsenic removal efficiency decreases with higher dissolved arsenic	Bedolla et al. (1999)
Stevens Institute technology (Coagulation, Sedimentation and Filtration)	Two buckets system: one for mixing the packet of iron coagulant and hypochlorite, the other one with sand bed to filter the flocs. Treated water is collected through a plastic pipe fitted with an outlet covered with a cloth filter to prevent sand	2001	hh	<50 ug/L	Bangladesh	n.r	n.r	enhanced coagulation and co-precipitation (ferrous sulphate) and less dependent on groundwater Iron	excessive bicarbonates may reduce the efficiency	Sutherland et al. (2001)

Technology	Description	Year	Scale	Efficiency	Location	Cost	Lifespan	Advantages	Disadvantages	Reference
Safe water treatment unit (Coagulation and filtration)	300 litres upper reaction vessel filled with contaminated water and BAT solution, after 30 minutes of reaction time allowed to pass through sand filter to store into lower storage vessel	2004	Semi-comm	>95%	Pakistan	USD 400	4 years	• no longer contact time required • arsenic removal from 1000 µg L^{-1} to <10 µg L^{-1}	regular backwashing required	Kahlown et al. (2005)
Fill and draw treatment unit (Flocculation and filtration)	600 litres reaction vessel filled with water and the required quantity of oxidant and coagulant, stirred for 30 seconds and left overnight for sedimentation, filtered through sand bed and collected through vessel tap.	n.r	Semi-community type	n.r	installed in schools/colleges/communities in Bangladesh	USD 265/ unit	n.r	semi-community level option	longer contact time	Ahmed (2006)
Tube well-attached arsenic treatment unit (coagulation, sedimentation, and filtration)	Unit attached to hand pump-operated tube well, involved addition of sodium hypochlorite and alum in diluted form followed by mixing, flocculation, sedimentation, and up flow filtration in a compact unit	2000	community	90%	West Bengal, India	n.r	n.r	effective in removing 90% of the arsenic from tube well water	operation of the system depends on regular washing of the filter bed.	Ahmed and Rahman (2000)
Iron-arsenic treatment unit (precipitation and adsorption)	natural iron in water precipitated to remove arsenic by oxidizing As^{+3} to As^{+5} and finally by adsorption.	1998	both	50-80%	Bangladesh	n.r	n.r	reduction in arsenic from half to one-fifth of the original concentration.	community ownership created issues with regular washing of the filter bed	Ahmed (2006)
Combination of aeration, sedimentation & rapid sand filtration	medium-scale iron-arsenic removal plants	n.r	comm.	40-80% for arsenic level of 100 µg/L	Bangladesh	variable according to size	n.r	arsenic removal by co-precipitation and adsorption on natural iron flocs has good potential for arsenic content up to about 100 µg/L	higher water requirement for washing the filter beds	Ahmed (2006)
Arsenic removal by softening	Calcium carbonate formation by lime in water used to adsorb arsenic. arsenic removal through sorption of arsenic onto magnesium hydroxide solids that form during softening.	n.r	both	40-70%	Multiple regions	n.r	n.r	efficient to treat water with high hardness, especially at pH >10.5.	large lime doses (800–1,200 mg L^{-1}) result in large volume of sludge. pH adjustment of treated water required, relatively low removal efficiencies	McNeill and Edward (1997)
Activated alumina filters (BUET activated alumina, Alcan enhanced activated alumina and Apyron Arsenic treatment units)	Adsorption of arsenic on active surface of the media	n.r	hh to sem-community level	moderate efficiency	Bangladesh and India	n. r	6 months	• no chemicals required • highly selective towards As^{+5} • effective with water with high total dissolved solids (TDS)	• with exhaustive sorptive sites media cannot remove arsenic • interference by iron and phosphate • 5–10% of the alumina is lost during removal process and the capacity of the regenerated medium is reduced by 30–40%. • replacement of activated alumina after 3–4 regenerations.	Ahmed (2006)
Activated aluminium hydroxide hydrogel	Hydrogel produced from hydrated aluminum sulfate, powdered calcium hypochlorite, ammonium hydroxide and demineralized water.	1994	n.r	>90%	Tucuman province (Argentina)	n.r	n.r	arsenic reduction (40–800 µg L^{-1}) to below 10 µg L^{-1}	not found	Litter et al. (2012)
Granular iron oxide (Bayoxide®, GFO)	contains less than 70% of Fe_2O_3	1999	comm	95%	Multiple regions	n.r	n.r	viable product with arsenic removal efficiency	interferences of other ions during arsenic adsorption	Dennis. (2016)
Granulated ferric hydroxide e.g. granular ferric hydroxide GFH® or (AdsorpAs®)	Arsenic removal by activated alumina controlled by the pH and arsenic level of water, Arsenic removal is optimum in the narrow pH range from 5.5 to 6.0 when the surface is positively charged.	n.r	both	>90%	India and Bangladesh	USD 4,300 for community	>3,600 litres of arsenic free water per day for 100 families	• highly effective adsorbent for As^{+5} and As^{+3} • adsorption capacity of 45 g/kg for arsenic on a dry weight basis	• requires aeration for oxidation of water and pre-filtration for removal of iron flocs before filtration through active media • regeneration of saturated alumina results in high-arsenic-contaminated caustic waste water.	Pal (2001) Matthews (2014)

Technology	Description	Year	Type	Removal	Region	Cost	Lifespan	Advantages	Disadvantages	Reference
Electro-Chemical Arsenic Remediation (ECAR)\n\n(electro-coagulation)	Uses a small electrical charge through an iron electrode to produce ferric hydroxides, oxy-hydroxides, and oxides, a form of rust. The rust reacts with the arsenic in the water to be filtered or allowed to settle out of the water.	n.r	both	>90%.	Argentina Bangladesh	n.r	n.r	• does not require continuous chemical supplies\n• electrode cleaning by reverse current once a day.	electricity dependent option	Matthews (2014)
The Shapla Arsenic Filter (Adsorption)	Iron-coated brick chips manufactured by treating brick chips with ferrous sulphate solution used as adsorption media	n.r	hh	80-90%	Bangladesh.	capital cost: USD10 media replacement cost/year: USD10-15	media lifespan of 3-6 months)	used filter media is non-toxic and can be disposed of safely	n.r	CAWST (2009)
READ-F Arsenic filter (Ion-exchange resins)	the READ-F is ethylene-vinyl alcohol co-polymer-borne hydrous cerium oxide (an adsorbent)	n.r	hh	>95%	Bangladesh and Japan	USD 50-70	3 years	• effective adsorption of As^{+5} and As^{+3}\n• regeneration by adding sodium hydroxide and then Sodium hypochloride and finally washing with water	pre-treatment of iron by sand filtration to avoid clogging of the resin bed.	Matthews (2014)
SORAS (solar oxidation and removal of Arsenic)	Based on principle of SODIS but lemon juice is added and kept under sunlight as a source of UV to cause oxidation of As^{+3} to As^{+5}. The $As(V)/Fe(OH)^3$ co-precipitate and settles at bottom.	n.r	hh	75- 90%	South East Asia, Latin America	minimal	na	reactive oxidants are produced photo chemically with sunlight	low scalability	CAWST (2009)
SAFI filter (adsorption & filtration)	Removes arsenic by filtration and adsorption through porous material of filter.	n.r	both	>73%	Bangladesh	46 USD	n.r	user friendly and readily available	reduced flow rate of water with the passage of time	Rahman et al. (2005)
Memstill® technology	combines multistage flash and multi-effect distillation modes into one membrane module	2007	hh	n.r	Bangladesh and India	n.r	n.r	• arsenic free water at cost lower than for reverse osmosis (RO) and distillation\n• Small scale applications using solar heat	improper cleaning of membrane may results in expiry of membrane	Feenstra et al. (2007)
Cerium oxide	CeO_2 nanoparticles firmly fixed on the walls of silica monoliths(SCO) and demonstrated a superior dynamic arsenic removal performance	2012	both	87%	Multiple regions	n.r	n.r	SCO composite easily desorped/regenerated for re-use	n.r	Shimoto (2007)
Magnetic micro-sorbents	the high saturation magnetization of $Fe_3O_4@TiO_2$ nanoparticles (45.56 emu/g) facilitates their separation from aqueous solutions by use of a moderate magnetic field and cause Arsenic adsorption	2003	both	n.r	n.r	n.r	n.r	faster adsorption of As^{+3}	tremendous application in water industry and no drawbacks found in literature	Lan (2013)
Nano-particulate ZVI(NZVI)\n\n(Adsorption)	rapid removal of As^{+3} and As^{+5} from subsurface environment	2005	both	99.9%	Multiple regions	n.r	variable	formation of arsenic neutral after reaction of As^{+5} and As^{+3} on the nano-particle surface.	efficiency decreases by increasing pH and arsenic concentration in solution	Ramos et al. (2009)
Ion exchange media	Resin made of cross-linked polymer skeleton having attached the charged functional groups through covalent bonding. Following pre-oxidation of As^{+3} to As^{+5} is removed is removed using the ion exchange process.	n.r	both	>90%	Multiple regions	USD 2,000.	variable	• effective technology even at higher flow rates of tube well water.\n• As^{+5} removal is relatively independent of pH and influent concentration.	• excess oxidant may damage the resin and thus needs to be removed.\n• Interference by competing anions to affect run length.\n• clogging by suspended solids and precipitated iron	Clifford (1999)
Nano-filtration	Separation of ionic species by nano-filtration membrane is dependent on membrane charge and pore size	n.r	both	95% of As^{+5} and >75% of As^{+3}	Multiple regions	variable	n.r	high pressure, high pH and low temperature favor more efficient arsenic removal.	• fouling or scaling of membrane by iron or manganese\n• backwashing cannot recover membrane fouling	Sato et al. (2002)

									• As^{+3} cannot be removed	
Reverse Osmosis (RO)	high-pressure membranes of RO (75–250 PSI or higher) causes reversal of natural osmotic flow resulting in rejection of polyvalent ions including arsenic oxy-anions	n.r	both hh and comm	40-99%	Argentina, e.g. in the provinces of Santa Fe, Córdoba and La Pampa	variable with size	n.r	• simple operation and maintenance (O&M) as no chemical addition • periodic membrane cleaning required • effective for community and household application • effective for treating water with high total dissolved solids (TDS) water	• water recovery rates of only 10–20% • higher electric power consumption • higher capital and operating costs • higher risk of membrane fouling • suitable for lower levels of arsenic • disposal of arsenic containing rejected brine water/sludge is a concern • poor removal of As^{+3} as oxidation to As^{+5} is difficult and may cause membrane damage • pre-treatment required	Clifford (1999) Litter et al. (2010) Robert (2002)
Capacitive Deionization (CI)	unit consists of low-cost filter of coal electrodes causes deionization by flow through a capacitor with electrostatic load	n.r	both	98.51%	Mexico	n.r	n.r	• system cleaning with smaller amount of chemical reagents • removal of As^{+5} and As^{+3} • rejection of 3-4% of treated water • lower operation and maintenance (O&M) cost	suitable for water with total dissolved solids (TDS) <3000 mg L^{-1}	Litter et al. (2010) Garrido et al.(2008)
Electrodialysis	Electrodialysis is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential	n.r	comm	80%	Multiple regions	n.r	n.r	• equally effective like RO in treating high total dissolved solids (TDS) water • reduced scaling	• very high costs • pre-treatment required	Litter et al. (2010)
In-situ remediation: Permeable Reactive Barriers(PRB)	Appropriate reactive material based on based on sorption, precipitation, chemical reaction and/or biogenic reactions, is able to induce physicochemical and/or biological processes to remediate groundwater contamination	1999	comm	n.r	Multiple regions	n.r	n.r	• significant cost benefits • low operational costs • low-cost local materials can be used	• efficiency affected by microbiological and geochemical processes • corrosion of materials. • diminished permeability by precipitation of sulfides, oxides, hydroxides and carbonates.	Litter et al. (2010)

hh: household, comm: community, USD: US Dollar, n.r: not reported